## Preparation of Organosiloxane Telechelics by Anionic Ring-opening Polymerization

Subjects: Polymer Science

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Polydimethylsiloxanes (PDMS) telechelics are important both in industry and in academic research. They are used both in the free state and as part of copolymers and cross-linked materials. The most important, practically used, and well-studied method for the preparation of such PDMS is diorganosiloxane ring-opening polymerization (ROP) in the presence of nucleophilic or electrophilic initiators. Anionic ring opening polymerization (AROP) under the action of various nucleophilic reagents is widely used for the synthesis of high molecular weight polydiorganosiloxane telechelics with various organic surroundings of the siloxane chain. In the process of cyclosiloxane opening and chain growth, side processes may occur: depolymerization due to the breaking of the linear chain by the active center (backbiting reaction) with the formation of low molecular weight cyclic products, and chain transfer reaction, in which the terminal active site attacks the siloxane bond of another polymer chain, leading to a redistribution of macromolecules, which is also called equilibration

Keywords: polysiloxanes ; ring-opening polymerization ; PDMS

### 1. Introduction

Polyorganosiloxanes are one of the most important classes of polymers with great practical importance. The nature of the backbone determines the set of unique characteristics of these macromolecular compounds, making them indispensable in the creation of materials widely used in various fields of practice, ranging from construction, engineering, agriculture, and environmental protection to medicine, cosmetics, pharmaceuticals, and home care products [1][2][3][4][5]. Siloxanes have low surface tension, hydrophobicity, good surface wettability, damping properties, low glass transition temperature and frost resistance, low temperature dependence of physical properties, low toxicity and flammability, and they are safe for the environment [6][Z][8]. The most important property of siloxanes is biocompatibility, which are already actively used in science and technology [9]. The development of new high-tech industries, such as organic electronics and photonics, 3D printing, gas separation, and drug delivery, has led to a further expansion of the applications for various types of organosiloxane polymers [8][9][10][11][12][13][14].

The significant feature of organosiloxane polymers in comparison with classical organic macromolecules is determined by a significantly higher Si–O bond energy than the C–C and C–O bonds in the main chains of organic polymers <sup>[15]</sup>; it determines high-temperature characteristics, and slight changes in physical properties over a wide temperature range. A longer bonds and wider angle of rotation compared to carbon analogues determine the high flexibility of the siloxane chain, low glass transition temperature, and high gas permeability. A weak intermolecular interaction also determines one of the significant disadvantages of organosiloxanes: their relatively low physical and mechanical properties <sup>[16]</sup>. Searching for ways to overcome this significant drawback, while maintaining the main advantages of this class of polymers, has continued throughout the history of their development.

More recently, however, these researches have reached the highest level of property control—the structure of synthesized polymers is improving. As a result, many highly organized polymeric structures have appeared, among which dendrimers, multi-arm stars, and molecular brushes can be noted [17][18]. These macromolecular systems have a number of unique properties that were first made available through the use of well-organized functional precursors. The appearance of dense molecular brushes in which polymer side chains were grafted to linear skeletons [19] marked other forms of intermolecular interaction. In particular, it facilitated the disentanglement of chains in polymer melts [20][21][22] and opened up prospects for creating a brush-like architecture for the creation of modern elastomers [23], thermoplastics [24][25], and molecular ensembles [26][27]. In contrast to linear-chain networks, brush-like networks are determined by three independent structural parameters: main chain length, side chain length, and grafting density. This transforms the one-dimensional parameter space of synthetic elastomers into a multidimensional landscape of available correlations.

However, for the synthesis of multi-arm stars and for obtaining dense molecular brushes, well-organized narrowly dispersed functional oligomers of various structures are needed as building blocks.

### 2. Anionic Ring Opening Polymerization (AROP) Initiators

Hydroxides of alkali metals, quaternary ammonium, and phosphonium bases and their derivatives, siloxanolates are most frequently used as process initiators, which leads to the formation of terminal silanolate anions that are active centers in the polymerization reaction.

Potassium hydroxide is one of the first initiators used for ROP of cyclic siloxanes. Its usage dates back to 1948, when ring-opening polymerization with alkali metals was first patented. With its usage, octamethylcyclotetrasiloxane was converted into a high molecular weight (HMW) polymer by heating for two hours at T = 140 °C. The polymer contained 13–15% low molecular weight volatile products; the MW of the main fraction varied from 100,000 at 10% conversion to 1,000,000 at equilibrium <sup>[28]</sup>. However, the active end groups remaining in the system caused the process of depolymerization at high temperatures; the polymer lost 99% of its mass when kept for 24 h at 250 °C. The formation of a stable product was achieved by neutralizing the product as quickly as possible.

Already in early works, it was demonstrated that the rates of polymerization under the action of hydroxide and siloxanolate of the same metal are the same  $^{[29][30]}$ . The activity of hydroxides and siloxanolates of alkali metals during bulk polymerization decreases in the series Cs > Rb > K > Na > Li  $^{[31]}$ . Tetramethylammonium and tetrabutylphosphonium siloxanolates are comparable in activity to Cs compounds  $^{[32]}$ . The great advantage of these compounds is the possibility of their deactivation and complete decomposition when the polymer is heated, which makes it possible to obtain a neutral thermostable polymer without using the end group blocking step.

In the middle of the last century, many research works were devoted to the mechanism of interaction between the anionic center and the siloxane bond. It was shown that silanolates exist in the polymerization system as associates of various sizes. During polymerization under the action of Na, K, and Cs silanolates, apparently, the initiator is present in the system in the active monomeric form and in the form of a low-active binary silanolate complex formed both intermolecularly and within one macromolecule <sup>[33]</sup>.

The size of associates significantly depends on a specific alkali metal atom and affects both the rate of polymerization and the occurrence of side processes <sup>[34]</sup>. An increase in the polarity of the polymerization medium by changing the nature of the solvent or introducing small amounts of polar additives leads to the destruction of inactive metal associates and the formation of solvated ion pairs, which significantly increases the rate of polymerization of cyclosiloxanes <sup>[35][36][37]</sup>. Butyllithium is the most popular catalyst for non-equilibrium anionic ROP <sup>[37][38]</sup>. Lithium compounds used as initiators, such as n-, sec- and tert-butyllithium, have a number of features that significantly differ their behavior in ring-opening anionic polymerization reactions, especially in the case of D3. In a non-polar medium, when D3 and BuLi react, the reaction products are exclusively the corresponding BuDLi and the remaining cyclosiloxane <sup>[39]</sup>:

 $BuLi + [Me_2SiO]_3 \rightarrow BuSiMe_2OLi + 2/3[Me_2SiO]_3$ 

Apparently, due to the abnormally low activity of the lithium counterion and the high tendency to aggregation, the formation of inactive associates leads to the appearance of the first silanolate groups. Then the attack proceeds only along the activated siloxane bond adjacent to the silanolate bond until they are completely exhausted, and the process of opening no cycles. This feature formed the basis for the creation of a two-stage procedure for carrying out ROP D3 polymerization. The first stage is carried out in solution in a non-polar medium to convert active groups into a silanolate form with equal activity, and at the second stage, with the introduction of activating polar agents, the process continues until the initial cyclosiloxanes are exhausted. This approach makes it possible to obtain monomodal narrowly dispersed polydimethylsiloxane.

An interesting effect of solvation and separation of associates of active sites, leading to an increase in the polymerization rate, is observed in the polymerization of dimethylcyclosiloxanes with n > 5. The rate of polymerization of cyclosiloxanes with n = 7 and 8 is more than 100 times higher than the rate of polymerization of octamethylcyclotetrasiloxane. This acceleration is explained by the coordination of the metal by the oxygen atoms in the cyclosiloxane molecule, similarly to the interaction between the cation and the crown ether <sup>[40]</sup>. However, this effect was not subsequently reproduced or somehow confirmed. Apparently, the "crown" is instantly exhausted during the reaction process.

A polymer with a polydispersity index close to 1 was obtained using strong complexing agents as polar additives, for example, crown ethers and cryptates of the appropriate size <sup>[37]</sup>. The complexes were formed in these cases with the

lithium counterion of the initiator. It led to the complete destruction of their aggregates and a significant increase in the polymerization rate in the almost complete absence of depolymerization processes. This technique was also successfully used in the polymerization of hexaethylcyclotrisiloxane, which is much less active than hexamethylcyclotrisiloxane <sup>[36]</sup>.

The results of the study of AROP with a lithium counterion in the presence of traces of water are of practical importance. In this case, even when using a monofunctional, widely used organolithium initiator, the formation of a telechelic occurs due to the fast exchange reaction  $\sim$ SiMe<sub>2</sub>-O-Li + HOH  $\leftrightarrow \sim$ SiMe<sub>2</sub>-OH + Li-OH and subsequent opening of cyclosiloxane in situ with lithium hydroxide, with the formation of a macromolecule with two terminal functional groups. It was shown that between the active end groups  $\sim$ SiMe<sub>2</sub>-OLi and  $\sim$ SiMe<sub>2</sub>-OH there is a rapid exchange and the formation of an associate, and these ends are equally active in the process. The ratio of the amounts of water and lithium initiator in the system determines the rate of the process; an increase in the amount of water leads to an increase in the induction period. In this case, when using a monofunctional initiator, a monomodal telechelic is formed at [init] << [HOH]. In the case of [init]~ [HOH], the polymerization product is bimodal with the presence of monofunctional macromolecules <sup>[41]</sup>.

The most important class of initiators are tetraalkylammonium and tetraalkylphosphonium hydroxides and silanolates, which are used both in earlier publications and today <sup>[42][43][44]</sup>. The advantage of this series of catalysts is that, compared to other catalysts, they are quite easily removed from the polymer—they undergo thermal decomposition with the formation of volatile by-products and a neutral, thermally stable polymer.

Another group of catalysts is quaternary phosphazene bases. They catalyze the polymerization of D4 in exactly the same way and decompose at high temperatures in the same way. Decomposition products are non-toxic and do not react with the polymer <sup>[45][46][47]</sup>.

Modern studies also mention new types of AROP catalysts. Jinfeng Shi et al. showed that the organic cyclic trimeric phosphazene base (CTPB) is highly efficient for the ring-opening polymerization (ROP) of octamethylcyclotetrasiloxane (D4) and the copolymerization of D4 with octaphenylcyclotetrasiloxane (P4) under mild conditions. The polymerization proceeds rapidly, and the obtained polymers have a rather high molecular weight (Mn up to 1,353,000 g/mol). For the copolymerization of D4 and P4, it is easy to prepare copolysiloxanes with different contents of diphenylsiloxane (up to 64 mol%). There was no observed Q- or T-branching for copolysiloxanes in all cases according to 29Si NMR analysis, indicating good ROP control with the current CTPB/BnOH catalyst system. DSC analysis confirms that the copolysiloxanes are amorphous and Tg increases with increasing diphenylsiloxane content in the polymer chain. TGA analysis shows that the increase in thermal stability is achieved by introducing a diphenylsiloxane unit <sup>[48]</sup>.

Recently there have been reports on the use of N-heterocyclic carbenes or bicyclic guanidines as AROP initiators. For example, Marta Rodriguez et al. report that N-heterocyclic carbenes are effective ROP catalysts for cyclotetrasiloxane D4 under mild conditions. Interestingly, a system using primary alcohols (MeOH and BnOH) more effectively controls the molecular weight of the polymer; the molecular weight of silicone polymers can be controlled by simply changing the amount of alcohol initiator. Due to neutral conditions, the only by-products are a catalytic amount of moisture sensitive NHC and volatile alcohol, which are easily removed<sup>[49]</sup>.

However, other types of catalysts are also mentioned in the current literature. For example, Bashim Yactine used potassium vinyldimethylsilanolate (KVDMS) and potassium trimethylsilanolate (KTMS) catalysts in his work to perform ROP. Anionic polymerization of D3 initiated by potassium vinylsilanolate proved to be very efficient for the synthesis of difunctional and monofunctional polydimethylsiloxanes, respectively <sup>[50]</sup>.

Oka et al. used the urea anion as a catalyst for ring-opening polymerization (ROP) of a cyclic siloxane initiated from silanols, which allowed control of the molecular weight and fineness of the final product. ROP of D3 was initiated with a trifunctional silanol ( $I_3$ ), to form star-shaped polysiloxanes. Trifunctional silanol  $I_3$  is relatively poorly soluble in THF; deprotonation of  $I_3$  with NaH in THF led to the formation of a precipitate. However, the addition of U(4CF<sub>3</sub>) to this mixture solubilized the ionic species to give a homogeneous compound. The D3 conversion reached 96% in 60 min, although the dispersity increased slightly. Urea anion catalysts are particularly useful for producing lower molecular weight polysiloxane stars. Moreover, the combination of silanols and urea anion catalysts overcomes the solubility problem arising from the polarity mismatch between the initiators, D3 and polydimethylsiloxanes (PDMS) <sup>[51]</sup>. However, this process remains rather complicated.

An organocatalytic controlled or living ROP of cyclotrisiloxanes using water as an initiator, strong organic bases as catalysts, and chlorosilanes as blocking agents was developed by the Keita Fuchise group for a convenient and efficient method for the synthesis of linear polysiloxane telechelics and their copolymers. It was shown that guanidines B, namely guanidines containing the R-N=C(N)-NH-R' unit, showed the highest catalytic activity depending on their Brønsted

basicity among the tested organic bases. In particular, TMnPG, monocyclic guanidine B, was the best in terms of its high catalytic activity and low number of side reactions <sup>[52]</sup>.

The polymerization rate of AROP depends on the nature of the initiator, the polymerization medium, and the selected monomer. However, the key factor controlling the kinetics of ring-opening polymerization is the counterionic interaction of silanolates leading to the formation of aggregates that are inactive in AROP <sup>[29]</sup>.

The polymerization itself can be carried out in the bulk, 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. In some examples, THF is used as a solvent in combination with a solid counterion <sup>[53]</sup>.

# 3. Influence of the Structure of the Initial Organocyclosiloxane on the AROP Process

The next parameter that determines the course of the AROP process is the structure of the starting organocyclosiloxane and the nature of the organic substituents at the silicon atom.

The influence of the size of the initial cyclosiloxane is clearly manifested in the case of the most widely used dimethylsiloxane cyclosiloxanes, hexamethylcyclotetrasiloxane (D3) and octamethylcyclotetrasiloxane (D4). The difference between these compounds and, accordingly, the conditions and results of their polymerization processes is quite large.

The similarity of the binding energies in dimethylcyclosiloxanes with n > 3, primarily in octamethylcyclotetrasiloxane and in linear dimethylsiloxanes, leads to the fact that the process is ongoing exclusively due to the thermodynamic component. Ionic active centers attack and break the Si–O bonds both in dimethylcyclosiloxane and in the resulting linear polymer, carrying out the depolymerization process parallel to polymerization. The result is a mixture of linear and cyclic siloxanes with different ring sizes. In the system, over time, an equilibrium is established between the polymer and the mixture of cyclosiloxanes. The equilibrium position in this case does not depend on temperature, because  $\Delta H$ ~0, same as the nature of catalyst and solvent [54].

The process of polymerization of hexamethylcyclotrisiloxane, which has a significant intensity of the three-link cycle, looks different, as a result of which the thermal effect of polymerization is  $\Delta$ H~3–4 kk/mol. The presence of an energy gain during the opening of hexamethylcyclotrisiloxane makes it possible, under certain conditions, to carry out polymerization in a nonequilibrium mode, which excludes depolymerization reactions and interchain exchange. The rate of polymerization of hexamethylcyclotrisiloxane under comparable conditions is almost 100 times higher than the rate of polymerization of octamethylcyclotrisiloxane. This method for the synthesis of polydimethylsiloxane makes it possible to obtain polymers with a controlled molecular weight, specified end groups, and a narrow molecular weight distribution (Mw/Mn = 1.0–1.2) [37][55][56], and the resulting dimethylsiloxane telechelics are widely used to obtain siloxane block copolymers polymer networks. The use of appropriate blocking reagents makes it possible to obtain polymer products with specified end groups [56]. The disadvantage of this method for obtaining polydimethylsiloxane telechelics is the need to obtain hexamethylcyclotrisiloxane, which is a more expensive monomer than unstrained cyclosiloxane, and stringent requirements for the process conditions for the purity of the system and temperature. Thus, from a commercial point of view, the polymerization of octamethylcyclotetrasiloxane is preferred [57][58].

The process of polymerization of diphenylcyclosiloxanes, both 6- and 8-membered, is completely different from other. Polydiphenylsiloxanes (PDFS) have very high thermal and radiation resistance, a very high melting point (about 265 °C), and mesophase properties <sup>[59]</sup>, in connection with which they are of great interest; however, the preparation of telechelics and, in general, polymers of this nature remained an unsolved problem for a very long time. The extremely high tendency to cyclization of the diphenyl chain, caused by the steric factor, apparently playing a decisive role in this case. In all polycondensation and polymerization processes, the reaction product was either tetraphenyldisiloxanediol, or further octaphenylcyclotetrasiloxane <sup>[60]</sup>. Under anionic conditions, the polymerization and depolymerization processes proceed simultaneously and at the same rate and lead to the formation of low molecular weight cyclic products. Moreover, only in this case, the differences in the tension of the initial 6- and 8-membered diphenylcyclosiloxanes do not play a significant role: apparently, the thermodynamic unfavourability of the polymer chain leads to its absence in the products of the equilibrium process. The implementation of a nonequilibrium process without a significant occurrence of depolymerization was only possible under the conditions of solid-state polymerization of hexaphenylcyclotetrasiloxane at temperatures close to the melting point of the cycle, but not reaching it. It was shown that polymerization proceeds under heterogeneous conditions; the reaction proceeds inward from the surface of HPTS crystals and leads to the formation of a

crystalline polymer, with polymerization and crystallization proceeding sequentially <sup>[61]</sup>. In this case, the crystallinity of polymerized PDPS samples is inversely proportional to its specific viscosity <sup>[62]</sup>.

From the point of view of the arrangement of functional groups, the literature considers the preparation of two types of siloxane telechelics obtained by ROP: siloxane oligomers with functional groups directly bonded to terminal silicon atoms (Si–X) and siloxane oligomers with an organofunctional end (Si–R–X). Moreover, in addition to functional ends, functional groups can also be attached to the backbone of the polysiloxane. This can be achieved by the aforementioned ROP of cyclotetrasiloxane as well as by catalytic rearrangement reactions. However, instead of the usual D4 or D3 that give known PDMS, the methyl group(s) attached to the Si atom of cyclic siloxanes can be replaced with different functional groups before polymerization <sup>[63][64]</sup>.

The above processes proceed according to one of three different basic reaction mechanisms: cationic, anionic, or coordination intercalation <sup>[65]</sup>.

The next factor that has a significant effect on the course of polymerization is the nature of the organic groups at the silicon atoms of siloxane cyclosiloxanes. The introduction of electron-donating substituents—longer hydrocarbons than the methyl group—reduces the rate of anionic polymerization of cyclosiloxane, while electron-withdrawing substituents— alkenyl, aromatic, phenyl, 3,3,3-trifluoropropyl or cyanoalkyl groups—increase the rate of polymerization [66][67][68]. In this case, electron-withdrawing substituents at the silicon atom during anionic polymerization lead to the formation of a siloxanolate anion with a lower nucleophilic activity, which somewhat levels out the increase in the activity of cycles during polymerization. In addition, the steric influence of bulky radicals leads to low reactivity of the corresponding cyclosiloxanes [69].

### 4. Preparation of Monochelical PDMS by AROP

Monofunctional PDMS, also referred to as "macromonomers", are usually synthesized by living anionic polymerization of hexamethylcyclotrisiloxane. These experiments were first carried out in the 1960s by Bostick <sup>[70]</sup> and Lee <sup>[37]</sup>, and showed the possibility of obtaining monofunctional polydimethylsiloxanes with controlled molecular weight and narrow molecular weight distribution by anionic polymerization of hexamethylcyclotrisiloxane (D<sub>3</sub>) using lithium silanolate salts (R-Li<sup>+</sup>) or lithium as initiators in the presence of promoters such as THF or diglyme.

Theoretically, anionic polymerization can be carried out using D4, however, the reaction will tend to equilibrate even at low conversions. Accordingly, the resulting polymers have a relatively broad molecular weight distribution and contain appreciable amounts of macrocyclic oligomers <sup>[37]</sup>. By using a cyclic trimer as a starting material, siloxane redistribution processes other than the desired ring-opening chain propagation reaction can be almost completely eliminated. This is mainly due to the ring tension in the D3 monomer, which significantly increases its reactivity towards anionic initiators. Selectivity is further enhanced by the use of initiators in which lithium is the counterion. Initiators containing lithium counterions are preferable to counterions of other alkali metals because of the lower catalytic activity of lithium in siloxane redistribution reactions  $^{[71]}$ . Monofunctional oligomers are characterized by low molecular weight (500–20,000 g\*mol<sup>-1</sup>).

Using the ROP  $D_3$  mechanism in the presence of BuLi, hydridesilyl monofunctional PDMS <sup>[72][73]</sup>, acrylate monofunctional PDMS <sup>[74]</sup>, and amine-containing monofunctional PDMS <sup>[75]</sup> are obtained.

Vysochinskaya Y.S. et al. <sup>[76]</sup> synthesized monofunctional vinyl PDMS from  $D_3$  in the presence of BuLi as a catalyst and dimethylvinylchlorosilane as a blocking agent. The resulting compounds were used to prepare star-shaped polymers by hydrosilylation reaction with cyclic nuclei with Si-H groups in the presence of Karstedt's catalyst.

Kawakami Y. et al. [77] used the same method to obtain monofunctional macromonomers of the styrene and methacrylate type, which are the starting compounds for obtaining graft polymers :

Martin Fauquignon et al. synthesized a series of PDMS-b-PEO diblock copolymers of various molar masses and hydrophilic mass fractions. He used monofunctional 3-chloropropyl-PDMS which were synthesized by anionic ring-opening polymerization of the hexamethylcyclotrisiloxane (D3) monomer in anhydrous THF at 80 °C. Butyllithium was used as the initiator, functionalization of the end of the chain was obtained using chloro-(3-chloropropyl)dimethylsilane as a termination agent <sup>[78]</sup>. The subsequent conversion of the chloropropyl group to the azidopropyl group made it possible to obtain poly(dimethylsiloxane)-block-poly(ethylene oxide) (PDMS-b-PEO) diblock copolymers by click chemistry. These polymers are applicable in the developing field of hybrid polymer/lipid vesicles. According to the same scheme, monofunctional azide PDMS were obtained in <sup>[79][80]</sup> for the subsequent preparation of copolymers.

The functional end group can be introduced either by the organo segment of the initiator or by the chlorosilane molecule. Functionalized initiation has been reviewed by Casey L. <sup>[81]</sup>. A number of poly(dimethylsiloxane) homopolymers in the molar mass range from 2400 to 15,000 have been synthesized using 3-[(N-benzyl-N-methyl)amino]-1-propyllithium. The protecting group on PDMS was quantitatively removed by hydrogenolysis to give a secondary amine:

A recent review by Goff J., Sulaiman S., and Arkles B. <sup>[82]</sup> is dedicated to the production of monofunctional PDMS and their application. However, the use of monofunctional PDMS in copolymerization reactions is rather limited. It is much more common to obtain difunctional terminal (telechelic) silicone oligomers, which are the starting compounds for a wide range of silicone copolymers.

### 5. Obtaining Functional Telechelics by AROP

For the further usage of organosiloxane telechelics, the nature of the terminal functional groups is an important parameter. Since the end of the last century, the most important PDMS-telechelics have been obtained by the AROP mechanism: vinyl-functional <sup>[83][84]</sup> and amine-functional <sup>[85][86][87]</sup>, etc.

Obtaining new functional PDMS-telechelics is also relevant in time. Li X. et al. <sup>[88]</sup> obtained aminopropyl terminated polydimethylsiloxane in the presence of a tetramethylammonium hydroxide catalyst by the AROP mechanism to subsequently obtain silicone elastomers with good mechanical properties, as well as high self-healing efficiency through a simple amino-ene addition reaction according to Michael. A basic TMAH catalyst is added to the system to provide a dynamically crosslinked silicone elastomer network. Tensile tests show that the silicone elastomer has very good mechanical properties for an unfilled silicone composition with a tensile strength and an elongation at break of  $1.08 \pm 0.06$  MPa and  $206.10 \pm 9.55\%$ , respectively. After holding at 105 °C for 24 h, the tensile strength of "broken" specimens can recover 91% of their original strength, and specimens cut into multiple pieces can regain their original shape.

Also, the preparation of aminopropyl terminated polydimethylsiloxane by the anionic ROP mechanism is reported in the work of V.V. Gorodov <sup>[89]</sup>. The resulting oligomeric amine-containing PDMS was subsequently treated with itaconic acid in an o-xylene solution in the presence of anhydrous magnesium sulfate as a dehydrating agent. Thus, telechelic oligodimethylsiloxanes with 4-carboxypyrrolidone fragments were synthesized and their thermal and rheological properties were studied. These polymers have been found to be prone to the formation of smectic-type mesophases. The introduction of carboxypyrrolidone groups into the siloxane chain significantly increases the viscosity and activation energy of the viscous flow of oligodimethylsiloxanes.

The group of Zuo Y. <sup>[90]</sup> obtained vinyl functional PDMS telechelics, as well as vinyl functional copolymers by the AROP D4 mechanism in the presence of a tetramethylammonium hydroxide catalyst. Then these polymers were functionalized with N-acetyl-L-cysteine using thiol-ene chemistry, subsequently forming new transparent, luminescent silicone elastomers. Luminescence centers were formed by complexation of lanthanide ions into a functionalized polysiloxane.

It should be noted that in modern studies on the ROP mechanism, it is possible to obtain telechelics with new functional groups. For example, F.V. Drozdov et al. reported the production of a number of unusual functional PDMS telechelics by the ring-opening polymerization D4 mechanism, using various functional trisiloxanes as a stopper and TfOH/Purolite/tetramethylammonium silanolate (TMAS) as a catalyst. If acid-resistant functional groups were present in the monomer, TfOH or Purolite was used as an acid catalyst and bulk polymerization was carried out. Otherwise, a basic catalyst was used and the reaction was carried out in toluene. For the polymerization of PDMS(St-CH<sub>2</sub>NHBoc)<sub>2</sub>, a number of catalysts were used: TfOH, Purolite, tetramethylammonium silanolate (TMAS), and KOH. In the case of acidic catalysts (TfOH and Purolite), only an insignificant part of the starting monomer participated in the polymerization even for 48 h at 60 °C. Using TMAS, a polymer with high conversion and molecular weight distribution was obtained. Thus, PDMS were obtained in the range of molecular weights from 1500 to 30,000. The synthesis of not only symmetrical oligosiloxanes but also asymmetric hydridosiloxane-containing analogs has potential applications as precursors for the preparation of functional siloxane derivatives by the hydrosilylation reaction. Thus, symmetrical or asymmetric telechelic oligo- or polydimethylsiloxanes with different functional groups are suitable as AA-type blocks for further synthesis of block copolymers <sup>[91]</sup>.

Moving on nonequilibrium processes, it is worth noting the work of Fei H.F. et al.  $^{[92]}$ , where they studied the anionic ringopening polymerization of 1,3,5-tris(trifluoropropylmethyl)cyclotrisiloxane in bulk using dilithium diphenylsilanediolate as initiator (I); and N,N-dimethylformamide (DMF), bis(2-methoxyethyl)ether (Diglyme), and 1,2-dimethoxyethane (DME) as promoters (P). A detailed study of the polymerization kinetics with various molar ratios of promoter to initiator ((P)/(I)), which were equal to 2.0, 4.0 and 6.0, showed that the yield of linear polymers was highest when (P)/(I) 2.0 for all promoters, among which DME was the most effective in suppressing side reactions. The reaction initiated by DME had a very wide "cutoff window" with the highest linear polymer yield and a very narrow molar mass distribution. PMTFPS with end groups such as vinyl, hydroxyl, hydrogen and chloromethyl were obtained and characterized by <sup>1</sup>H NMR, <sup>29</sup>Si NMR, and FT-IR. Vinyl-terminated polymers showed higher thermal stability than hydroxyl-terminated polymers under nitrogen atmosphere.

In a review by Köhler T. <sup>[1]</sup>, the process of obtaining OH-terminated polydimethylsiloxanes by the ROP mechanism is considered in detail. US Pat. No. 5475077 describes a batch process for the synthesis of certain OH-terminated silicones by AROP. To do this, a mixture of cyclic siloxanes (mainly  $D_3$ ,  $D_4$ , and  $D_5$ ) is subjected to interaction 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 chlorohydrin is added to neutralize KOH, which precipitates in the mixture in the form of a salt. The reaction product is then desorbed and silanol-terminated PDMS is obtained. The viscosity of the resulting 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.

In a recent study by Sato K. et al. <sup>[93]</sup>, the researchers obtained of  $\alpha,\omega$ -chain-end-functionalized PDMS with bromomethyl groups also by the ROP mechanism from D3 in the presence of water and a catalyst from the guanidine series using bromomethyldimethylchlorosilane as a blocking agent. The advantages of this approach include the narrow dispersity of the obtained compounds, a fairly wide range of molecular weights, and the disadvantages are a rather laborious synthesis scheme. The resulting compounds were subsequently converted into azide PDMS for subsequent azide-alkyne cycloaddition reactions, model variants of which are also presented in the work.

In another work by the same group of Japanese scientists <sup>[94]</sup>, functional linear polysiloxanes were obtained, namely vinyl, 3-chloropropyl, and allyl by an organocatalytic controlled/living ring-opening polymerization (ROP) of monofunctional cyclotrisiloxanes using water or silanols as initiators, guanidines as catalysts, and chlorosilanes as blocking groups. The AROP method has made it possible to obtain polymers with a controlled number average molar mass (Mn), a narrow molar mass distribution, desirable end structures, and a good distribution of side chain functional groups. It can be expected that this convenient new method for the synthesis of linear polysiloxanes with well-defined functionalized side chains will allow the preparation of organosilicon compounds, hybrid materials with a variety of polymer structures, such as block copolymers, star polymers, comb polymers, and surface modified materials, which will ultimately contribute to the development of new advanced materials with improved properties. The vinyl, 3-chloropropyl, and allyl groups on the side chains can be further converted to other structures through a variety of reactions, including hydrosilylation, thiol-ene, oxidation, and nucleophilic substitution.

The same group of scientists carried out the synthesis of linear polysiloxanes functionalized with disubstituted and monosubstituted alkynyl groups, also by the method of controlled/living ring-opening polymerization of cyclotrisiloxanes using water or silanols as initiators, guanidines as catalysts, and alkynyl (amino) silanes as end blockers agents <sup>[95]</sup>. Two alkynyl(amino)silanes, (diethylamino)dimethyl(phenylethynyl)silane and (diethylamino)ethynyldimethylsilane were synthesized by alkynylation of chloro(diethylamino)dimethylsilane. In addition, the resulting alkynyl-terminated polysiloxanes were subjected to non-catalytic and catalytic Huisgen reactions with organoazide compounds. The resulting polysiloxanes can be used in other reactions involving alkynyl groups, especially alkynylsilyl groups. These new polysiloxanes will provide great opportunities in molecular design and for obtaining polymer structures and cross-linked materials, hybrid materials with controlled molecular or network structure, which, in turn, should lead to the development of new advanced materials with improved properties and/or unprecedented functionalities.

Thus, anionic ROP has been a universal method for the preparation of a wide range of functional PDMS telechelics for many years. At present, the reaction remains relevant, and scientists are able to introduce new types of functional groups (for example, azide and acetylene) into the structure of PDMS, which, of course, expands the scope of such compounds.

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