# Preparation of Organosiloxane Telechelics by Cationic Ring-Opening Polymerization

Contributor: Kseniya A. Bezlepkina, Sergey A. Milenin, Nataliya G. Vasilenko, Aziz Muzafarov

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. Cationic ROP is also of interest for the preparation of functional PDMS. The advantage of this process is that it can be carried out at a relatively low temperature, the catalyst can be easily deactivated, and the process can also be used to synthesize polysiloxanes having base-sensitive substituents such as Si–H or Si–(CH2)3–SH.

## 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][7][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 [15]; 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 [16]. 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.

Siloxane telechelics with various organic surroundings are the earliest well-defined structure products in this class of macromolecular compounds; they are used as starting reagents for the directed molecular design of siloxane polymers and materials for various applications, the importance of which is growing every day [28].

Linear organosiloxane telechelics have been obtained from the beginning of the development of the chemistry of siloxane polymers in the synthesis of high-molecular products, both by polycondensation of difunctional monomers and by ring-opening polymerization of diorganocyclosiloxanes with ionic initiators. Variation of organic substituents in the structure of polydiorganosiloxane telechelics significantly affects the properties of the obtained products; for example, the introduction of aromatic groups increases the thermal, oxidative, and radiation stability, and the introduction of long alkyl groups leads to an improvement in lubricating properties but reduces their thermal stability. The introduction of highly polar 3,3,3-trifluoropropyl substituents increases the resistance of the polymer to the action of nonpolar solvents while maintaining thermal and thermo-oxidative stability [29].

## 2. CROP Initiators

The first high molecular weight siloxane polymer was obtained by ring-opening D4 cationic polymerization in the presence of sulfuric acid. Polymerization in the presence of sulfuric acid proceeds in several stages. Acid is usually introduced in an amount of 1–3% (wt.). Polymerization lasts from two to eight hours at room temperature and leads to the formation of low molecular weight polymers, therefore, at the end of polymerization, a small amount of water is added to the system for subsequent growth of molecular weight. However, the polymerization mechanism is complex and is still a subject of debate in the literature due to the fact that some unusual kinetic patterns have been observed. There is a negative order in monomer concentration and a negative activation energy [30][31]. The role of water in the polymerization process is also a matter of debate as it can act as a promoter and inhibitor in CROP [32].

The mechanism of polymerization using trifluoromethanesulfonic acid as an initiator has been studied in more depth [33][34]. It is generally accepted that the Si–O bond is cleaved by strong protonic acids during the initiation of the reaction. Thus, the corresponding silanol based on the silyl ester is formed, which starts chain growth.

Other catalyst systems have been reported in the literature such as $HClO_4$, aryl and alkyl sulfonic acids, heterogeneous catalysts such as ion exchange resins, acid treated graphite and acid treated clays, and some Lewis acids such as $SnCl_4$ [35][36][37][38][39]. Polymerization in the presence of Lewis acids is a matter of controversy. Strong protonic acids such as $HSnCl_5$, the reaction product of a Lewis acid with water or other protonic impurities, are also suggested as catalysts [40]. However, it was reported that some non-protic systems, such as ethyl boron sesquitriflate [41] and antimony chloride vapors-acid chloride pairs [42], are capable of initiating the polymerization of cyclotrisiloxane. However, they have not received wide distribution due to either insufficiently good process control or their high cost.

Other unusual types of catalysts are also mentioned in the literature. V.M. Djinovic at al. synthesized a series of α,ω-dicarboxypropyloligodimethylsiloxanes with a given molecular weight from octamethylcyclotetrasiloxane and 1,3-bis-(3-carboxypropyl)tetramethyldisiloxane (BCPTMDS) using a macroporous cation exchange resin as an acid catalyst. At the same time, the expected molecular weights in the range from 600 to 3500 were achieved with acceptable accuracy. However, the researchers did not provide data confirming the effectiveness of this catalyst at higher molecular weights [43].

In Yactine B. [44], acid-treated bentonite (sold under the trade name TONSIL1) was chosen as the CROP catalyst because of its ability to catalyze the polymerization of cyclosiloxanes at a relatively low temperature (typically 70 °C) and because of its easy filtration departments. The novelty here is to compare conventional ROP D4 (and sometimes $D^H4$) using a conventional terminating agent with redistribution reactions starting with telechelic polydimethylsiloxanes (PDMS) and D4 commonly practiced in the industry. Such methods will make it possible to obtain Si–H or Si–vinyl terminated telechelic homopolymers and copolymers [45][46].

Javier Vallejo-Montesinos and colleagues have used synthetic and natural silicon aluminates as inorganic acid catalysts for ring-opening polymerization of cyclosiloxanes. In particular, aluminosilicate and bentonite were used as catalysts in the opening of D3 and D4. Such catalysts have proven to be a good choice for the heterogeneous ROP cationic polymerization of cyclosiloxanes. The increase in acid sites due to acid treatment led to the dealumination of materials, which made possible the polymerization of cyclosiloxanes. The structural change in the material caused by the loss of aluminum created the necessary chemical conditions to facilitate the polymerization process. The catalysts were obtained by a relatively simple and economical procedure and were easily separated from the reaction medium. However, product yields were extremely low [47].

In recent years, biocatalysis has become increasingly popular; that is, the use of natural catalysts such as clays in an organic synthesis reaction [48][49]. Djamal Eddine Kherroub and researchers have developed and implemented an alternative method for the synthesis of silicone polymers. This method involves the use of Magnet-H$^+$, an aluminosilicate ecocatalyst designed to initiate the polymerization reaction of pentavinylpentamethylcyclopentasiloxane ($V_5D_5$). A total of 0.1 g of Maghnite-H$^+$ was heated under vacuum with mechanical agitation for 30 min before to use. The polymerization was carried out in bulk. The dried amount of Maghnite-H+ was added to a flask containing 5 g of $V_5D_5$, the flask was carried out in an oil bath at 60 °C under reflux with stirring. After 6 h the reaction was stopped by deactivating Maghnite-H$^+$ by adding cold water to the reaction mixture. However, the presence of additional steps makes the process more complex and less preferable compared to using standard catalysts [50].

## 3. Obtaining Siloxane Telechelics by CROP

The CROP mechanism is used to obtain functional PDMS telechelics widely used in industry: hydride [51][52][53], mercaptopropyl [54], vinyl [55], as well as hydroxybutyl [56], carboxyl [57], and hydroxyl [58].

Today, PDMS-telechelics with "standard" functional groups are obtained for the purpose of their further modification [10]. Thus, Gorodov et al. obtained a series of hydride-containing polymers and copolymers by cationic polymerization of octamethylcyclotetrasiloxane with 1,1,3,3-tetramethyldisiloxane or polymethylhydrosiloxane and hexamethyldisiloxane. The process was carried out at various ratios of reagents in the presence of sulfonic acid resin for 8–10 h at 70 °C. Subsequently, siloxane copolymers containing fragments of undecylenic acid and its esters were synthesized by adding a trimethylsilyl group or tert-butyl undecenoate to the silicon hydride groups of polydimethylmethylhydrosiloxanes by hydrosilylation [59]. In addition, Gorodov V.V. et al. [60] in their review considered the preparation of hydride-containing PDMS and their subsequent functionalization to obtain carboxyl-containing PDMS.

According to the same principle with the same catalyst, polydimethylsiloxanes with side functional hydrosilanes were obtained by Drozdov F.V. et al. [61]. Based on polydimethylsiloxanes (PDMS) with terminal dimethylhydrosilyl or distributed methylhydrosilyl groups in the polymer chain and methyl esters of boronic or phenylboronic acid, cross-linked polyborosiloxanes were obtained by the Pierce–Rubinstein reaction (PBS). Depending on the number and location of methylhydrosilyl groups in the initial PDMS, as well as on the functionality of the boron component, PBS with different macromolecular structures and crosslinking densities were obtained.

In the work of Tasic et al., a cation exchange resin based on macroporous sulfonated cross-linked polystyrene was used as a heterogeneous catalyst for the synthesis of PDMS-telechelics with trimethyl-, hydrido-, vinyl-, and carboxypropyl end groups [62]. In all cases, polymers with a low molecular weight (2500) were obtained, so that later they could be used for the synthesis of block copolymers. Syntheses were performed starting from D4, while the disiloxane co-reagents for inclusion of the functional group were hexamethyldisiloxane (HMDS), 1,1,3,3-tetramethyldisiloxane (TMDS), 1,3-divinyltetramethyldisiloxane (DVTMDS), 1,3- bis(3-carboxypropyl)tetramethyldisiloxane (DCPTMDS).

Benjamin T. Cheesmana et al. prepared acrylate PDMS telechelics by the ROP mechanism in the presence of a trifluoromethanesulfonic acid catalyst. 1,3-bis(methacryl)tetramethyldisiloxane obtained by hydrosilylation of allyl methacrylate was used as a blocking agent [63]. The methacrylate-terminated PDMS macromonomers synthesized have been successfully used to form films by UV-induced crosslinking, and studies of the properties of crosslinked films are the subject of future publications.

In the work of Drozdov F.V. [64], the preparation of limonene functional PDMS by the mechanism of cationic ROP from D4 and difunctional siloxane derivative of limonene in the presence of Purolite ST-175 catalyst was considered. A series of prepolymers based on difunctional siloxane derivatives of limonene and dithiols with different methylene spacer lengths was obtained by a photoinitiated thiol polyaddition reaction. It has been shown that an increase in both the siloxane and methylene moieties in the starting monomers results in higher molecular weight products (4000–15,000 Da).

Zhang C. et al. [65] report the preparation of hydroxyl-functional PDMS from D4 with water in the presence of solid super acid. An effective method for improving the thermal insulation and stability of polysiloxane foam (SIF) by adjusting the chain length of hydroxyl-terminated polydimethylsiloxane (OH–PDMS) has been described. A series of SIFs were obtained through foaming and crosslinking processes with different crosslinking densities.

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