REVIEW

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Industrial synthesis of reactive silicones: reaction mechanisms and processes

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Silicones and silicone rubbers are ubiquitous in our daily lives, being used in a broad range of applications ranging from consumer products and adhesives to medicinal and electronic devices. The chemistry and synthesis of these versatile materials have been reviewed so many times that it is difficult to have a comprehensive overview. Hence, with this tutorial review we aim to provide a concise account of the most important reactions and industrial processes to furnish silicones, focusing specially on reactive silicones, specifically in telechelic OH-terminated polysiloxanes, which represent one of the most relevant members of this important materials family.

1. Introduction

Silicones or polyorganosiloxanes are a class of hybrid organic/inorganic polymers whose chains are characterized by a backbone of alternating silicon and oxygen atoms which might be linear or branched (Fig. 1). They represent an important materials class with special properties compared to common organic polymers.[1] They find multiple applications in the construction sector, the automotive industry, electronics, medicine, personal care as well as many consumer goods. Due to their special characteristics they are widely used as insulating materials, spreading agents, defoamers, parting agents, implants, matrices in drug delivery systems, adhesives and sealants.[2-4]

The term "silicone" was coined by Frederick S. Kipping who studied silicon and its compounds at the beginning of the 20th century.[5] He called the resin-like materials which he eventually obtained "silicon ketones" or "silicones" as he regarded them as aggregates of discrete molecules rather than as polymers. Because of their limited variety and their virtual inertness, Kipping did not foresee any application.[6,7] Later on, James F. Hyde produced silicone resins for impregnating and coating glass in the 1930s building on Kipping's work.[8,9] Before the development of the direct synthesis of organohalosilanes[10,11] – also known as the Müller–Rochow process – in the 1940s, the availability of the raw materials for its preparation was limited to silica and mineral silicates, leading to a very slow develop-

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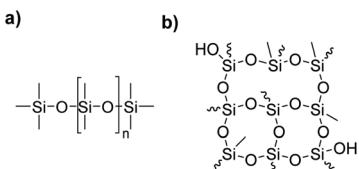
Fig. 1 Exemplary structures of silicone materials: (a) linear polydimethylsiloxane (PDMS) and (b) highly branched hydroxy functional silicone resin.

ment of silicone chemistry.[6] After a "dark period" of intensive research owing to World War II (keeping most of the advances in silicone chemistry unknown to the public for decades), the silicone field flourished dramatically.[12] In 2008, an estimated 480 000 t per a of silicone products were produced by the biggest European silicone companies.[13] In 2011 the worldwide production of silicones was around 7.3 million t per a and it was increased to 7.4 million t per a in 2017.[14] Other market studies state an increase in sales of approximately 4% per a until 2024.[15] This indicates a growing demand for basic siloxane products and a constant innovation potential in this area.

The unique properties of silicones are mostly attributed to the special characteristics of the Si–O bond.[1] For instance, silicones show only slight changes of their physical properties over broad temperature ranges as well as low glass transition temperatures and high gas permeability. This results from the high flexibility of the silicone chains.[16,17] The Si–O bond is longer than the C–O bond and the Si–O–Si bond angle is wider than that in its carbon analogues.[18,19] The angle might change with variations in the organic moieties attached to the silicon atoms. Both the longer bonds and the wider angles allow easier rotation of the substituents, leading to the said high flexibility of the polysiloxane chains.[19]

Silicones show good dielectric behavior due to the partial ionic character of the Si–O bond (∼50%) resulting from the high difference in electronegativity (ΔEN_{Si-O} = 1.76).[20] Thus, silicones are widely used as insulator materials.[21] Moreover,

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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, allowing the preparation of organofunctional terminated silicones.[19] Furthermore, silicones show high thermal and oxidative stability which results from the high bond dissociation energy (BDE) of the Si–O bond (460 kJ mol^{−1}), much higher than that for the C–O bond (318 kJ mol^{−1}).[18,19]

Linear polyorganosiloxanes, mainly polydimethylsiloxanes (PDMS), are among the most important silicone products (besides cyclic siloxanes). There are many processes to obtain these linear polymers and new processes are being developed constantly.[22–35] A key element of these transformations is controlling the nature of the functional groups that will end up at the ends of the chains, since, depending of their reactivity, these end-groups determine the subsequent use of these materials. Alkyl-terminated PDMS are used as lubricants, plasticizers, and heating oils due to their inertness, while hydroxy, alkoxy, hydrido and vinyl terminated telechelic PDMS are employed as the base of household and structural adhesives and curable formulations for sealings and coatings. These groups are especially important for curing these polymers to obtain solid silicone rubbers.[21] From these reactive silicones, OH-terminated PDMS are arguably the most relevant in industry.

The term "telechelic" refers to polymers with reactive chain-ends which can undergo further polymerization reactions or polymer analogue reactions.[36,37] Polymer analogue reactions are defined as those 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] It is important to mention that the reactive end-groups in telechelic polymers derive from the initiator, or terminating or chain-transfer agents used in the polymerization, 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.[37]

Many reviews and book chapters are devoted to the preparation of linear polyorganosiloxanes and their corresponding mechanisms from a purely academic viewpoint.[21,39–43] However, there very few (if any) collecting the synthesis of linear polysiloxanes from both academic and industrial perspectives, and importantly, there are no reviews focusing on OH-terminated reactive silicones. With this contribution, and without aiming to be comprehensive, we want to fill this gap and provide an overview of the academic and industrial processes to produce these important materials.

2. Methods for the synthesis of OH-terminated PDMS

OH-terminated PDMS are commonly synthesized by hydrolysis and condensation reactions of organochlorosilanes or by the

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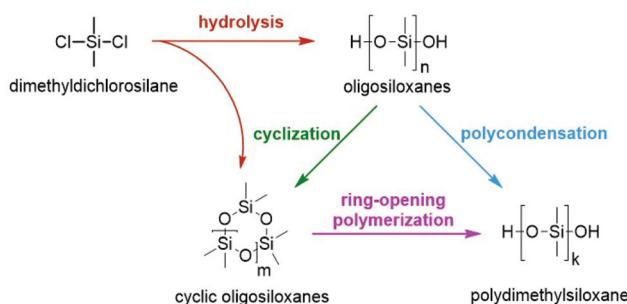
Scheme 1 Possible synthesis routes for OH-terminated polydimethyl-siloxanes starting from dimethyldichlorosilane.

Scheme 2 Reactions for the synthesis of methylchlorosilanes by the Müller−Rochow process.

ROP of cyclic polyorganosiloxanes (Scheme 1). The synthesis *via* condensation is not well-controlled and leads to broad polydispersities of the obtained polymers. In contrast, by the ROP of cyclic siloxanes, which also represents the main pathway in industry, silicones with tailored molecular weights can be obtained in a highly controlled fashion. The variety of suitable initiators, end-capping agents, additives, reactors *etc.* is broad.[39,44] In particular, for the anionic ring-opening polymerization (*vide infra*) many new initiators have been reported in the past few years. Metal hydroxides (like KOH, which is one of the earliest examples)[27] can be replaced with metal-free initiators such as tetraethylammonium or tetraethylphosphonium salts and phosphazene bases.[39] The most recent reports have dealt with nitrogen-containing bases such as N-heterocyclic carbenes,[45] bycyclic guanidines[46] and phosphatranes.[47]

In general, producing a silicone comprises at least three essential steps: first, synthesis of oligomeric silicone prepolymers from dimethyldichlorosilane followed by condensation polymerization or ring-opening polymerization (ROP); second, neutralizing or quenching the catalyst; and third, stripping the silicone polymer from volatiles.[33] The neutralization of the catalyst is especially crucial for the success of the overall process since basic or acidic catalyst residues lead to degradation of the polymer.[21]

Depending on the chosen polymerization method, the technical requirements must be adjusted. Considering these requirements, the following reactor setups have performed remarkably well at an industrial scale: (a) polymerization vessel; (b) stirred-tank cascade; (c) screw extruder reactor; (d) cell reactor/plug-flow-reactor; and (e) fixed bed reactor.[21,41]

2.1. From silicon to silicone

2.1.1. Synthesis of organochlorosilanes. Organochlorosilanes are mainly produced by direct synthesis, also known as the Müller−Rochow process, developed independently by E. Rochow[11] and R. Müller[10] in the early 1940s and still in use 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
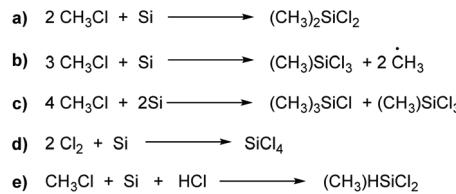
alkyl or unsaturated moieties show low yields and are not applicable in this process. They can also be obtained *via* Grignard reaction, hydrosilylation or radical additions.[44,48]

The main reactions for the synthesis of methylchlorosilanes by the Müller−Rochow process are presented in Scheme 2.[49] The main reaction (a) leads to dimethyldichlorosilane:[48] other methylchlorosilanes are products of side reactions (b and c) leading to a broad mixture of silanes (also referred to as "crude silanes"). This mixture also includes hydride-containing silanes such as $(CH_3)SiHCl_2$ (e), which are crucial raw materials for hydrosilation reactions.[50] The mixture is normally separated *via* laborious distillation. However, through adjustment of reaction temperature and the usage of promoters, the composition of the different silanes can be influenced. Anyhow, the main product always is dimethyldichlorosilane. An exemplary composition is given in Table 1.[48]

Organochlorosilanes are very sensitive to decomposition in the presence of protic compounds such as water or alcohols under the release of hydrochloric acid or chloroalkanes. This feature is exploited for the synthesis of polymeric silicone materials, by which the purified organochlorosilanes are converted to cyclic, linear[21,40,41] or branched polyorganosiloxanes or highly branched silicone resins[51] *via* methanolysis or hydrolysis reactions.[3,4,52,53]

2.1.2. Hydrolysis and polycondensation processes. Linear polyorganosiloxanes, also referred to as silicone oils or fluids, are commonly produced in a two-step process starting from dichlorosilanes (Scheme 3). The first step is the hydrolysis or methanolysis of a dichlorosilane which, as mentioned above, leads to a mixture of linear and cyclic oligomeric siloxanes. Hydrolysis or methanolysis can be performed in a way that

Table 1 Typical composition of a crude silane mixture from the Müller−Rochow process

Compound	Boiling point [°C]	Proportion in the "crude silane" [wt%]
$(CH_3)_2SiCl_2$	70	70–90
$(CH_3)SiCl_3$	66	5–15
$(CH_3)_3SiCl$	57	2–4
$(CH_3)HSiCl_2$	41	1–4
$(CH_3)_2HSiCl$	35	0.1–0.5

Typical reaction conditions: 0.5–3 wt% copper catalyst; zinc or zinc oxide as a promoter; 250–320 °C.[54]

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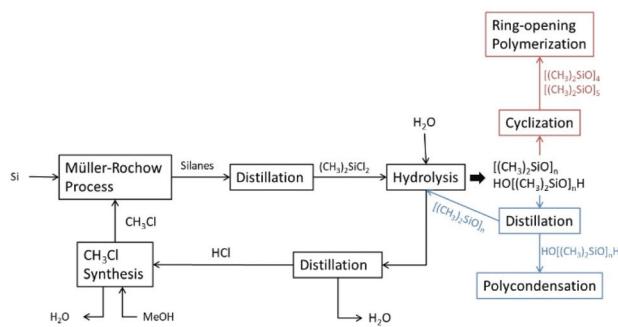
Scheme 3 Simplified flow diagram of the two-step process for the synthesis of OH-terminated PDMS *via* hydrolysis.

either linear or cyclic oligomeric siloxanes are obtained selectively.[26] The products can be also inter-converted into each other.[55,56] The hydrolysate is then further converted to high-weight polymers by polycondensation or ROP.[21,40,41]

Commonly, the silicone synthesis process is directly connected to the Müller–Rochow process. For this procedure chloromethane is needed as the starting material to furnish the chlorosilanes. Therefore, aqueous hydrochloric acid which accumulates in the hydrolysis reaction is first distilled to yield pure HCl, which is then reacted with methanol. The prepared chloromethane is then used for the Müller–Rochow process. Instead of hydrolysis, methanolysis of dichlorosilanes can be performed. This bears the advantage that chloromethane is recovered directly instead of aqueous hydrochloric acid, reducing the overall cost of the process.[21,40,41]

In patent US 4960850[35] they describe a batch process for the polycondensation of oligomeric siloxanediols in order to obtain a silanol (Si–OH) end-capped polymer. Therein, the oligomeric siloxane diols are first stirred under reduced pressure to remove volatile compounds out of the substrate. Then they return to atmospheric pressure by purging with nitrogen. The reaction mixture is heated to a certain temperature (50–130 °C) and triflic acid is added to the reaction mixture. Again, the pressure is reduced, and the mixture can react until the desired viscosity of the product is obtained. The reaction is quenched by adding hexamethylcyclotrisilazane. The obtained polymer is then stripped to remove volatile contents.[35]

## 2.2. Ring-opening polymerization of cyclic siloxanes

The ROP of cyclic siloxanes is commonly not the method of choice in industrial processes due to its higher cost compared to hydrolysis and polycondensation approaches. However, it is still highly relevant for special applications in which a careful control of the molecular weight and polydispersity of the produced polysiloxanes is required. The cyclic monomers used are mainly organocyclotetrasiloxanes (like octamethyl-cyclotetrasiloxane, also called D_4) or organocyclotrisiloxanes (like hexamethylcyclotrisiloxane, also called D_3). Other monomers include cyclic carbosiloxanes such as 2,2,5,5-tetramethyl-2,5-disila-1-oxacyclopentane. Known ROP techniques are: ionic, radical, and peroxide- or plasma-initiated ROP.[17] 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.[17]

Anionic or cationic ROP of both strained (D_3) and unstrained (D_4, D_5 and D_6) cyclic siloxanes leads to the same equilibrium in which the polymer and cyclic byproducts co-exist. Nevertheless, the mechanism leading to this equilibrium is different, which also results in two possible pathways for ROP: kinetically or thermodynamically controlled (Scheme 4).[57,58] 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.[57]

Thermodynamically controlled ROP: The thermodynamically controlled ROP is entropy-driven and is mainly applied for the polymerization of cyclotetrasiloxanes or higher cyclosiloxanes due to the fact that all bonds in both monomers and polymers are thermodynamically equivalent.[59] This leads to the parallel formation of linear poly- and oligocyclosiloxanes. Thereby, the polymer concentration increases until equilibrium is achieved. This kind of polymerization is also known as equilibrium polymerization or equilibration because it stops after reaching the equilibrium state.[57]

An advantage of this process is that it is not dependent on the nature of the used initiators. Therefore, initiators which achieve equilibrium fast and under mild conditions can be chosen; they 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.[57] A limitation of this approach is the formation of oligocycles. Therefore, the thermodynamically controlled ROP should be used for polymerizations which give a high yield of the polymer in the equilibrium state. The ratio of linear polymers 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).[57]
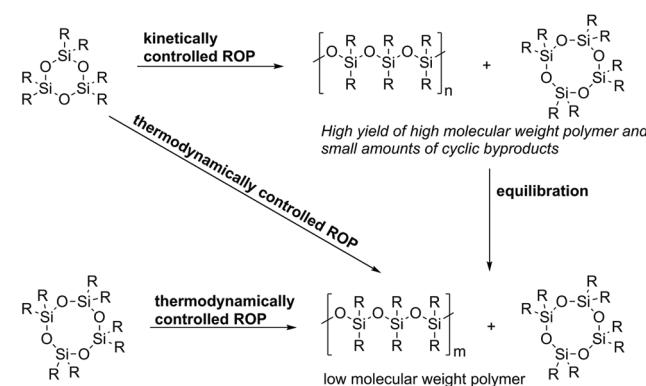
Scheme 4 Differences between thermodynamically and kinetically controlled ROP of cyclic siloxanes.

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, with the ring strain release being the driving force of the reaction.[57] The reaction has to be quenched directly after reaching the highest monomer conversion in order to avoid equilibration reactions. If the reaction is stopped before equilibrium is attained, a high molecular weight polymer with only small amounts of cyclic byproducts is obtained. An advantage of this process is that polymers with controlled structures and higher yields can be obtained. Conversely, the processes require more expensive monomers and very pure reactants and only selected initiators can be used.[57]

2.2.1. Anionic ROP. The anionic ring-opening polymerization is often used for the synthesis of high molecular weight polymers and its mechanism is well understood.[60] The initiation step requires a base and leads to the formation of silanolate anions, which are the active center in the propagation reaction in which the chain length is extended (Scheme 5a).

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 the formation of cyclic siloxanes. As a consequence, smaller and bigger cyclic siloxanes are generated as by-products when equilibrium is achieved (Scheme 5b).[39] This can be avoided under certain conditions by stopping the reaction directly before equilibrium is achieved and it is commonly called non-equilibrium polymerization.[57] Chain transfer is another side reaction which can occur (Scheme 5c). Herein, the active center attacks a silicon atom at another polymer chain, breaking the siloxane bond and leading to chain randomization which is also called equilibration. 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 (*i.e.* water) in the reaction. It can also be forced by using the initiator in an aqueous solution or by quenching the reaction with water or alcohols.[40] Importantly, the molecular weight can be controlled by the amount of water used.[61] An alternative is the usage of end-capping agents, typically disiloxanes including tetramethyldisiloxane (TMDS), hexamethyldisiloxane (HMDS) or divinyltetramethyldisiloxane (DVS).[33] These end-capping agents may also be used to regulate the molecular weight of the polymer and/or to add a functionality different from OH, for instance a vinyl group.[62]

The polymerization rate depends on many factors such as the nature of the initiator, the polymerization medium and the chosen monomer. However, the key factor governing the kinetics of the ring-opening polymerization is the silanolate–counterion interaction (K^+ and Na^+ being the most common in industry) leading to the formation of aggregates which are inactive in AROP.[63,64]

Initiators: Many different initiators are well known for this route and those widely described are alkali metal or alkali earth metal hydroxides (*e.g.* KOH and NaOH),[27] alcoholic complexes thereof, alkali metal or alkali earth metal silanolates,[65] tetraalkylammonium hydroxide, phosphazene bases[66] and, recently, N-heterocyclic carbenes[45] or bicyclic guanidines (Scheme 6).[39,67] It has been observed that the polymerization rate increases with the size of the counterion: $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+ \sim Et_4N^+ \sim Et_4P^+$. With increasing size, the cations become less electrophilic and therefore the concentration of free anions increases. Therefore, the most active initiators are phosphazenes.[63]

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.[27] Potassium hydroxide is neither soluble in the monomer nor in the polysiloxane. Therefore, it needs to be dispersed as a fine powder in the reaction system and high temperatures (>150 °C) are necessary to start the polymerization.[30] Nowadays, potassium silanolates are often used as initiators for the synthesis of silicones. They represent a KOH-surrogate
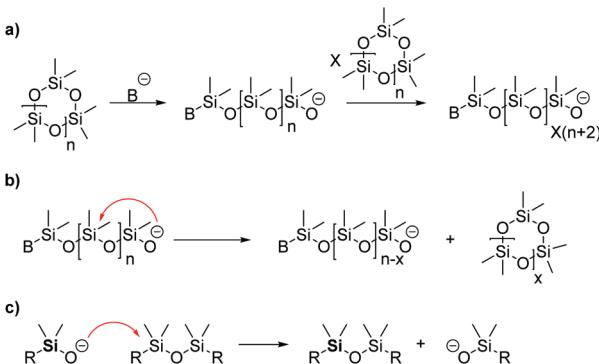
Scheme 5 Anionic ring-opening polymerization of cyclosiloxanes. (a) Initiation reaction by the formation of silanolate anions and propagation. (b) Back-biting reaction on a growing PDMS chain. (c) Chain-transfer reaction.
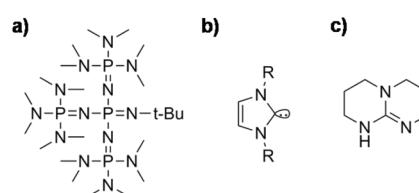
Scheme 6 Modern initiators for ROP of cyclosiloxanes: (a) an exemplary molecular structure of a phosphazene: (1-*tert*-butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)-phosphoranyliden-amino]-$2\lambda^5,4\lambda5$-catenadi(phosphazene)) (P_4-*t*Bu phosphazene), (b) the general molecular structure of a N-heterocyclic carbene (NHC), and (c) the molecular structure of 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD).

which is soluble in siloxanes[68,69] and may also be used for polycondensation.[69] They can be obtained by reacting potassium hydroxide with siloxanes.[65]

Phosphazene bases (Scheme 6a), 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 for the ring-opening polymerization, especially in the presence of proton donors such as methanol or traces of water.[66] 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.[29,32,70] For example, Möller et al. showed that P_4-tBu phosphazene is very active at room temperature at very low concentrations (10^{-3} mol L^{-1}). Polymerization of D_4 starts immediately and equilibrium is achieved after 1 min.[66,71,72]

In the past few years, initiation via Lewis bases has been of special interest in silicone research. In particular, the use of metal-free organocatalysts such as N-heterocyclic carbenes (NHCs, Scheme 6b) or guanidines has been reported,[73] even for the ROP of other cyclic monomers such as caprolactones.[74] In the literature, NHCs with cyclohexyl or tert-butyl moieties have been reported as active initiators for the ROP of cyclic oligosiloxanes using primary alcohols such as methanol or benzyl alcohol as co-initiators.[45] NHCs act as nucleophilic reagents, where the electron rich carbon of the NHC attacks a silicon atom of the cyclic monomer and binds to it while the monomer undergoes ring-opening. The formed zwitterionic intermediate contains the silanolate center which is needed for the chain propagation described above. The alcohols described as co-initiators are necessary for chain termination. By releasing the initiator they form a heterotelechelic silicone which is alkoxy end-capped on one side and silanol-terminated on the other (Scheme 7).[75,76] NHCs have the great disadvantage of being very sensitive to moisture. In the literature, CO_2-protected NHCs are also described, which can be thermally deprotected and allow a premixing of the reactants under normal conditions. This is especially advantageous for industrial applications.[77]

Molecules such as 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) (Scheme 6c) have been successfully used for the ROP of cyclic carbosiloxanes such as 2,2,5,5-tetramethyl-1-oxa-2,5-disilacyclopentane or hexamethylcyclotrisiloxane. Hedrick et al. used TBD at a concentration of 1.2 mol% in combination with an alcohol and could confirm via NMR that they obtained heterotelechelic polymers with an alkoxy and silanol terminated chain-end. TBD acts in this polymerization as a co-initiator by deprotonation of the added alcohol. The formed alcoholate acts as an initiator for the ring opening polymerization.[67] TBD is less active than NHCs but the obtained polymers show a smaller polydispersity which indicates a more controlled process.[78] In Patent US 0215097 a process for preparing silicones by ROP of cyclosiloxanes in the presence of bicyclic guanidines (especially TBD) is described. Therein, alcohols are not necessarily used and additionally disiloxanes are used as end-capping agents.[46]

Influence of solvents and activators: The polymerization itself can be carried out neatly in solvents or in emulsion. However, the solubility of the initiator in the reaction medium plays an important role in the reaction kinetics. Suitable solvents are liquid hydrocarbons such as hexane or silicone fluids.[33] In some examples THF is used as the solvent in combination with a hard counter-ion, namely Li^+, in the ROP of D_3.[79–83] Reaction conditions were found under which backbiting and chain-transfer reactions have been avoided and polymers with very narrow polydispersities (<1.1) have been obtained. Advantageous to this process is the absence of any additives which could contaminate the polymer. The reason for these results is the stronger interaction of the counter-ion with the solvent than with the active center at the chain-ends.[81] Morton and Bostick reported a solution polymerization of D_4 in THF, showing 71% conversion after 24 h at 60 °C. Under neat conditions, a reaction temperature of 140 °C was necessary, demonstrating that the choice of solvent has an accelerating effect.[84,85]

Various additives and coinitiators which improve the polymerization rate have been described and these include hexamethylphosphoric triamide,[86–88] dimethyl sulfoxide,[86,89–92] 2,5,8-trioxanonane (diglyme),[93] 2,5,8,11-tetra-oxadodecane (triglyme),[94] 1,2-dimethoxyethane,[86] dimethylformamide,[95] and N-methylpyrrolidone.[96] The success of these approaches lies in the fact that the counter-ion shows a stronger interaction with these activators compared to that with the active center of the polymer chain.[88,91,97–99] For instance, when crown ethers are used, they form a complex with the counter-ion and thereby reduce the silanolate–cation interaction and the formation of aggregates resulting in an increase in the polymerization rate.[100] Some of these additives and some other polar aprotic substances such as acetonitrile and acetone have been studied in the ROP of 1,3,5-tri(3,3,3-trifluoropropyl-)-1,3,5-trimethylcyclotrisiloxane (D^F_3) with sodium siloxanolate as an initiator. The reaction is of first
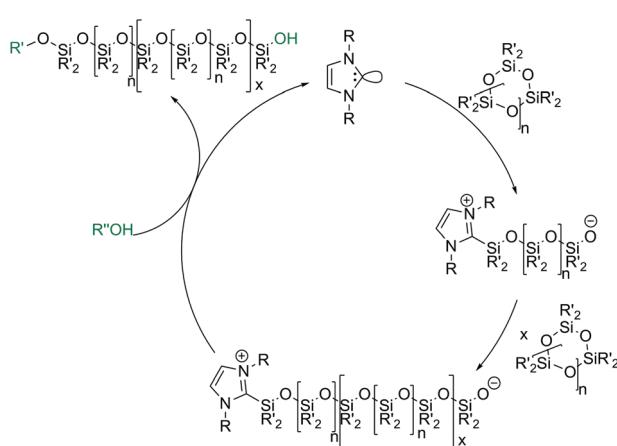
Scheme 7 Proposed reaction mechanism for the NHC initiated ring-opening polymerization of cyclic siloxanes by monomer activation.

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Table 2 Relative rates k/k_0 of polymerization of D^F_3 initiated by sodium siloxanolate in the presence of different solvents

Solvent	$c_{Additive}$ [mol L^{-1}]	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

[Sodium siloxanolate] = 2×10^{-2} mol L^{-1}. k_0 is the observed first-order rate constant in the absence of an activator.


Scheme 8 Mechanistic details of the CROP of cyclosiloxanes. (a) Chain propagation (as postulated by Toskas et al.) and (b) chain transfer reaction.

order with the monomer if no additive is used. Some of these results are summarized in Table 2.[95,101]

Effect of the monomer structure: In general, the reactivity of the monomers decreases with increasing ring size: $D_3 \gg D_4 > D_5 > D_6$. Hexamethyltrisiloxane (D_3) has the largest ring strain among cyclic siloxanes and shows very high reactivity in ROP and therefore, is often used in non-equilibrium polymerization processes.[58] This has the advantage that minimal back-biting and chain randomization take place.[39] Nevertheless, the preparation of D_3 is complex and therefore its commercial availability is limited.[41] The reactivity order of cyclosiloxanes is reversed if the polymerization is performed under neat conditions or in a non-polar solvent in combination with an alkali metal silanolate.[40,102] This might be explained by the formation of crown ether-like complexes due to a multidentate interaction of D_6 or D_7 rings with the cation.[103]

2.2.2. Cationic ROP. CROP is initiated by either Brønsted or Lewis acids and it is used specially for monomers with reactive functional groups such as Si–H or Si–Cl, which are not stable in the presence of strong bases. The simultaneous generation of linear polymers and cyclic oligomers is disadvantageous to this process.[104] The polymerization mechanism is complex and is still a subject of debate in the literature due to the fact that some unusual kinetic behaviors have been observed.[105–108] These are, for instance, a negative order in monomer concentration and negative activation energy.[106] The role of water in the polymerization process is also a subject of discussion since it can act as both a promotor and an inhibitor in the CROP.[104]

The polymerization mechanism using triflic acid as an initiator has been studied in depth, and will serve as an example for the following mechanistic considerations.[105,109] In general, it is accepted that the Si–O-bond is cleaved by strong protic acids during the initiation reaction. Thereby, the corresponding silyl ester silanol is formed which starts the chain propagation.[104] It is proposed that homocomplexes of the acid (TfOH·TfO$^-$; [(TfO$_2$)H]$^-$) or the hydrate of the acid ([TfO·H$_2$O]$^-$) are formed and they act as initiators since the ester group is inactive.[110] Toskas et al. proposed that chain propagation is based on the formation of trisiloxonium ions (Scheme 8a).[107] The most relevant side reactions during CROP are chain-trans-

fer (Scheme 8b)[111] and back-biting. The latter, unlike in the AROP, takes place via intramolecular condensation processes leading to a product mixture of macrocyclic rings and linear polymers.[104,107]
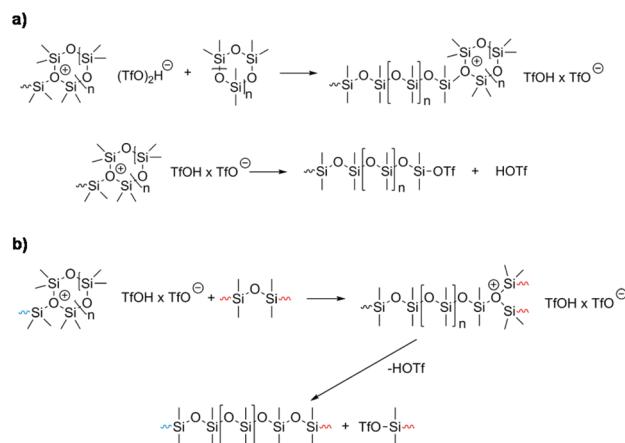
Strong protic acids such as sulfuric,[25,112] sulfonic[31,107,109,113] and perchloric acid initiators are used in the CROP.[101] Sulfuric acid is the earliest reported initiator for the CROP of cyclic siloxanes.[112] Sulfonic acids which are described in the literature as successful initiators include triflic acid (HOTf)[107] and bis(trifluoromethyl)sulfonimide (TFSI-H).[114] Heterogeneous initiators such as ion exchange resins, acid-treated graphite[115] or acid treated clays[116] can also be used in CROP.[101] They bear the advantage that they can be easily separated from the product after the reaction.

An alternative method for initiating the CROP is the generation of trisiloxonium ions by an in situ hydride transfer. It has the advantage that a simple addition polymerization takes place since the chain-propagation takes place only in one direction.[108] Another alternative is the CROP of D_3 with trimethylsilyl triflate in the absence of strong protic acids.[117]

2.2.3. Industrial processes for obtaining OH-terminated PDMS via ROP. In most patents dealing with the ROP of cyclic siloxanes, the inventors do not specify the end-groups of their polymers. However, since most of them use disiloxanes as end-capping agents, it can be expected that these moieties can be found at the chain termination of the obtained polymers. As mentioned above, silanol-terminated polysiloxanes can be obtained by quenching the polymerization with water or by introducing water during the polymerization process. Patent US 5475077 describes a batch process for the synthesis of defined OH-terminated silicones via AROP.[22] For this, a mixture of cyclic siloxanes (mainly D_3, D_4, and D_5) is reacted with an aqueous solution of KOH at 170 °C. The reaction mixture is purged with steam to remove air and other gases. After keeping the reaction mixture for some time at this temperature and under a certain pressure of water vapor, ethylene

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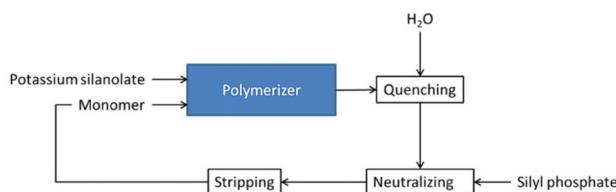
Scheme 9 Simplified flow diagram of the process for the production of OH-terminated silicones *via* AROP.[24]

chlorohydrin is added to neutralize the KOH, which precipitates as salt in the mixture. The reaction product is then stripped and a silanol terminated PDMS is obtained. The viscosity of the obtained polymer, which depends on the molecular weight and polydispersity, is controlled by the water vapor pressure in the vessel. The higher the water vapor pressure, the lower the viscosity of the resulting product.[22]

A continuous process for the synthesis of silanol-terminated polymers *via* AROP has been described in patent US 4250290 (Scheme 9).[24] It is a cascade of plug-flow reactors where the monomer is fed continuously. The reaction is conducted at 145 °C. Potassium silanolate is used as an initiator and the reaction is quenched with water at an early stage. This is necessary to control the rapidly increasing viscosity of the reaction mixture, hence avoiding mixing problems.[24]

Another patent describes the synthesis of silanol-terminated PDMS *via* CROP. The polymerization of a mixture of cyclic siloxanes with either aqueous H_2SO_4 or a combination of aqueous HCl with tetramethylammonium tetrachloroferrate is performed in a loop-type reactor (Scheme 10). Both the time of residence and the reaction temperature depend on the chosen initiator. The unstripped polymer is obtained *via* phase separation. In the case of sulfuric acid as an initiator the yield is about 55% and the polymer contains less than 1 ppm of H_2SO_4.[25]

Phosphazene bases can also catalyze condensation reactions.[29,32,70] For example patent EP 1008611 claims the synthesis of silicone polymers *via* ring-opening polymerization and condensation polymerization at the same time in an equi-

librium state.[70] In the reaction mixture, the siloxanes and the catalyst are mixed with water along with a OH-terminated polysiloxane or an alcohol to yield a polymer. Additionally, an end-capping agent may be used to produce a polymer with a targeted molecular weight. In general, a silanol-terminated siloxane or an alkoxy- and silanol-terminated siloxane is used as a starting material.[70] With this method also hydroxyl-terminated polymers can be obtained.[70]

2.3. Emulsion polymerization

First patented in 1959,[118] the polymerization of organosiloxanes in aqueous emulsions either by ROP[31,113] or polycondensation,[119,120] is of great importance regarding sustainability.[39] Silicone emulsions of polyorganosilanols in water are obtained as a product, which can be used in disperse dyes,[121] disperse adhesives,[122] and in personal-[123] or home-care applications.[124]

Regarding the emulsion polymerization of cyclic siloxanes, the process itself and the mechanism behind it are relatively complex. The process involves a delicate balance among chemical reactions, physico-chemical phenomena such as diffusion processes, phase equilibria and the nature of the interface, commonly modified by the use of surfactants.[40] Favored surfactants 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 initiate the polymerization themselves. Nevertheless, they can be used in combination with classic initiators. Cationic emulsifiers may be used in addition to basic initiators, whereas anionic emulsifiers are used in combination with acidic initiators.[40]

Besides the basic reactions of the ROP (initiation, chain growth and termination), condensation reactions of the OH-terminated oligomers and polymers can occur. Other side reactions are back-biting and redistribution as well as depolymerization. Recent reports propose that the initiation and propagation of the ROP of cyclic siloxanes take place *via* homogeneous nucleation in the continuous phase.[125,126]

The reaction mechanism of the emulsion polymerization of cyclic siloxanes can be divided into three stages (Scheme 11).[125,126] In *Stage I* ROP is initiated by the emulsifier itself, leading to small oligomeric silanolates which undergo propagation until the chain becomes 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 in the absence of micelles. 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,
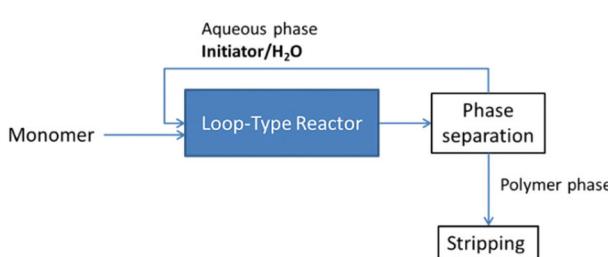
Scheme 10 Simplified flow diagram of the process for the synthesis of silanol terminated PDMS *via* CROP.[25]

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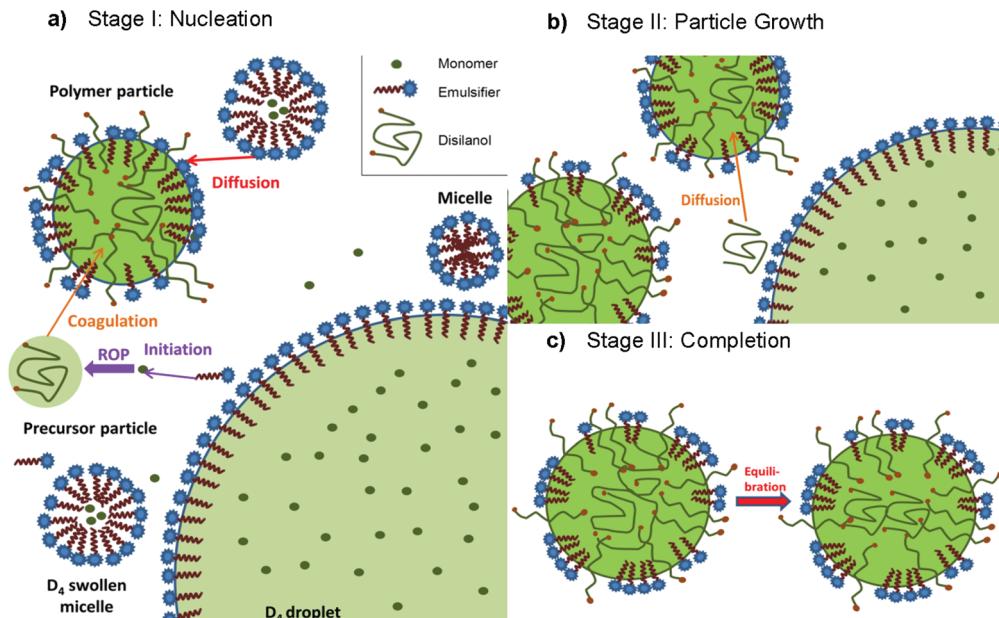
Scheme 11 Schematic presentation of the three stages of emulsion polymerization of cyclic siloxanes (exemplary for D_4).[125,126]

since step-growth polymerization occurs *via* condensation of small oligomers which subsequently form macrocyclic siloxanes by intramolecular condensation.[125,126]

As already mentioned, emulsifiers can initiate the polymerization process themselves. In patent US 4999398 the inventors describe that dodecylbenzenesulfonic acid is capable of forming a stable microemulsion with D_4 in aqueous media as well as initiating CROP.[113] In patent US 3294725 the same phenomena are observed by using a combination of dodecylbenzene sulfonic acid and its sodium salt.[31] Polycondensation in emulsions is also possible. In patent US 6232396 they use dodecylbenzenesulfonic acid as an emulsifier, which is neutralized with Na_2SO_4 at the beginning of the reaction. Then, an emulsion is prepared with water and a low molecular weight silanol-terminated PDMS. The condensation is then initiated by the addition of concentrated sulfuric acid.[119] In patent US 9156954 they describe a similar process to yield silanol terminating groups in the final polymer.[120] All the described processes have an occurrence in common that in the end a stable aqueous polysiloxane emulsion is obtained which is not further treated. Interestingly, the polymerization reaction can be terminated by simply adding a salt such as NaCl.

3. Conclusions

There is broad palette of available synthetic methodologies to prepare reactive silicones, specially telechelic OH-terminated polysiloxanes, making use of many catalytic technologies. These methods include the classic anionic and cationic ring-opening polymerizations and more "sophisticated" modern approaches such as aqueous emulsion polymerization and

polycondensation reactions. Interestingly, even though these reactions are currently a subject of multi-ton industrial processes, their underlying reaction mechanisms are still a subject of debate.

Consequently, as it is common practice in industry, the control of these polymerization processes and the tailoring of the physico-chemical properties of the produced materials are done mostly empirically, hampering the further advancement of the field. Hence, it is necessary to deepen the chemical knowledge available on silicon(e) chemistry by applying modern analysis and modeling techniques for mechanistic investigations.

Moreover, considering the current society's drive towards a "greener" and more sustainable chemical industry, it is foreseeable that novel reactive silicone materials will emerge, displaying novel properties and reactivities (including biodegradability, hydrolysability, bio-compatibility, *etc.*) which will enable their use in even more applications in tune with the current human needs.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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