Chojnowski, J. Ring-Opening Polymerization of Cyclosiloxanes, in *Silicon Compounds: Silanes and Silicones 4000A*, Ed. B. Arkles, G. Larson, Gelest Inc. 2008, Morrisville, PA, 389-405

RING-OPENING POLYMERIZATION OF CYCLOSILOXANES

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1. INTRODUCTION

Ring-opening polymerization (ROP) of cyclic siloxanes is a process of the transformation of a cyclosiloxane monomer* into a linear siloxane polymer as a result of the cleavage of the SiOSi bond in the monomer ring and the subsequent reformation of this bond in the polymer chain, equation 1.


(1)

For over 50 years this reaction has been extensively used in industry and in chemical laboratories as the basic method of the generation of high molecular weight linear polysiloxanes. It gives advantages over the polycondensation of difunctional silanes – the alternative route to linear polysiloxanes – as it allows for a better control of the size and structure of macromolecules. In contrast with the polycondensation, no low molecular weight side product is formed during the ROP process and the concentration of the reactive end groups remains at a low stationary level during the chain growth. Comprehensive reviews are available [1-5].

A suitable monomer for the ROP of siloxanes may be any cyclic compound containing a reactive SiOSi group in its ring skeleton which is thermodynamically less stable as compared with its open chain structure. Many cyclic oligosiloxanes of general formula $(R_1R_2SiO)_n$*) having various substituents at silicon and various ring size fulfill this condition. Thus the family of monomers of the ROP process is broad. This family extends over many cyclosiloxanes comprising different siloxane units as well as over numerous cyclics, which, besides the siloxane moiety, have also other atoms or groups of atoms in their rings. Examples of some typical monomers of the ROP of cyclic siloxanes are shown in Figure 1.

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* Cyclosiloxanes, although usually cyclopolysiloxanes composed of more than one repeating units, are here referred to as monomers if they are substrates in the ROP process.

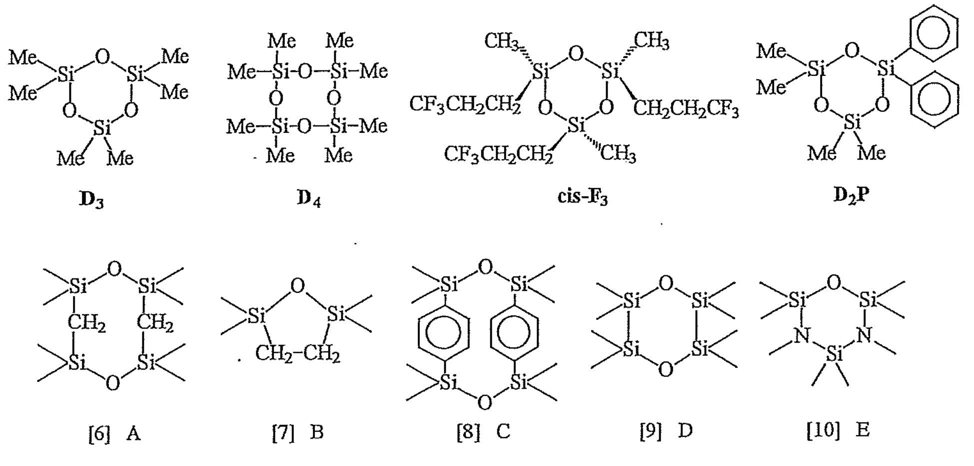


Figure 1. Examples of monomers of ROP of cyclosiloxanes.

The most important are: octamethylcyclotetrasiloxane, denoted by symbol D_4 (D marks the Me_2SiO unit) and hexamethylcyclotrisiloxane, D_3. Monomer D_4 is by far the most common as it is the basic substrate in the industrial synthesis of polydimethylsiloxanes (PDMS), in particular those of high molecular weights [1]. While D_4 is the monomer most often used in the equilibrium polymerization of cyclosiloxanes (section 3.1), D_3 is a common monomer in kinetically controlled syntheses of polysiloxanes [2-5] (section 3.2). Cyclosiloxane cis-F_3 in Figure 1 is an example of the monomer having configurational units. The ROP of this type of monomers may lead to polymers of various tacticities, i.e., various stereochemical structures [11]. Instead, the polymerization of monomer D_2P (Figure 1), which is representative of cyclosiloxanes with mixed units, may lead to various sequences of units [12]. Structures in the lower row of Figure 1 represent examples of monomers having other atoms in the ring skeleton able to form linear polymers by the siloxane bond breaking and making.

The ROP of cyclosiloxanes is classified as anionic (AROP) or cationic (CROP) according to the anionic or cationic character of their reactive intermediates. The other classification is based on the way in which the polymer product is controlled. We can distinguish the equilibrium ROP with thermodynamic control of products and non-equilibrium ROP with kinetic control of products. Finally, the ROP of cyclosiloxane may be performed in different ways: in bulk, in solution, in emulsion or microemulsion and in solid state.

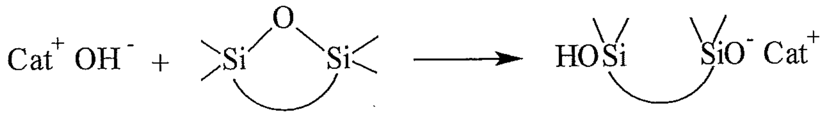
2. ANIONIC AND CATIONIC ROUTES OF ROP OF CYCLOSILOXANES

2.1 Anionic ring-opening polymerization (AROP) of cyclosiloxanes

The AROP of cyclosiloxanes is initited by strong inorganic or organic bases. Alkali metal hydroxides, KOH in particular, and silanolates derived from them are common catalysts [1-5]. Quarternary ammonium and phosphonium hydroxides and silanolates, such as Me_4NOH and Bu_4POH, are very effective [13] and the additional benefit is connected to their thermolability, which permits to stabilize the polymer by the thermal decomposition of the active propagation centers. Organic bases, such as numerous organolithium compounds are very important initiators, often used for precision syntheses of polysiloxanes. More recently, organic superbases, peraminooligophosphazenium hydroxides or alkoxides [14-16] were proposed. They initiate very fast polymerization under mild conditions.

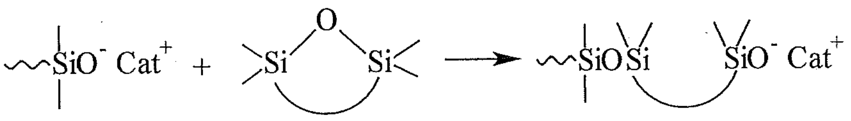
General mechanism of anionic ROP of cyclosiloxanes, illustrated by equations 2 and 3 is simple and was recognized about 50 years ago [17]. The initiator opens the monomer ring producing a silanolate ion which is able to propagate the polymer chain.

initiation



(2)

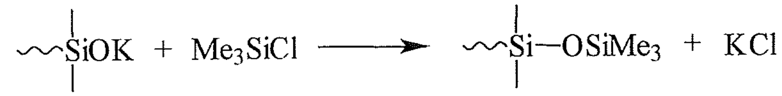
propagation



(3)

In the absence of water and CO_2 from atmosphere and other acidic contamination the active propagation center is stable. Thus, there is no termination and the reaction must be quenched. Trimethylchlorosilane is the readily used quencher as it introduces neutral trimethylsiloxane unit at the polymer chain end, equation 4.

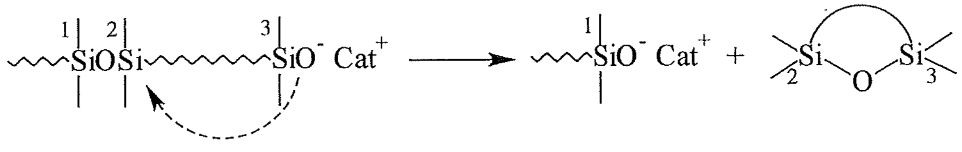
quenching



$$\sim\!\sim\mathrm{SiOK} + \mathrm{Me_3SiCl} \longrightarrow \sim\!\sim\mathrm{Si{-}OSiMe_3} + \mathrm{KCl} \qquad (4)$$

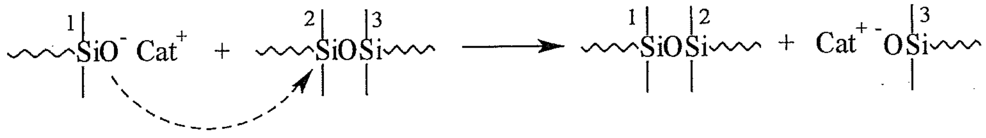
The propagation is accompanied by 'backbiting' which leads to cyclic oligomers and macrocycles, equation 5. The other accompanying reaction is chain transfer to polymer chain, equation 6, resulting in chain randomization.

backbiting



(5)

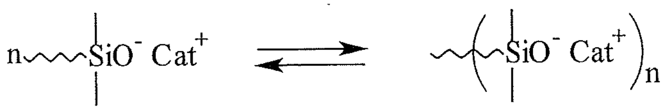
chain transfer



(6)

Silanol end groups should be avoided as they make control of the polymer structure difficult [18]. In particular, the polycondensation of silanol and the interchain exchange of terminal siloxane units occur [18-20] affecting the polydispersity of the polymer and its chain microstructure. The control of end groups is aggravated as well. This is the reason for which the initiation step according to equation 1 is often omitted by using as initiator oligosiloxane-α,ω-diolates, e.g., $KO(SiMe_2O)_nK$. If n is sufficiently high this initiator, in contrast to KOH, is soluble in the polymerization system.

The anionic ROP of cyclosiloxanes is strongly affected by various types of the interaction of the ionic propagation centers, for review see ref. [18]. The usual active form of the propagation center is an ion pair. The silanolate ion pair exhibits a great tendency for aggregation according to equation 7 [21].



$$n\sim\!\sim\mathrm{SiO^-\,Cat^+} \rightleftharpoons \sim\!\left(\sim\mathrm{SiO^-\,Cat^+}\right)_n \qquad (7)$$

The aggregates are not able to propagate, thus they form dormant centers. The kinetics of the polymerization is greatly affected by this phenomenon. Since the equilibrium of aggregation usually lies well to the side of the complex the polymerization is strongly inhibited and exhibits fractional order in initiator. Without promoter the rate increases in the series of counter-ions $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+ \sim R_4N^+ \sim R_4P^+$.

Addition of a promoter is commonly practiced. A strong uncharged nucleophile, such as dimethylsulfoxide (DMSO), hexamethyltriamide of orthophosphoric acid (HMPA) or dimethylformamide (DMF) effectively increases the rate of polymerization by forming more reactive, nucleophile separated, ion pairs and by increasing the concentration of unaggregated silanolate [18,22]. The same effect is attained when the reaction is performed in a solvent interacting with the countercation. This is the reason for which the polymerization of D_3 on lithium silanolate in THF at room temperature is completed within several hours, while it does not occur at a measurable rate in bulk or hydrocarbon solvent even at 100°C.

Crown ethers and cryptands accelerate the reaction particularly effectively as they multidentally coordinate the counter-ion [23,24]. Bases having cations with a highly delocalized charge, such as peraminooligophosphazenium ions, induce very fast polymerization. Even D_4 may be polymerized in 1 min at room temperature [14-16].

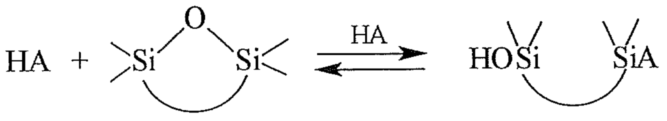
Rate of the anionic ROP depends much upon the monomer structure – the ring size and substituents [2-5,18,22-25]. Within the same cyclic homologue series the most reactive are small strained rings, such as six membered rings of cyclotrisiloxanes and five-membered rings of cyclo-1-oxa-2,5-disilacyclopentanes (Figure 1, structure B). Thus, D_3 is opened faster than D_4 by a factor of about 10^2-10^3. With further increase of the ring size the reactivity may change in different way depending on the initiator [18,22-25]. Electronegative substituents at silicon increase the reactivity, while the steric effect decreases the rate [18,22]. Both factors, steric and polar, are responsible for the decrease in the reactivity with elongation of the alkyl chain of substituent in the series D_3>$[Et_2SiO]_3$>$[n\text{-}Pr_2SiO]_3$ [26]. Finally, the reactivity may be strongly affected by the direct interaction of a functional group in the organic substituent with active propagation center [27,28].

2.2 Cationic ring opening polymerization (CROP) of cyclosiloxanes

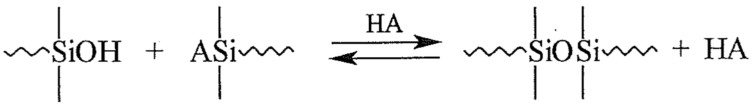
The most common initiators of the cationic ROP of cyclosiloxanes are strong protic acids. Among them the most often used are: H_2SO_4, CF_3SO_3H, $HClO_4$, CH_3SO_3H [1-3]. CF_3SO_3H being very effective is preferred for synthetic use in laboratories, while industry prefers to use the cheaper and safer H_2SO_4. Very effective are initiators composed of a protic and Lewis acid, such as $HCl+FeCl_3$ [29] or $HCl+SbCl_6$ [30]. Heterogenic systems, acid-activated minerals [31] or cation exchange resins [32] are readily used as they can be easily separated from the polymer product. Some non-protic initiators such as $SbCl_5 + CH_3C(O)Cl$ [33] or $(C_6H_5)_3C^+B(C_6F_5)_4^-$ + R_3SiH [34] were proved to initiate the polymerization, but they are of minor importance in synthesis of polysiloxanes. The high-initiating activity of some Lewis acids can be attributed to products of their interaction with protic contaminants.

The mechanism of the polymerization is very complex comprising many component reactions. Relative rates of these reactions differ considerably for various monomers, initiators and reaction conditions. The initiation is opening of the monomer ring by acid (HA), equation 8 [2-5,18]. Since the reverse condensation processes occur inter- and intramolecularly, equations 9 and 10, stationary concentrations are established of the acid water and reactive terminal groups. The acid is necessary to activate the end group for the monomer addition and to catalyze reactions 8-10. Water forms strong hydrogen bond complexes with the acid, equation 11, which greatly affects the acid activity [35-37].

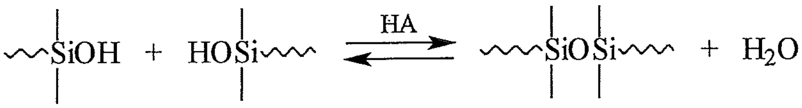
initiation



(8)



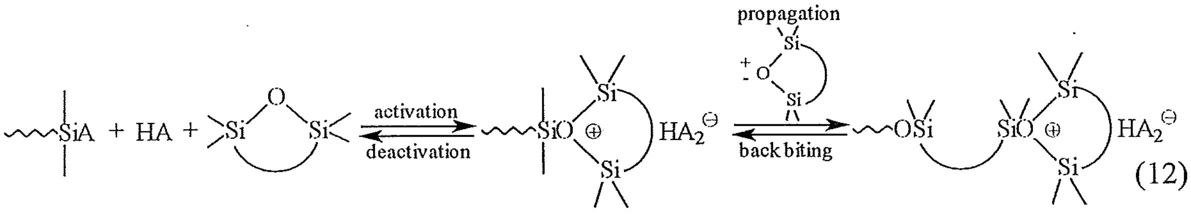
$$\sim\sim\text{SiOH} + \text{ASi}\sim\sim \xrightleftharpoons{\text{HA}} \sim\sim\text{SiOSi}\sim\sim + \text{HA} \qquad (9)$$



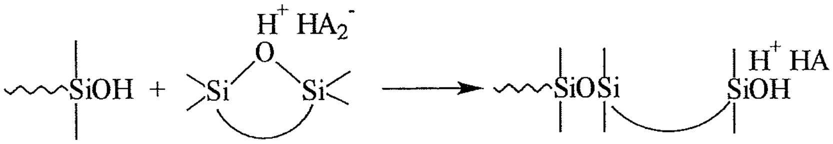
$$\sim\sim\text{SiOH} + \text{HOSi}\sim\sim \xrightleftharpoons{\text{HA}} \sim\sim\text{SiOSi}\sim\sim + H_2O \qquad (10)$$

$$n\,\text{HA} + m\,H_2O \rightleftharpoons [(\text{HA})_n \cdot (H_2O)_m] \qquad (11)$$

There are at least three pathways of the growth of the siloxane macromolecule. The contribution of the condensation processes, equations 9, 10, to the chain formation may be considerable [35]. However, it is generally accepted that the polymer is formed mostly by addition of monomer to the end group, which requires an activation of the end group or the monomer by acid [34-39]. The activation may occur by the generation of a tertiary or secondary silyloxonium ion as shown on simplified schemes 12 or 13.



(12)



(13)

However, the oxonium ions are transitory species. Deactivation processes dominate over propagation so the polymer chain grows stepwise and the molecular weight of the polymer increases linearly with monomer conversion.

Since the stationary concentration of acid is maintained throughout the process, the initiation according to equation 8 occurs all the time during the polymer growth, which leads to a broadening of the molecular weight distribution. Another feature of this polymerization is the formation of considerable amounts of cyclic products. They are formed by intramolecular reactions of end groups [18,40] and by ring-expansion isomerization of the tertiary oxonium ion [37,39]. Backbiting and chain transfer contribute to the polymerization of unstrained cyclics but are of minor importance in the CROP of cyclotrisiloxanes [41].

Strained ring monomers such as D_3 polymerize much faster than the unstrained ones, such as D_4. Polar and steric effects of substituents seem to play an important role affecting the reactivity [3]. In contrast to anionic polymerization, the rate is decreased by electron withdrawing polar substituents. The rate of the polymerization depends to a considerable extent upon the acid strength, thus CF_3SO_3H is a much more active initiator than CH_3SO_3H [9].

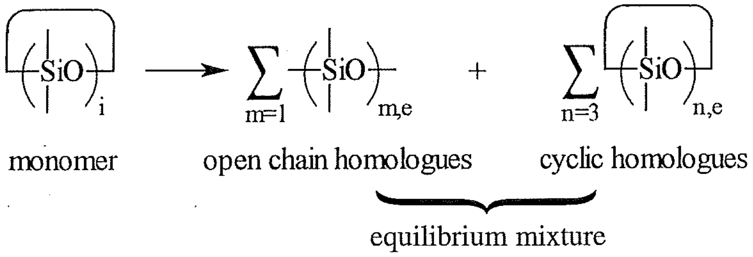
The cationic route is extensively exploited in the equilibrium polymerization (section 3.1), but rather rarely used in the processes performed with kinetic control (Section 3.2). Recent investigations showed, however, that some initiation systems permit to gain a fairly good control of the polymer structure [30]. The CROP of D_3 initiated by $SbCl_5$ + HCl + Me_2SiCl_2 leads to polymers of controlled molecular weight and a low cyclic content. Addition of an excess of a triorganosilyl ester to the polymerization system initiated by CF_3SO_3H considerably reduces cyclic products and permits good molecular weight control [41,42].

3 EQUILIBRIUM AND KINETIC CONTROL OF THE PRODUCT IN THE ROP OF CYCLOSILOXANE

3.1 Equilibrium polymerization (equilibration)

Basic knowledge

The equilibrium ROP is carried out until the whole process achieves the equilibrium state. Since the equilibrium is independent of the reaction mechanism, virtually the same polymer yield and the same polymer structure is obtained from both anionic and cationic routes. The knowledge of the equilibrium state is the most important issue in understanding this process. The equilibrium is complex as two series of polymerohomologues are formed according to equation 14 [3,5].



(14)

The equilibrium established between all cyclic and linear homologues, may be characterized by three dependencies: equilibrium distribution of linear homologues, equilibrium distribution of cyclic homologues and equilibrium between linear and cyclic fractions.

The distribution of the size of the open chains is mostly controlled by the chain transfer (equation 6*) which occurs at random and leads to the most probable distribution often referred to as the Flory distribution [43]. Polydispersity factor (PDI = M_w/M_n)** for this distribution is equal 2.

In general, the equilibrium concentrations of cyclics decrease in a homologous series with the increase of the ring size. The exceptions are strained ring cyclotrisiloxanes which often appear in very low concentrations at equilibrium. For example, the equilibrium concentration of D_3 is negligible at room temperature although it becomes significant at high temperatures. The most abundant is D_4, 6.3 wt% of total undiluted equilibrated PDMS, then D_5, 3.7%, and D_6, 1.5% [44].

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* Equation 6 represents the chain transfer for the anionic route. Similar process occurs in CROP.

** M_n and M_w denote molecular weights, number average and weight average, respectively.

Since the cyclic fraction contains mostly oligomers, the equilibrium between cyclic and open chain fractions gives us direct information about the yield of polymer. This equilibrium as well as the equilibrium distribution of cyclics are controlled by the elementary ring closure–ring opening equilibria. These equilibria are described by a very simple approximate equation 15***, according to which the equilibrium concentration of a cyclic $\left[\overline{\lfloor (\mathrm{SiO})_n \rfloor} \right]_e$ is equal to the equilibrium constant of the cyclic formation [44].

$$K_{cn} = \left[\overline{\lfloor (\mathrm{SiO})_n \rfloor} \right]_e \qquad (15)$$

Since equation 15 holds for all cyclic homologues in the series, the total weight concentration of cyclics in a system coexisting in equilibrium with linear polymer, $\sum_{n=3} n\, M_0\, K_{cn}$,**** is also constant independent of the total weight concentration of cyclic and linear polysiloxanes. Consequently, the dilution of the system at equilibrium with a solvent must convert some amount of linear polymer to cyclics to fulfill equation 15. The yield of polymer is decreasing with dilution of the polymerization system, which is illustrated in Figure 2. For each polysiloxane there exists a critical concentration below which linear polymer is not formed.

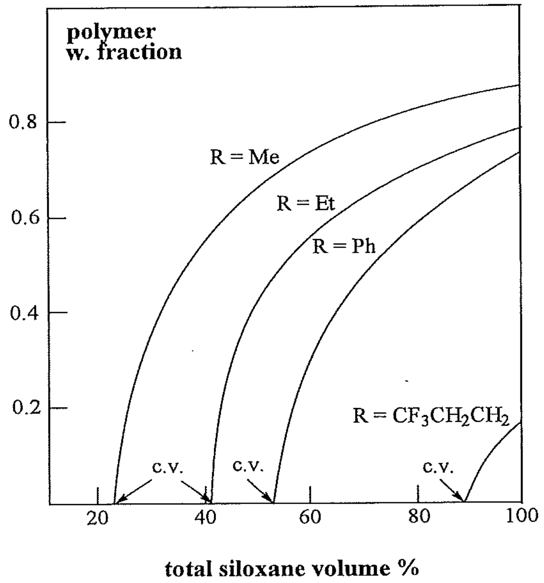


Figure. 2
Weight fraction of polymer in total siloxane vs volume percent of total siloxane in toluene at 100°C at equilibrium in the polymerization of $(\mathrm{RMeSiO})_n$, R=Me, Et, Ph, (CH2)2 CF3, c.v. marks - critical siloxane volume for the polymer formaton.

(Adapted from Ref. [44] with kind permission of Kluwer Academic Press).

Another feature of this equilibrium is its independence of temperature [46]. This is because rings that appear in equilibrium at significant concentrations are virtually strainless. The number and character of chemical bonds is not changed in the ROP process. The enthalpy of ring opening is equal, or almost equal, to zero. Conformational entropy controls the position of the ring-chain equilibria. The entropy gain in ring opening, which is the driving force for the polymerization, is due to high flexibility, i.e., conformational freedom, of the siloxane chain. All modifications of the monomer structure decreasing the conformational freedom of the siloxane chain shift the equilibrium towards cyclics. Thus, the increasing size or polar character of substituents at silicon reduces the yield of polymer at equilibrium, which is well illustrated by low yields and high critical concentrations of poly-3,3,3-trifluoropropylmethylsiloxane in the equilibrium ROP (Figure 2). Linear polydiphenyl-siloxane cannot be obtained by this method.

*** For more rigorous treatment, needed if molecular weight is low, see ref. [45].

**** n – number of units in cyclic homologue, Mo – molecular weight of the unit.

Practical use

The equilibrium polymerization of cyclosiloxanes are very often used in the synthesis of polysiloxanes both in industrial processes and in research laboratories as it gives many advantages shortly discussed below.

1. This method itself does not impose any restriction on initiator. Variety of them, anionic and cationic, may be used. Thus, it is easy to find an initiator which, being tolerated by functional groups in polymer, drive the system to the equilibrium state relatively fast under mild conditions and may be easily removed from the polymer.
2. There are no stringent requirements of quenching the reaction in a narrow range of time.
3. There are no requirements for the size of the monomer ring. The same results are obtained using various monomers of the same homologous series. A mixture of cyclics or a mixture of cyclic and linear polysiloxanes is often equilibrated.
4. Molecular weight is readily controlled by using chain blockers which are disiloxanes or short chain oligosiloxanes introducing end groups according to equation 16 [1].

$$\mathrm{Me_3SiOSiMe_3} + \mathrm{n\,(Me_2SiO)_4} \longrightarrow \mathrm{Me_3SiO(Me_2SiO)_{4n\text{-}mp}SiMe_3} + \mathrm{m\,(Me_2SiO)_p} \qquad (16)$$

The initial concentration of initiator, which is the other source of end groups, must be much lower than that of the blocker.

5. Functionalization of both chain ends is possible by using functionalized blockers which is exemplified by equation 17 [47].

$$\mathrm{H_2N(CH_2)_3Me_2SiOSiMe_2(CH_2)_3NH_2} + \mathrm{n\,D_4} \xrightarrow{\text{equilibrium ROP}} \qquad (17)$$

$$\longrightarrow \mathrm{H_2N(CH_2)_3Me_2Si(OSiMe_2)_mOSi(CH_2)_3NH_2} + \text{cyclics}$$

If the blocker is an organic polymer containing the SiOSi group, an organic siloxane block copolymer may be obtained [48a].

6. The equilibrium ROP of cyclosiloxane is a very convenient route to statistical copolymers of various siloxanes. The example of this synthesis is presented in equation 18 [49].

$$\mathrm{Me_3SiOSiMe_3} + \mathrm{n\,(Me_2SiO)_4} + \mathrm{m\,(ViMeSiO)_4} \xrightarrow[\text{}]{\substack{\text{equilibrium ROP}\\ \text{(equilibration)}}} \mathrm{Me_3SiO[SiMe_2O]_p\,[SiMeViO]_rSiMe_3} \qquad (18)$$

Macromolecules of these copolymers have a uniform composition and random distribution of units [49]. Thus, it is possible to introduce functional groups pendant to polysiloxane chain which are statistically spread along the polymer chain.

There are also some limitations of using the equilibrium ROP of cyclosiloxanes in synthesis [3]. The main restraint is concerned with the formation of cyclic oligomers which reduce the yield of polymer. Since the yield decreases dramatically with the increase of the size and polar character of substituents the process is usually used in the synthesis of dimethylsiloxane and hydridomethylsiloxane polymers as well as their copolymers. The equilibrium ROP is carried out in bulk as any dilution of the polymerization system leads to a decrease in the polymer yield. The reaction cannot be used for the synthesis of polysiloxanes with a narrow molecular weight distribution and precisely functionalized at the single extremity of the polymer chain. It is not suitable for the synthesis of copolymers with specific distribution of siloxane units, such as alternate or gradient copolymers.

The important application of the equilibrium ROP of cyclosiloxanes is the industrial synthesis of high temperature vulcanized (HTV) silicone rubber [1]. Most of these technologies are based on the AROP of D_4. Addition of vinyl-substituted cyclosiloxanes is often practiced to introduce pendant vinyl groups used for cross-linking in the vulcanization process. Monomer purity requirements are very stringent, because molecular weights of these polymers are very high, up to 10^6 g·mol^{-1}, which means that the linear macromolecule having 10^4 siloxane units must be formed. Any small contamination may considerably change the rheological properties of the material.

The equilibration of siloxanes is also a fundamental method of industrial syntheses of various silicone liquids [1]. Since in these cases the molecular weight of the polymer is much lower, the purity of the monomer does not need to be so high and often a mixture of siloxane oligomers is used as the substrate.

The great interest in using of the equilibrium ROP of cyclosiloxanes in the laboratory synthesis of polymers continues. The polymerization is often applied to the synthesis of end-functionalized polysiloxanes used farther in synthesis of siloxane-organic block copolymers [50-52] or polymer networks [53]. The equilibrium copolymerization is often exploited in the syntheses of polysiloxanes functionalized in side groups [32,54-56].

3.2 Kinetically controlled ROP of cyclosiloxanes

Basic knowledge

The fundamental principle of the kinetic control of the polymer formed in the ROP of cyclosiloxanes is explained in Figure 3. The ROP of a strained ring cyclotrisiloxane and its strainless homologue, e.g., cyclotetrasiloxane, both lead to the same equilibrium state, however, on different routes. The strainless cyclosiloxane produces in parallel polymer and cyclic oligomers, the latter being formed by back-biting. The polymer concentration steadily increase to eventually achieve its equilibrium value. Instead, the strained cyclotrisiloxane is mostly transformed into linear polymer which in the second step is randomized and partly decomposed to cyclics. The system attains the equilibrium state according to general scheme, equation 19:

$$\text{monomer} \xrightarrow{\text{polymerization}} \text{linear polymer} \xrightarrow[\left(\begin{array}{l}\text{back biting}\\ \text{chain scrambling}\end{array}\right)]{\text{equilibration}} \begin{array}{l}\text{equilibrium mixture}\\ \text{of polymer and cyclics}\end{array} \qquad (19)$$

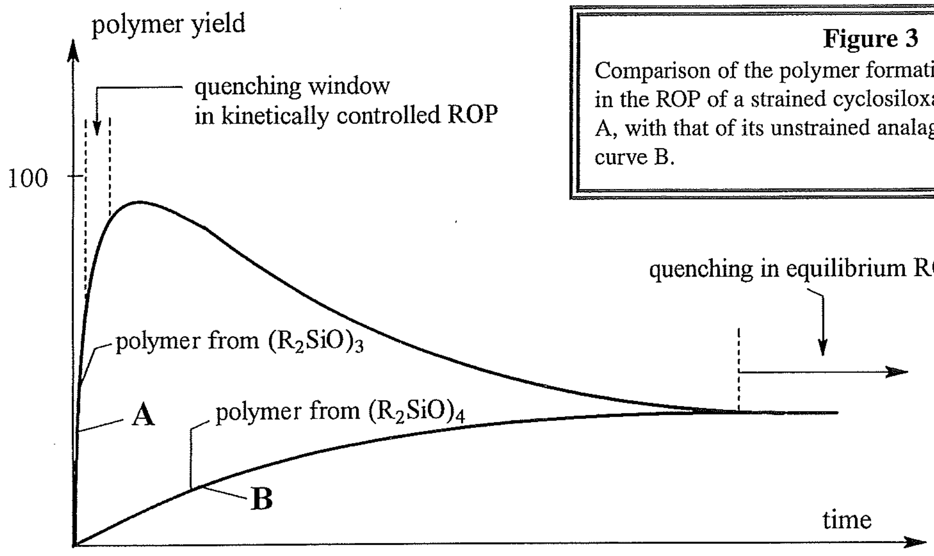


Figure 3
Comparison of the polymer formation - time dependence in the ROP of a strained cyclosiloxane $(R_2SiO)_3$ - curve A, with that of its unstrained analague, e.g., $(R_2SiO)_4$ - curve B.

This is because the propagation of the strained ring monomers is much faster than back-biting and chain transfer. In contrast to the entropy driven polymerization of strainless cyclosiloxanes, the driving force for the polymerization of cyclotrisiloxane is the enthalpy decrease related to the release of the ring strain. If the polymerization is quenched at a suitable moment a high yield of polymer may be obtained even in the case when the linear polysiloxane does not exist in the equilibrium state. A good example is the polymerization of $(Ar_2SiO)_3$ [57].

The AROP of cyclotrisiloxanes may gain the features of living polymerization under two conditions. First, the initiation must be fast and quantitative. Second, the difference in rates of propagation and the undesired back-biting and chain randomization processes should be high enough to eliminate the influence of these processes on the polymer structure. When both of these conditions are fulfilled all macromolecules are growing in parallel without chain breaking. If the polymerization is quenched in due time the polymer having a narrow molecular weight distribution with PDI below 1.1 may be obtained [58,59]. The precise functionalization of the polymer at a single chain end is possible. The functional group may be introduced either by additionally functionalized initiator, or more often, by using a terminator bearing an additional function. Examples are presented in equations 21 and 22. Thus, the kinetically controlled AROP of cyclotrisiloxane using the selective polymerization system is a good method for the precision synthesis of functionalized polysiloxanes. In contrast, the kinetically controlled CROP is rarely used for this purpose as it is difficult to eliminate the formation of cyclics, PDI is high and terminal group exchange makes the functionalization at single chain end impossible [41] (section 2.2).

The AROP of cyclotrisiloxanes, when used for the precision synthesis, requires selective polymerization systems. The most often used initiators for the selective AROP of cyclotrisiloxane are numerous organolithium compounds in combination with various promoters such as THF (usually used as solvent), DMSO, HMPA, DMF and cryptand [211] [3-5].

In a hydrocarbon solvent the transformation of the RLi initiator into the silanolate propagation center occurs quantitatively according to equation 20 [60].

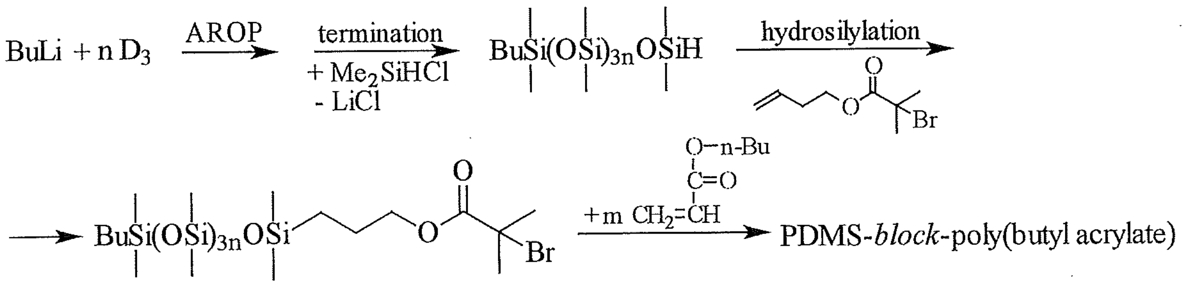
$$\left\lfloor (Me_2SiO)_3 \right\rfloor + 3\ RLi \longrightarrow 3\ RMe_2SiOLi \qquad (20)$$

This reaction proceeds fast and under mild conditions in which no propagation on the formed silanolate takes place without a promoter. A two step initiation is often practiced. First, the organolithium is quantitatively transformed into the silanolate and then the propagation is induced by introduction of a promoter. This procedure gives a better precision in synthesis as some possible side reactions of RLi are avoided [58].

Practical use

The kinetically controlled ROP of cyclotrisiloxanes is more difficult to perform than the equilibrium process. It requires more expensive monomers, selected initiators and more stringent conditions. This method is used in the technology of silicones for the fabrication of polysiloxanes which cannot be obtained in reasonable yield by the equilibrium polymerization, such as poly-($CF_3CH_2CH_2MeSiO$) [1]. The AROP of cyclotrisiloxanes is also extensively used in research laboratories in cases where the polymerization of unstrained cyclosiloxanes proceeds very slowly or leads to low yields of polymer because of unfavorable thermodynamics of the process [26,61]. However, the most important use of this process in research laboratories is the controlled synthesis of functionalized polysiloxanes for numerous applications, as discussed below. **Diblock and triblock copolymers** are obtained by three techniques exploiting the AROP of cyclotrisiloxanes: 1) macroinitiator [61-64], 2) sequential polymerization [63,65-68], 3) end functional group coupling [59,68,69].

The controlled AROP of cyclotrisiloxanes is a convenient route to macroinitiators of various types of polymerization. Equation 21 exemplifies synthesis and use of the monofunctional macroinitiator of atom transfer radical polymerization (ARTP) the precursor of which is obtained by functionalized terminator method [64]. The functionalized initiator method is also used for the generation of macroinitiators, e.g., ref. [70].



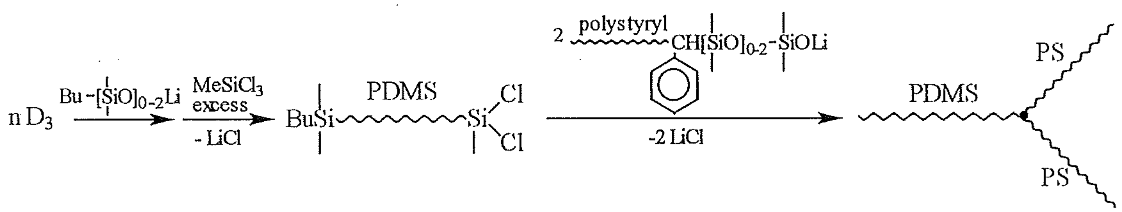
(21)
[64]

Conversely, the block copolymers are generated when organic macroinitiators or living polymers are used to initiate the controlled AROP of cyclotrisiloxane [62-65,68].

The sequential copolymerization of two or more cyclotrisiloxanes is a good method for the precision synthesis of all-siloxane block copolymers [66,67,71].

Synthesis of various branched organic-siloxane and siloxane-siloxane copolymers is often accomplished using the AROP of a cyclotrisiloxane. The reaction is exploited for the synthesis of macromonomers used further for copolymerization with vinyl monomers to obtain organic polymers with grafted polysiloxanes [72]. The other approach is the grafting of an end-functionalized polysiloxane, generated by the AROP, on a side organic polymer with functionalized side groups [68].

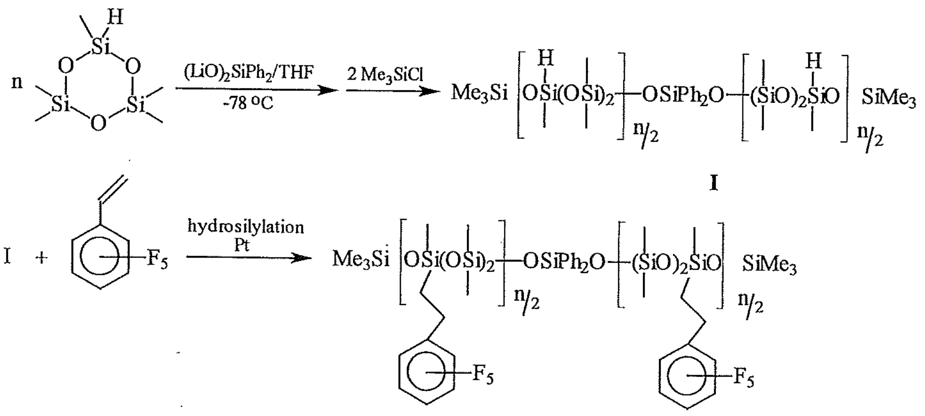
Star-branched polysiloxanes are obtained by using polyfunctional quenchers [73] or by using polyfunctional initiators [48b]. The precision two step synthesis of a branched miktoarms organic-siloxane copolymer is shown in equation 22. Dendritic branched polysiloxanes may be obtained by graft on graft or graft on star techniques [73].



(22)
[59]

A variety of all-siloxane and siloxane-organic cross-linked materials was prepared using the AROP of cyclotrisiloxanes for the synthesis of precursor functionalized polysiloxanes [53,61,74]. Besides conventional networks various kinds of interpenetrating networks were obtained [74,75]. The kinetically controlled sol-gel ROP of bicyclic siloxane monomers was used to form densely cross-linked materials in a solventless process [76].

Polysiloxanes with organofunctional groups pendant to siloxane chain are readily obtained by the controlled AROP. For this purpose a precursor groups such as $SiCH=CH_2$ [71,77], SiH [78,79], $Si(CH_2)_3Cl$ [67], $Si(CH_2)_2PPh_2$ [27] are introduced to cyclotrisiloxane. The AROP of these monomers leads to the controlled synthesis of polysiloxanes bearing the precursor which is further transformed to a variety of functionalities. An example is presented in equations 23.



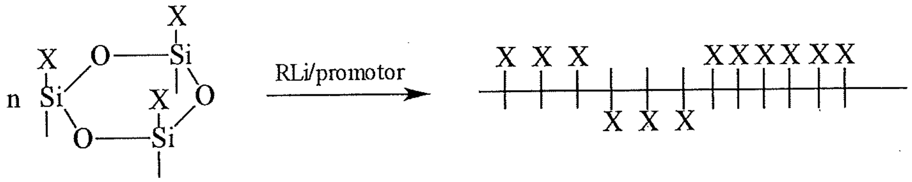
(23)

[78]

The functional groups may be arranged along the chain in a specific way. A uniform distribution of units is obtained when a cyclotrisiloxane with mixed units is used as no cleavage of the polymer chain occurs during the polymerization [12]. In some cases the propagation is regioselective [78-80] leading to regular alternative order of units. This is the case shown in equations 23 [78] where Si-H appears at every third silicon atom along the chain.

The simultaneous anionic copolymerization of two cyclotrisiloxane monomers leads to the uniform composition and chain microstructure of macromolecules. If the comonomers differ in reactivity the unit distribution is gradient. The vinyl-substituted monomer VD_2 reacts faster than D_3, $r_{VD2}=8.1$, $r_{D3}=0.22$ [80], thus the density of vinyl groups along the chain gradually decreases as the chain grows.

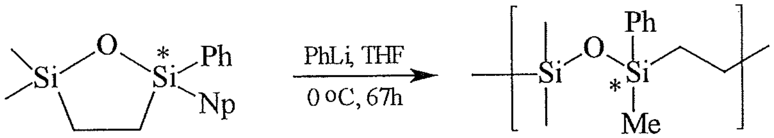
The stereocontrolled synthesis of polysiloxane was performed by the AROP of cyclotrisiloxanes having different geminal substituents at silicon, such as monomer F_3 presented in Figure 1. In some cases cis isomer can be isolated and its ROP gives partially stereoregular polymer as schematically presented in equation 24. Such polymers show a crystalline phase while the polymers obtained from the mixtures of cis and trans isomers are completely amorphous. The mechanical strength of silicone elastomers may be improved using a stereoregular polysiloxane [11].



(24)

X = Ph [65] or $CH_2CH_2CF_3$ [11]

Optically active all-siloxane polymers may be obtained by the AROP only if monomer bears an optically active substituent, e.g., ref. [82]. On the other hand, the controlled AROP of a cyclocarbosiloxane with a chiral center in the ring skeleton may lead to an optically active polymer. The example of a highly stereospecific polymerization of an optically active enantiomer of oxy-2,5-disilacyclopentane is shown in equation 25 [83].



(25)

$[\alpha]_D^{25} = -17.5^o$ $[\alpha]_D^{25} = -8.5^o$ Mn = 20 800

ee > 98.2 PDI = 1.12

4. SPECIAL METHODS OF THE ROP OF CYCLOSILOXANES

4.1 Polymerization in the solid state

High molecular weight materials may be synthesized by solid state ROP of cyclic siloxanes [84,85]. This may be a convenient mode of the polymerization of monomers, such as $(Ph_2SiO)_3$ difficult to dissolve in a commonly used solvent and having a high melting point. The AROP of this monomer was initiated by KOH spread on the monomer crystal surface. The propagation proceeds inward from the surface of the monomer crystals and leads to a crystalline polymer. Polymerization and polymer crystallization proceeds successively. An interplay between the rates of polymer chain growth and the polymer crystallization is suggested to control the polymer yield, its molecular weight, polydispersity and crystallinity. The rate is also sensitive to structural defects in monomer crystals.

4.2 Polymerization in emulsion

The ROP of cyclosiloxanes in emulsion and microemulsion, both anionic and cationic, attracted the attention of chemists as it gives some advantages over the classical ROP process [86-88]. The emulsion AROP is particularly useful for synthesis of α,ω-hydroxy-polysiloxanes of relatively low molecular weight 10^3-$3{\cdot}10^4$ g/mol [88]. These polymers may be obtained under mild conditions using cheap unstrained monomers such as D_4. The polymerization permits to obtain a high yield of the polymer with a controlled molecular weight and a relatively narrow molecular weight distribution (PDI 1.1-1.5 unless the conversion is higher than 70%). The yield of cyclics is lower than in classical AROP, because the polymerization mechanism is different. The process occurs in particles of siloxane of diameter ranging 0.05-0.5 μm. Each particle acts as an independent minireactor of polymerization. A considerable role is played by emulsifier, which usually is a tetraorganoammonium bromide with one or more longer chain alkyl substituent, such as didodecyldimethylammonium bromide. It stabilizes the particle being at its surface. Sodium hydroxide used as initiator exchanges partly anion with the emulsifier. Thus OH^- is present in the interface initiating there the polymer chain. The propagation and termination takes place at the interface too. Steric hindrance of the surfactant suppresses backbiting leading to low content of cyclics in polymer.

Kinetic control of the emulsion AROP of $[CF_3(CH_2)_2MeSiO]_3$ permits to obtain polymer with almost theoretical yield as the selectivity of the process is very high [87].

The emulsion CROP exploits dodecylbenzenesulfonic acid as initiator and emulsifier. The CROP of unstrained D_4 occurs fast and leads to high polymer with M_n up to $2{\cdot}10^5$ g/mol [88,89].

4.3 Radiation polymerization

The ROP of cyclic trisiloxane may be initiated by γ-radiation [90-91]. The polymerization is performed in bulk in the solid or liquid state. It requires extremely high purity of the system as traces of nucleophiles arrest the reaction. The interesting feature of this reaction is that D_3, D_4 and D_5 react at the same rate [91]. The polymerization is cationic in nature. It is suggested that the silylenium ion, the analogue of carbenium ion, is formed on monomer in result of CH_3^- cleavage.

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