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**THE EFFECT OF THE STRUCTURE OF  
CYCLIC MONOMERS ON THE COURSE  
OF ANIONIC POLYMERIZATION AND  
THE PROPERTIES OF VINYL-  
-TERMINATED POLYSILOXANES**

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**UTICAJ STRUKTURE CIKLIČNIH  
MONOMERA NA TOK ANJONSKE  
POLIMERIZACIJE I SVOJSTVA  
VINIL-TERMINIRANIH POLISILOKSANA**

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## The Effect of the Structure of Cyclic Monomers on the Course of Anionic Polymerization and the Properties of Vinyl-Terminated Polysiloxanes

### ABSTRACT

Two main goals of the present study include the development of novel, completely amorphous and strictly linear polysiloxanes, suitable for extreme temperature applications, and comprehensive evaluation of silanolate-initiated ring opening polymerization (ROP) of selected cyclosiloxanes.

Suppression of crystallization of polydimethylsiloxane, PDMS, was achieved by random incorporation of small amounts of diphenylsiloxy, DiPhS, diethylsiloxy, DiEtS, or methylphenylsiloxy, MePhS, repeat units along polymer chains. While the presence of DiPhS units in copolysiloxanes caused the occurrence of chain branching, affecting molecular weight distribution and the chain conformation, their replacement by DiEtS or MePhS units yielded linear polymers. Based on the results of  $^{29}\text{Si}$  NMR and SEC-MALS-VIS studies, it is proposed that branching in DiPhS-containing polymers is caused by a nucleophilic attack of initiating silanolate anions on their Si-C<sub>Ar</sub> side bonds and a resulting formation of Ph-T-branches.

The dynamics of ROP of octamethylcyclotetrasiloxane, D<sub>4</sub>, and three copolymerizations of D<sub>4</sub> with octaphenylcyclotetrasiloxane, D<sub>4</sub><sup>Ph2</sup>, hexaethylcyclotrisiloxane, D<sub>3</sub><sup>Et2</sup>, and tetramethyltetraphenylcyclotetrasiloxane, D<sub>4</sub><sup>MePh</sup>, were monitored using SEC, TGA and  $^{29}\text{Si}$  NMR methods. While ROP of D<sub>4</sub> and its copolymerizations with D<sub>3</sub><sup>Et2</sup> and D<sub>4</sub><sup>MePh</sup> occurred similarly, with characteristic fast initial polymer growth, the copolymerization of D<sub>4</sub> with D<sub>4</sub><sup>Ph2</sup> exhibited a distinct induction period caused by limited solubility of solid D<sub>4</sub><sup>Ph2</sup> in D<sub>4</sub> and far greater reactivity of D<sub>4</sub><sup>Ph2</sup> than D<sub>4</sub> toward the dimethylsilanolate. A new mechanism for the copolymerization of D<sub>4</sub> with D<sub>4</sub><sup>Ph2</sup> is proposed which includes: a) initial formation of B-A-B triblocks of DiMeS (A) and DiPhS (B) segments, followed by b) formation of A-B-A-B-A pentablock species, and c) redistribution of the multiblocks through a siloxane equilibration reaction into copolymers containing single DiPhS units separated by extended PDMS segments.

Investigated terpolysiloxanes are intended for use in 3D-printing technology as well-defined precursors for preparation of elastomers with tunable properties.

Keywords: polysiloxane, crystallization, branching, anionic ring opening polymerization, equilibration

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# Uticaj strukture cikličnih monomera na tok anjonske polimerizacije i svojstva vinil-terminiranih polisiloksana

## SAŽETAK

Osnovni ciljevi ovog rada obuhvataju razvoj novih, potpuno amorfnih i isključivo linearnih polisiloksana, pogodnih za primenu na ekstremnim temperaturama, kao i detaljnu analizu mehanizma anjonske polimerizacije otvaranjem prstena odabranih ciklosiloksana.

Potpuno suzbijanje kristalizacije polidimetilsiloksana, PDMS, postignuto je nasumičnom ugradnjom malih količina difenilsiloksanskih, DiPhS, dietilsiloksanskih, DiEtS, ili metilfenilsiloksiloksanskih, MePhS, monomernih ostataka duž lanaca polimera. Dok je prisustvo DiPhS jedinica u kopolisiloksanima uzrokovalo grananje lanaca, koje značajno remeti raspodelu molskih masa i konformaciju lanaca polimera, njihova zamena uporedivim količinama DiEtS ili MePhS ostataka proizvela je kompletno linearne polimere. Na osnovu rezultata dobijenih uz pomoć  $^{29}\text{Si}$  NMR i SEC-MALS-VIS analiza, predloženo je da je grananje lanaca u polimerima koji sadrže DiPhS ostatke uzrokovano nukleofilnim napadom inicirajućeg silanolatnog anjona na bočne  $\text{Si-C}_{\text{Ar}}$  grupe koji rezultira formiranjem Ph-T-grana.

Odvijanje homopolimerizacije oktametilciklotetrasiloksana,  $\text{D}_4$ , i tri kopolimerizacije ovog monomera sa oktafenilciklotetrasiloksanom,  $\text{D}_4^{\text{Ph}_2}$ , heksaetilciklotrisiloksanom,  $\text{D}_3^{\text{Et}_2}$ , i tetrametiltetrafenilciklotetrasiloksanom,  $\text{D}_4^{\text{MePh}}$ , praćeno je korišćenjem SEC, TGA i  $^{29}\text{Si}$  NMR metoda. Dok su se homopolimerizacija  $\text{D}_4$  i kopolimerizacije  $\text{D}_4$  sa  $\text{D}_3^{\text{Et}_2}$  i  $\text{D}_4^{\text{MePh}}$  odvijale na skoro identičan način, sa karakterističnim brzim rastom polimera, kopolimerizaciju  $\text{D}_4$  sa  $\text{D}_4^{\text{Ph}_2}$  pratio je izražen indukcion period usled umanjene rastvorljivosti  $\text{D}_4^{\text{Ph}_2}$  u  $\text{D}_4$  i znatno veće reaktivnosti  $\text{D}_4^{\text{Ph}_2}$  od  $\text{D}_4$  ka dimetilsilanolatu. Predložen je novi mehanizam kopolimerizacije  $\text{D}_4$  i  $\text{D}_4^{\text{Ph}_2}$  koji obuhvata a) inicijalno formiranje B-A-B triblokova koji se sastoje od DiMeS (A) i DiPhS (B) segmenata, b) formiranje A-B-A-B-A pentablok vrsta i c) redistribuciju multiblokova reakcijom ekvilibracije siloksana, rezultirajući formiranjem polimera u kome alterniraju izolovane DiPhS monomerne jedinice i PDMS segmenti.



Ispitivani terpolisiloksani su namenjeni za upotrebu u tehnologiji 3D štampanja kao dobro definisani prekursori za pripremu elastomera sa podesivim osobinama.

Ključne reči: polisiloksan, kristalizacija, grananje, anjonska polimerizacija otvaranjem prstena, ekvilibracija

Naučna oblast: Hemijske nauke

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## Abbreviations

3D	Three-dimensional
AM	Additive manufacturing
A-ROP	Anionic ring opening polymerization
CDCl <sub>3</sub>	Deuterated chloroform, chloroform <i>d</i>
CER	Cation exchange resin
Cr(acac) <sub>3</sub>	<i>Chromium(III) acetylacetonate</i>
C-ROP	Cationic ring opening polymerization
D <sub>3</sub>	Hexamethylcyclotrisiloxane
D <sub>4</sub>	Octamethylcyclotetrasiloxane
D <sub>5</sub>	Decamethylcyclopentasiloxane
D <sub>6</sub>	Dodecamethylcyclohexasiloxane
D <sub>3</sub> <sup>Et2</sup>	Hexaethylcyclotrisiloxane
D <sub>4</sub> <sup>Et2</sup>	Octaethylcyclotetrasiloxane
D <sub>3</sub> <sup>MePh</sup>	Trimethyltriphenylcyclotrisiloxane
D <sub>4</sub> <sup>MePh</sup>	Tetramethyltetraphenylcyclotetrasiloxane
D <sub>5</sub> <sup>MePh</sup>	Pentamethylpentaphenylcyclopentasiloxane
D <sub>3</sub> <sup>MeVi</sup>	Trimethyltrivinylcyclotrisiloxane
D <sub>4</sub> <sup>MeVi</sup>	Tetramethyltetravinylcyclotetrasiloxane
D <sub>3</sub> <sup>Ph2</sup>	Hexaphenylcyclotrisiloxane

D <sub>4</sub> <sup>Ph2</sup>	Octaphenylcyclotetrasiloxane
DiMeS	Dimethylsiloxo- repeat unit
DiPhS	Diphenylsiloxo- repeat unit
DiViEB	Divinyl end-blocker
DMA	Dynamic mechanical analysis
DMF	Dimethylformamide
DMSO	Dimethylsulfoxide
DP	Degree of polymerization
DSC	Differential scanning calorimetry
DVTMDS	Divinyltetramethyldisiloxane
EtPhS	Ethylphenylsiloxo- repeat unit
GPC	Gel permeation chromatography
HMDS	Hexamethyldisiloxane
HMPT	Hexamethylphosphorotriamide
HPLC	High performance liquid chromatography
IV	Iodine value
LC	Liquid crystal
LS	Light scattering

MALS	Multi-angle light scattering
MePhS	Methylphenylsiloxy- repeat unit
MHS	Mark Houwink Sakurada equation
$M_n$	Number-average molecular weight
$M_p$	Peak molecular weight
$M_t$	Targeted number-average molecular weight
$M_w$	Weight-average molecular weight
MW	Molecular weight
MWD	Molecular weight distribution
NMR	Nuclear magnetic resonance
PDES	Polydiethylsiloxane
PDI	Polydispersity index
PDMS	Polydimethylsiloxane
PD- <i>n</i> BS	Polydi- <i>n</i> -butylsiloxane
PD- <i>n</i> PrS	Polydi- <i>n</i> -propylsiloxane
PDPS	Polydiphenylsiloxane
$R$	Run number
$R_h$	Hydrodynamic radius
RI	Refractive index
RMS	Root-mean-square radius
ROP	Ring opening polymerization
$R_z$	Root-mean-square radius, radius of gyration

SARSOX	Silarylene Siloxane
SEC	Size exclusion chromatography
SER	Siloxane equilibration reaction
TFPMeS	Trifluoropropylmethylsiloxyl- repeat unit
$T_g$	Glass transition temperature
TGA	Thermal gravimetric analysis
THF	Tetrahydrofuran
$T_m$	Melting temperature
TMAS	Tetramethylammonium silanolate
TMS	Tetramethylsilane
$[\eta]$	Intrinsic viscosity
$\eta$	Dynamic viscosity



## 1. INTRODUCTION

Additive manufacturing, AM, also known as 3D printing, is rapidly becoming a technology of choice for future manufacturing of an extremely wide variety of different objects ranging from complete houses or automobile, plane and/or ship bodies, to replacement human organs, from ears, to lungs, to intestines, to even hearts. However, while development of machinery required for realization of AM, including computer hardware and software, printers and supporting parts, is developing at an extremely rapid pace, the development of polymer materials required for this purpose has seriously lagged behind. Thus, at present, only a few families of synthetic polymers have gained a prominent status among materials used, including, acrylonitrile-butadiene-styrene copolymers, ABS, nylons, polyesters, polycarbonates, polyether imides. Notably, there are no elastomers among these materials, and the need for their introduction into AM technology is becoming painfully clear and quite urgent. Naturally, among elastomers that are considered, polysiloxanes, also often referred to as silicones and well-recognized as some of the best rubbers known to polymer science, have assumed center-stage in interest, and significant amount of research is presently ongoing in this direction.

Polysiloxanes, the long chain molecules with alternating arrangement of silicon and oxygen atoms in their repeat units,  $-\text{[SiR}_2\text{O]}_n-$ , are well recognized for having some of the lowest glass transition temperatures,  $T_g$ , known to polymer science and consequently, being excellent precursors for exceptional low-temperature elastomers. Pronounced elasticity of polysiloxanes at low temperatures is a consequence of their inherent chain flexibility derived from unusually long Si-O bond, large bond angle of Si-O-Si linkage as well as very low intersegmental interactions. The major drawback toward this application, however, results from their unfavorable crystallization behavior. This, for example, for the parent polymer of the family, polydimethylsiloxane, PDMS,  $-\text{[Si(CH}_3)_2\text{-O]}_n-$ , results in the crystalline melting transition at around  $-50\text{ }^\circ\text{C}$  to  $-40\text{ }^\circ\text{C}$  and therefore limits the low temperature usefulness of their elastomers to about  $10\text{ }^\circ\text{C}$  above it. Fortunately, as it has been well documented in literature, complete suppression of crystallization in linear PDMS, and therefore extension of elastomeric properties of the resulting rubbers to well below crystallization temperatures, can be achieved by substitution of small amounts

(often less than 5 mol %) of methyl side groups by crystallization disruptors, typically large and bulky phenyl units. On the other hand, for many applications of siloxane elastomers, formation of well-defined crosslinked networks is critical, requiring synthetic strategies for preparation of siloxane network precursors often to be focused on achieving the linearity and well-defined functionalization. Nonlinearity of their structures (branching) would lead to formation of network imperfections such as elastically inactive dangling chains, which would not perform as load-bearing elements of the final elastomer structure. It is therefore highly desirable to eliminate such branching while preventing polymer crystallization, in order to provide for predictable rubberlike elasticity at very low temperatures.

The first objective of this research was to investigate the effect of various cyclic siloxane monomers on the linearity and thermal behavior of their polymers aimed for the preparation of well-defined precursors for low temperature elastomers for additive manufacturing (3D printing). Towards this end, a series of polymers containing dimethylsiloxo-, DiMeS, methylvinylsiloxo-, MeViS, and diphenylsiloxo-, DiPhS, or methylphenylsiloxo-, MePhS, or diethylsiloxo-, DiEtS, repeat units, with dimethylvinylsiloxo-, DiMeViS chain ends was synthesized and evaluated. These polymers were prepared by anionic ring opening polymerization (ROP)-equilibration of different mixtures of cyclic siloxanes, including octamethylcyclotetrasiloxane,  $D_4$ , octaphenylcyclotetrasiloxane,  $D_4^{Ph2}$ , tetramethyltetraphenylcyclotetrasiloxane,  $D_4^{MePh}$ , octaethylcyclotetrasiloxane,  $D_4^{Et2}$ , hexaethylcyclotrisiloxane,  $D_3^{Et2}$ , and tetramethyltetravinylcyclotetrasiloxane,  $D_4^{MeVi}$ , initiated with oligodimethylsiloxo tetramethylammonium disilanolate, TMAS, in the presence of  $\alpha,\omega$ -telechelic dimethylvinylsiloxo-terminated oligodimethylsiloxane, end-blocker, DiViEB (see Reaction Scheme 2.1). It was found that, under the employed reaction conditions, the DiPhS-containing polymers underwent significant amount of chain branching, which was studied in detail and plausible reaction mechanism was proposed. To the best of this author's knowledge no such finding has been described previously in the literature. Formation of trisiloxo-, Ph-T-branches,  $Ph-Si-[OSi(CH_3)_2]_3$ , produced by desilylation of Si-Ph side bonds from DiPhS units by the nucleophilic attack of dimethylsilanolate anions, was identified and quantified by  $^{29}Si$  NMR analysis. In addition, it was also found that substitution of one Ph group from a DiPhS unit by a polydimethylsiloxo branch

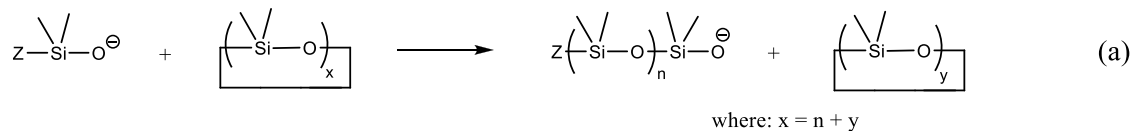
segment stabilized the remaining Ph group on the same silicon atom, since no indication of the formation of quaternary Q-branches could be detected. Furthermore, replacement of Ph side groups in such copolymers with large and bulky Et units resulted in complete prevention of branching, and both DiEtS cyclic trimer and tetramer were found equally effective for random incorporation into the polymer products. In contrast to this, an attempt to utilize DiEtS "hydrolyzate" for this purpose led to polymers that apparently contained extended PDES blocks and therefore showed some extent of crystallinity, not found in their completely random homologues from cyclic monomers. Finally, replacement of  $D_4^{\text{Ph}_2}$  cyclic comonomer by its  $D_4^{\text{MePh}}$  counterpart yielded perfectly linear terpolymers which required very low incorporation of phenyl side groups to completely prevent the PDMS-like crystallization, provided that randomization of repeat units is achieved by equilibration.

Taken together, all these results present a coherent picture that unexpectedly pronounced electrophilicity of DiPhS silicons makes them highly susceptible to attack by dimethylsilanolate nucleophiles, but that it is enough to replace one of two Ph groups with more electron-donating units (such as Et, Me or  $-\text{[O-Si(CH}_3\text{)}_2\text{]}-$  segments) to eliminate the driving force for this reaction and prevent the scission of the other Ph substituent from occurring. At the same time, if the replacing groups are equally large and bulky as Ph units, and randomly distribute along polymer chains, the resulting polymers become not only perfectly linear, but also perfectly amorphous (at least within the sensitivity ranges of the experimental techniques used in this work).

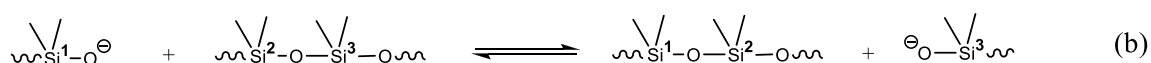
Silanolate-initiated polymerizations of cyclic siloxanes are complex processes generally consisting of two parallel, simultaneous reactions: (a) the anionic ring-opening polymerization, ROP, of cyclic monomers and (b) the siloxane equilibration (or redistribution) reaction, SER, in which nucleophilic silanolate active sites react with any siloxane bond in any cyclic or linear species present in the reaction system. Because of such complexity, and because of the well-known, extremely pronounced inherent flexibility of polysiloxane chains, at any given moment of the occurrence of such a process, the reaction system represents a complex mixture of linear and cyclic species. The relative contents and the molecular size distributions of these species, as well as the overall kinetics of the process, depend on a variety of factors, including the type of the initiator and monomer(s) used, the degree of monomer conversion, the nature of the

reaction medium (solution or bulk), and the reaction temperature. A general case of such a polymerization reaction can be represented by the following Reaction Scheme 1.1:

ROP:



SER:



where digits 1-3 denote different Si atoms

**Reaction Scheme 1.1. Ring-opening polymerization, ROP, and siloxane equilibration reaction, SER, in polymerization of cyclic siloxanes**

In an attempt to better understand this complex process, the objective of the second part of this dissertation was development and application of several practical methods for real-time monitoring of selected process variables during its occurrence. Such methods may focus on a variety of different process parameters, which reflect the reaction progress, including the increasing yield of the polymer product, its growing molecular size, increasing monomer conversion, etc. Monitoring methods employed in this work included size exclusion chromatography, SEC, thermal gravimetric analysis, TGA, and  $^{29}\text{Si}$  NMR spectroscopy, and it was found that all of them proved extremely useful for the purpose, complementing each other and enabling a better understanding of the reaction mechanism by which these polymers are formed. Dimethylsilanolate-initiated bulk copolymerizations of mixtures of  $\text{D}_4$  with  $\text{D}_4^{\text{Ph}_2}$  or  $\text{D}_4^{\text{MePh}}$  or  $\text{D}_3^{\text{Et}_2}$  as well as homopolymerization of pure  $\text{D}_4$  were investigated. Particular attention was devoted to the most complex of the systems examined, the copolymerization of  $\text{D}_4$  and  $\text{D}_4^{\text{Ph}_2}$ , which, in addition to complexities resulting from the simultaneous occurrence of the two reactions of Reaction Scheme 1.1, also featured an added subtlety of starting as a two-phase, heterogeneous system of two very differently reactive monomers. The  $\text{D}_4^{\text{Ph}_2}$  is much more reactive toward dimethylsilanolate than  $\text{D}_4$ , and is also very poorly soluble (i.e., practically insoluble) in its all-methyl  $\text{D}_4$  counterpart. Based on the data obtained, a new

three-stage reaction mechanism is proposed to describe the course of occurrence of this complex process.

## **2. THEORETICAL PART**

### **2.1 Overview**

This chapter focuses on literature resources closely related to the research study reported in this work. It is divided in several sections. In the first part, a brief historical background of research activities and discoveries that led to recognition and commercialization of polysiloxanes is presented. It is followed by the discussion of the unique features of siloxane bond and their impact on the properties and applications of polysiloxanes. The greater part of this chapter is devoted to chemistry of polysiloxane preparations with particular focus on both kinetically and thermodynamically controlled ring opening polymerization (ROP) of cyclic siloxanes. Low-temperature crystallization of polysiloxanes and mechanisms of its suppression are discussed in detail in the section that follows. The relation between reactivity of cyclic siloxanes and microstructure of resulting copolysiloxanes is reviewed in detail together with general theories of copolymerization. The final sections disclose the details on two powerful characterization methods explored in this dissertation:  $^{29}\text{Si}$  NMR spectroscopy and size exclusion chromatography (SEC).

### **2.2 Chemistry of Organosiloxanes - Historical Background**

Polyorganosiloxanes are an important and widely studied class of semi-inorganic polymers. The first successful attempts of establishing/developing the routes and methods for the preparation of organosilicon compounds which contain silicon-carbon bonds (which do not normally occur in nature), belong to Friedel and Crafts, who in the period 1863-1880 reported on preparation of tetraalkylsilanes utilizing the reaction between dialkylzinc and tetrachlorosilanes at elevated temperature.<sup>1</sup> Further development of this concept by Ladenburg, Pape, Polis, and others resulted in synthesis of various partially and fully alkylated silanes and chlorosilanes.<sup>1</sup> The major impact on the development of organosilicon chemistry came, however, at the very beginning of the twentieth century, from the work of Kipping and his coworkers, who, experimenting with newly discovered magnesium-based organometallic compound, Grignard reagent, invented a new general path for the preparation of organosilicon compounds.<sup>2</sup> Kipping's primary research interest

was in the field of optically active compounds and his initial intention was to prepare silicon-containing analogues of ketones, because of which he named these hypothetical compounds “silicones”. The expectation was to obtain these silicon-based optical compounds, described by the empirical formula  $R_2SiO$ , through hydrolysis of alkyl disubstituted chlorosilanes. These attempts, however, resulted in the compounds quite different from ketones, which readily agglomerated. At the later stage of research, after detailed analysis of the frequently overlooked products obtained by hydrolysis of chlorosilanes, Kipping characterized polymers of alternating silicon and oxygen atoms as macromolecules, but never considered them significant enough for advanced research, failing to foresee the potential commercial value of his work. Regardless, his research formed the basis for the worldwide development of the synthetic rubber and silicone-based lubricant industries.

Industrial interest in organosilicon polymers began in the early 1930s at the Corning Glass Works as well as at the General Electric Company. The first commercial polysiloxane product (heat-resistant electrical insulating material) was launched during the World War II by Corning Glass Works in a joint partnership with the Dow Chemical Company, and it was the result of research of Hyde,<sup>3</sup> based on Grignard route, pioneered by Kipping. He demonstrated superior thermal stability and electrical resistance of siloxane resins relative to other polymer materials.

Another breakthrough achievement occurred in 1940s, when preparation of main siloxane intermediates, organochlorosilanes, by the so-called “Direct Process”, was developed by Rochow<sup>4,5</sup> of General Electric Company. The Direct Process technology, which was the key step towards the commercialization of polysiloxanes, essentially consists of passing alkyl chlorides over elemental silicon in the presence of copper catalyst and is still the dominant technology for preparation of organochlorosilanes.

### **2.3. The Siloxane Bond**

The extraordinary versatility of polysiloxanes arises from their unique combination of advantageous properties, which in turn are due to the electronic character of the siloxane bond (Si-O bond). The siloxane bond is one of the thermodynamically most stable chemical bonds. Having the length of  $1.64 \pm 0.03 \text{ \AA}$ , the Si-O bond of polysiloxanes

is much shorter than the expected interatomic bond length of 1.8 Å (calculated from the simple addition of covalent radii of 1.17 Å and 0.66 Å for Si and O atoms, respectively). This 0.2 Å difference in Si-O bond length is attributed to both its substantial ionic and partial double bond character.

The concept of three combined contributions, covalent, polar and double-bond, to the siloxane bond is at the core of understanding of the physical and chemical properties of not only polysiloxanes but also of the silicates.

The first efforts to explain the shortening of the distance between Si and O to less than the sum of their interatomic radii postulated that the siloxane bond had both ionic and covalent bond component.<sup>1,6</sup> Pauling was the first to explain the ionic contribution using the difference in electronegativities of silicon and oxygen of 1.8 and 3.5, respectively.<sup>7,8</sup> Based on the results of experiments where electric dipole moments were measured, he derived the empirical formula for calculation of polar bond contribution as a function of absolute difference in electronegativity of bonded atoms  $|X_A - X_B|$ :

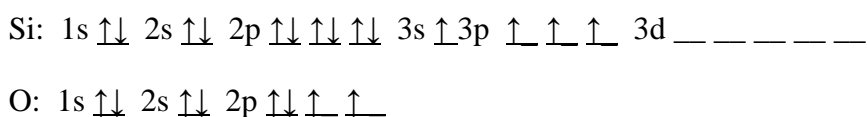
$$\text{Polar bond contribution, \%} = 100[1 - e^{0.25(X_A - X_B)^2}] \quad (2.1)$$

from which he estimated, taking into account the difference in electronegativities between silicon and oxygen of 1.7, that polar and covalent contributions of the siloxane bond were equal (50-50). Further revisions of Pauling's formula resulted in improved and more accurate expressions for determination of polar contribution of chemical bonds, such as the one derived by Hannay<sup>9</sup>:

$$\text{Polar bond contribution, \%} = 16(X_A - X_B) + 3.5(X_A - X_B)^2 \quad (2.2)$$

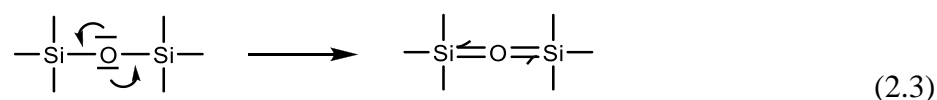
based on which the polarity of the siloxane bond was reduced to 38 %.

The double bond contribution to the siloxane bond arises from the ability and tendency of silicon atom to use its vacant 3d orbitals shown in the scheme of orbital arrangements below.





Except for normal  $\sigma$  bonding which involves  $3s$  and  $3p$  electrons of silicon and  $2p$  electrons of oxygen, there is also formation of  $d\pi - p\pi$  bonds, responsible for the double bond character contribution.  $d\pi - p\pi$  bonds are produced by partial delocalization of oxygen lone electron pairs from  $p$  orbitals to unoccupied  $d$  orbitals of silicon, schematically described by equation 3.<sup>1, 10</sup>



Unlike conventional  $p\pi - p\pi$  conjugation, the  $p\pi - d\pi$  type does not restrict rotation around the  $\sigma$  bond. This additional  $p\pi - d\pi$  interaction is also responsible for larger than expected valence angles in polysiloxanes.<sup>1, 10</sup>

The length of the siloxane bond can be altered by the electronegativity of attached organic substituents. Electron accepting groups on the silicon atom, for example, lower the energy of the vacant orbitals raising the double bond character of the bond. The bond order for most of organosiloxane compounds vary between 1.2 – 1.5.<sup>10</sup>

Electron delocalization along the O–Si–O linkage is responsible for the fact that siloxane bond exhibits unusually low *reactivity*. Both ionic and double bond components contribute to a high Si-O bond energy (445 kJ/mol or 108 kcal/mol), which is considerably higher than the bond energy of its carbon analog, C-O bond (358 kJ/mol or 82.6 kcal/mol).<sup>1, 11, 12</sup> This high dissociation energy makes siloxane bond very resistant to homolytic cleavage, which is directly related to considerable *thermal stability* of polysiloxanes.<sup>13, 14</sup> Generally, the onset of purely thermal degradation of polydimethylsiloxane occurs at about 350 °C, while its aryl-substituted versions can withstand even higher temperatures before irreversible degradation begins. At the same time, the siloxane bond is highly susceptible to heterolytic cleavage in the presence of acids or bases due to its pronounced polarity, the relatively large size of the silicon atom, and its accessibility within a polysiloxane chain.

The electronic configuration of the siloxane bond as well as the minimal steric hindrance of side groups (as the latter are attached at every other atom within the polysiloxane backbone), explains extremely high mobility of polysiloxane chains.<sup>10, 13</sup> The fact that Si-O bond of polydimethylsiloxane (PDMS) of 1.64 Å is longer than typical C-C organic bond of 1.54 Å allows for a broader range of valence angles.<sup>10</sup> The bond

angle for Si-O-Si linkage in organosiloxane compounds varies widely between  $105^\circ$  and  $180^\circ$ . For PDMS, this angle around the Si-O-Si linkage is ca.  $145^\circ$ , as illustrated in Figure 2.1, which greatly exceeds the expected valence angle of oxygen in a  $sp^3$  hybridized bond of about  $109^\circ$ .<sup>1, 10</sup> The length of the Si-O bond is also responsible for the enhanced mobility of organic substituents in polysiloxanes, due to their increased spatial separation and therefore minimal steric hindrances.<sup>13</sup> In addition, the oxygen atoms of the siloxane backbone are relatively small and unburdened with side group, thus allowing for more rotational freedom of the chains. Wide bond angles coupled with a very low energy barrier for rotation around the siloxane bond (less than 0.8 kcal/mol or 3.3 kJ/mol for Si-O versus 3.3 kcal/mol or 14 kJ/mol for rotation around C-C bond in polyethylene and more than 4.8 kcal/mol or 20 kJ/mol for rotation around C-C bond in polytetrafluoroethylene, PTFE)<sup>15</sup> results in a remarkable conformational freedom of polysiloxane chains, making them the most *flexible* family of polymers known to polymer science. The glass transition temperature,  $T_g$ , which reflects the extent of segmental mobility along the polymers chains, reaches the lowest known values for polydiethylsiloxane, PDES, of ca.  $-135^\circ\text{C}$ , and for PDMS, typically below  $-120^\circ\text{C}$ .<sup>13, 14</sup>

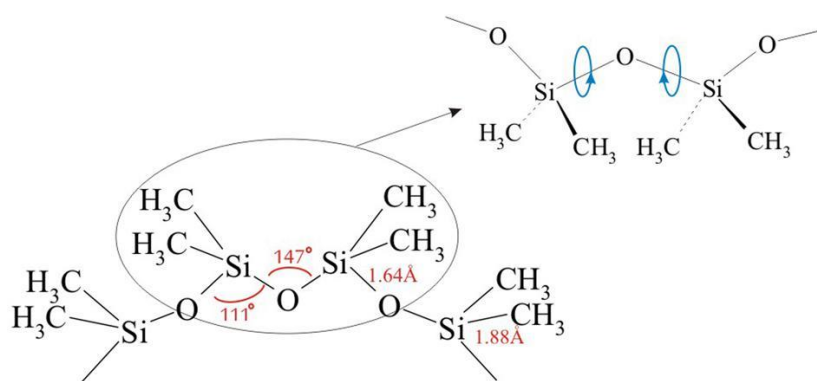


Figure 2.1. Fundamental structural features of a polydimethylsiloxane chain.<sup>16</sup>

The high segmental and rotational mobility of polysiloxane chains also plays important role in another unique characteristic of these polymers, their *surface properties*.<sup>17</sup> Although the inorganic backbone of polysiloxanes is highly polar, it is effectively shielded by non-polar organic pendent groups, which results in weak intermolecular forces in polysiloxanes.<sup>15</sup> Furthermore, chain-to-chain interactions are low due to the low

cohesive energy, and the distance between neighboring chains is noticeably larger than in organic analogues, which also contributes to the great flexibility of the former. Due to great flexibility of the chain backbone and weak intermolecular forces, the activation energy of viscous flow is very low, and the viscosity of polysiloxanes is less dependent on temperature compared to hydrocarbon polymers. Extremely low rotational barriers allow polysiloxane molecules to easily orient to thermodynamically favored conformations in a variety of environments such as at interfaces. This feature, combined with weak intramolecular interactions, gives rise to very low surface tension (20 to 25 mN/m for PDMS) and therefore capability of wetting most surfaces. Silicones have the lowest surface tension of all polymers excluding fluoropolymers.<sup>15</sup> With the methyl groups pointing to the outside, this gives very *hydrophobic* films and a surface with good release properties. Siloxane fluids readily spread over the surfaces of many substances, making them useful in a variety of applications such as surfactants, antifoaming agents, lubricants, release agents, and water repellents. The very low intermolecular forces and consequently high free volumes of polysiloxanes are responsible for their exceptionally high *permeability* to gases such as oxygen, nitrogen and even water vapor. This feature found applications as membranes for blood oxygenation, gas separation, drug delivery etc.<sup>18, 19</sup> Expectedly, *compressibility* of polysiloxanes is also high with application found as liquid springs, shock absorbers, and damping devices.<sup>20</sup>

### **2.3.1 Applications of Polysiloxanes**

The remarkable combination of properties of polysiloxanes that are attributed in large part to the chemistry and electronic configuration of their siloxane bonds, have been the main reason behind their unprecedented success and diverse uses, some examples of which are listed in Table 2.1.

Table 2.1. Some traditional applications of polysiloxanes.<sup>21</sup>

<b>Automotive</b>	<b>Electrical/Electronic</b>
Wire insulation Transmission seals Spark-plug boots Special lubricants Hydraulic bumpers Truck hose	Motor and transformer insulation Wire and cable insulation Circuit board laminates Telephone wire connectors Transistor encapsulants Circuit encapsulants Television insulation Rubber tapes (adhesive)
<b>Military/Aerospace</b>	<b>Paper</b>
Aircraft seals Firewall insulation Special lubricants Heat shields	Antistick surfaces Process defoamers
<b>Textiles</b>	<b>Rubber</b>
Water repellents Fabric softeners Dyeing-process defoamers	Tire release coatings
<b>Food</b>	<b>Construction</b>
Coffee defoamers Bread pan coatings Milk-carton release coatings Cooking-process defoamers	Window and building sealants Roof coatings Masonry water repellents Weather-durable paints Heat-resistant paints
<b>Plastic Tooling</b>	<b>Consumer Products</b>
Furniture molding Vinyl shoe molding Jewelry molding	RTV sealants Tile grout Shoe water repellents Eye-glass tissues Lubricant sprays
<b>Chemical Specialties and Cosmetics</b>	<b>Medical</b>
Auto and furniture polish Antiperspirants Hair sprays Hand creams Bath oils Foaming agents	Prostheses Artificial organs and skin Facial reconstruction Contact lenses Catheters Drug delivery systems

In recent years, an increased number of scientific reports focused on possible application of polysiloxanes in three-dimensional, 3D, printing (or additive manufacturing, AM). 3D printing, which is defined as the action or process of making a physical object from a three-dimensional digital model, typically by laying down many thin layers of a material in succession, represents a highly flexible and versatile novel processing technique which can apply polymers, metals, ceramic, concrete and other building materials. 3D-printed functional soft materials would have a diverse range of potential applications in the fields of materials engineering, bioengineering, and electronics. Through precise control over the deposition of highly engineered viscoelastic inks in the form of continuous filaments, complex 3D architectures can be additively fabricated, layer-by-layer, to generate parts that are directly applicable to cutting-edge technologies. 3D-printed silicones would be particularly well suited to soft materials applications including high-performance foams and cellular solids,<sup>22-25</sup> soft robots,<sup>26-29</sup> and highly flexible and stretchable electronics.<sup>30, 31</sup>

## **2.4. Synthesis of Polysiloxanes**

### **2.4.1 Synthesis of Organochlorosilanes**

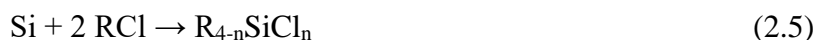
The precursors for the synthesis of polysiloxanes are organosilicon compounds of general formula  $R_4-nSiX_n$ , where R denotes organic substituent and X denotes easily hydrolyzable groups such as Cl, -OR, -NR<sub>2</sub>. Dimethyldichlorosilane, Me<sub>2</sub>SiCl<sub>2</sub>, is organochlorosilane predominantly used as polymerization precursor in siloxane industry.<sup>1, 32, 33</sup>

The preparation of organochlorosilanes is a two-step process. In the first step, the silica (SiO<sub>2</sub>) is reduced by carbon at high temperature by the carbothermal method<sup>34-36</sup> to obtain elemental silicon:



The elemental silicon is, in the second step, transformed into organochlorosilanes, most commonly using one of the following routes:

Direct Process,<sup>4, 5, 37-39</sup> involving the reaction of elemental silicon with organic compound such as alkylchloride in the presence of copper catalyst, at elevated temperature (250 – 300 °C), as illustrated by equation:



Chlorination of elemental silicone:



followed by partial substitution of chlorine by organic groups using organometallic compounds such as Grignard reagents:<sup>40</sup>

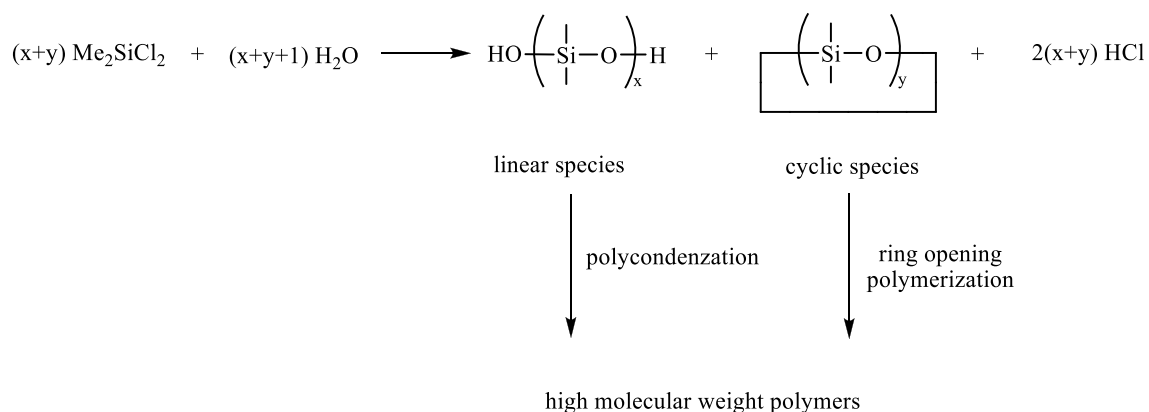


While the latter process is relatively complicated, Direct Process became the most common technology for preparing organosilicon compounds on an industrial scale worldwide. Over the years, Direct Process evolved considerably with regard to yield and selectivity as a result of comprehensive research in the area of promoters and additives.<sup>37, 38</sup>

#### 2.4.2 Preparation of Linear Polysiloxanes from Organochlorosilanes

Hydrolytic polycondensation of bifunctional silane precursor, typically dimethyldichlorosilane, produces a mixture of linear (silanol-terminated) and cyclic siloxy oligomers, frequently referred as “hydrolyzate”. The composition, i.e., the ratio of cyclic to linear component in a hydrolyzate depends greatly on the reaction conditions.<sup>1, 41-45</sup> For example, formation of the linear fraction of higher molecular weight is greatly promoted by the use of basic catalysts at higher temperatures, while acidic catalysts tend to produce larger fraction of cyclic molecules together with linear oligomers of lower molecular weights.<sup>46</sup> Since the composition of siloxane hydrolyzate depends on the kinetics of unimolecular and bimolecular condensation yielding cyclics and linear species, respectively, the cyclization is promoted if reaction is performed in diluted solution.<sup>47-51</sup>

Preparation of hydrolyzate from dimethyldichlorosilane is schematically illustrated in Reaction Scheme 2.1.



Reaction Scheme 2.1. Preparation of hydrolyzate from dimethyldichlorosilane

Generally, the path to high molecular weight polysiloxanes consists of either a) polycondensation of silanol-terminated oligosiloxanes, or b) ring opening of cyclic siloxane oligomers.

Various polycondensation reactions involving disilanol oligomeric fraction of hydrolyzate may be applied for preparation of linear polysiloxanes. They involve homofunctional polycondensation of disilanol as well as the variety of heterofunctional polycondensations based on reaction of silanol group with different silyl-functional groups such as SiOR, SiH, SiCl, SiOC(O)R, SiNR<sub>2</sub>, SiONR<sub>2</sub> etc.<sup>1, 32, 52, 53</sup> Heterofunctional polycondensation reactions are of importance in preparation of siloxane copolymers<sup>54-59</sup> as well as for the preparation of modified siloxane polymers containing non-siloxy repeat units in their main chains<sup>60-71</sup> A representative example of the latter group of copolymers are exactly alternating silarylene-siloxane polymers (SARSOX), which exhibit a promising combination of high temperature stability and low temperature flexibility.<sup>62-71</sup>

The ring-opening polymerization (ROP) of cyclic siloxane oligomers is, on the other side, the primary route to the majority of silicon polymers and copolymers and the method of choice when greater precision is required for the synthesis of high molecular weight polysiloxanes.<sup>32, 45, 52, 72-76</sup>

## **2.5 Synthesis of Polysiloxanes via Ring Opening Polymerization of Cyclic Siloxanes**

### **2.5.1 General Considerations**

Ring-opening polymerization, ROP, of cyclic siloxanes is a chain-growth reaction which occurs readily in the presence of ionic initiators. According to the chemical nature of active propagation center, the ROP reactions of cyclic siloxanes are classified as anionic and cationic. Even though these reactions are kinetically controlled chain-growth reactions, in most of the cases they are accompanied with reactions of equilibration, leading to the resulting product being a polydisperse mixture of linear and cyclic species. There are two general methods of ROP of cyclosiloxanes: 1) kinetically controlled, non-equilibrium polymerization which must be quenched at the proper moment before the onset of equilibration and 2) thermodynamically controlled equilibration or siloxane redistribution, SER, which is commonly used method but applicable only when polymer yield is reasonably high.

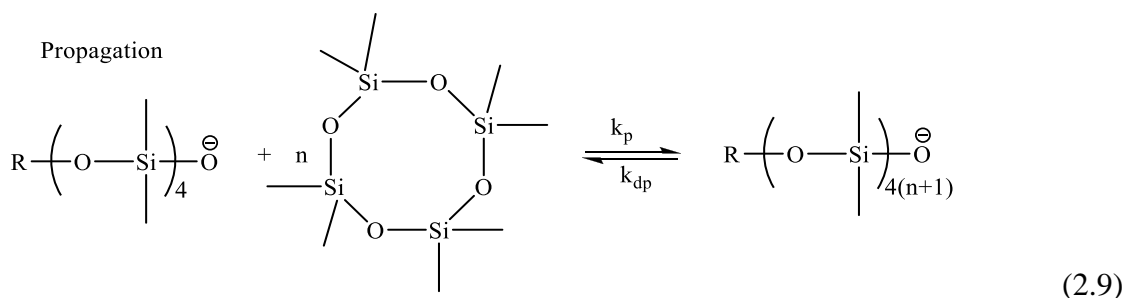
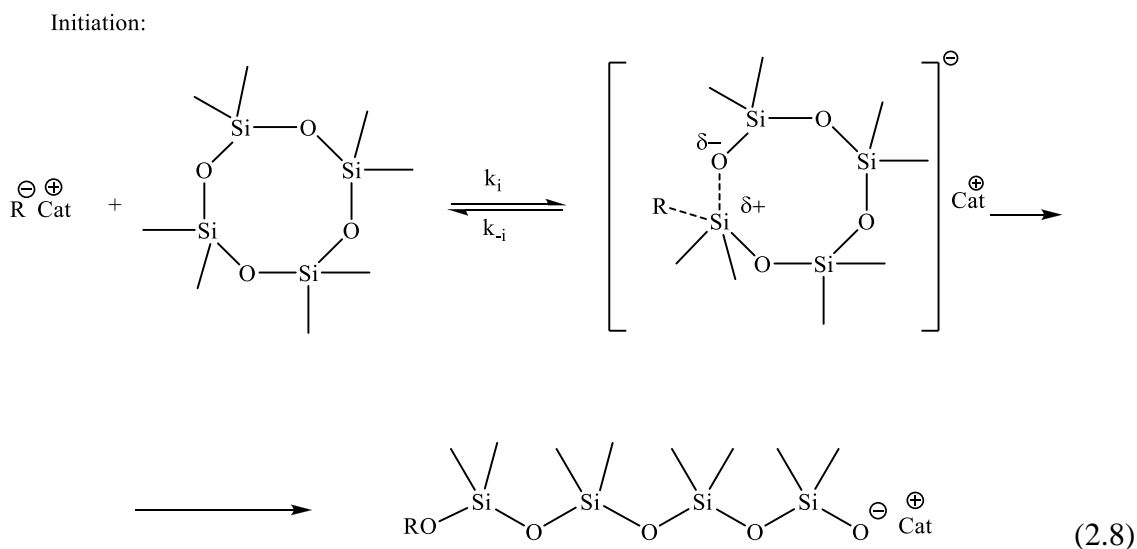
From the perspective of controlled design of the polymer structure, anionic, A-ROP of cyclic siloxanes is far more important than cationic. A-ROP has been broadly used in the industrial synthesis of polysiloxanes since late 1940s<sup>77</sup> and the interest in development of the process still persists. Thermodynamically driven, equilibrium A-ROP of cyclic siloxanes (see Reaction Scheme 1.1), which usually takes place in bulk at elevated temperatures, is technology of choice when well-randomized copolysiloxanes are required, while kinetically controlled processes (or non-equilibrium A-ROP) are used when a precise control of molecular weight, molecular weight distribution and functionalization is necessary.

### **2.5.2. Anionic Ring Opening Polymerization of Cyclic Siloxanes**

The initiation of an A-ROP of cyclosiloxanes proceeds by nucleophilic attack of the base on Si atom of the cyclic monomer. The initiators commonly used include strong inorganic, organic and organometallic bases such as hydroxides and oxides of alkali metals, quaternary ammonium hydroxides and silanolates, phosphonium hydroxides, organometallic compounds such as butyllithium, organic bases such as alkoxides, etc. The cleavage of the polar siloxane bond of the cyclic monomer is accomplished via rearrangement of a transition complex containing pentacoordinated Si atom. This leads



to the formation of an active propagation center, silanolate anion, capable of extending the polysiloxane chain by the addition of monomers, as shown in the Equations 2.8 and 2.9.



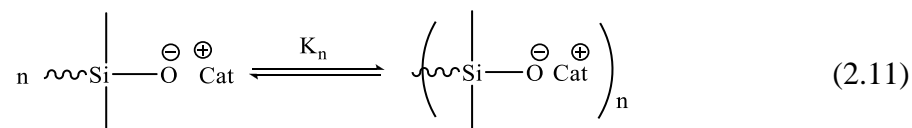
The overall rate of an A-ROP of cyclic siloxanes, as well as the average degree of polymerization of the polymer obtained, depend on the type and concentration of both initiator and monomer(s) and on the reaction temperature. The polymerization rate  $R_p$ , in its ideal form, can be described as the product of the bimolecular rate constant,  $k_p$ , the concentration of active silanolate ends,  $[\text{SiO}^-]$ , and the concentration of monomer,  $[\text{M}]$ :

$$R_p = k_p [\text{SiO}^-][\text{M}] \quad (2.10)$$

However, the rate law for A-ROP of cyclic siloxane is much more complicated due to aggregation of initiator ion pairs, the presence of accelerators as well as intra- and

intermolecular reactions between active silanolate and polymer, which produce cyclic siloxanes and broaden molecular weight distribution of polymer.

The free silanolate anions, in most systems, do not appear in any kinetically significant concentrations, and consequently the ion pairs serve as the active propagation species. Because of the effective ion-ion interactions, higher, inactive ion pair aggregates are formed in a fast and reversible reaction, as shown in equation 2.11.<sup>52, 78-80</sup>



where  $K_n$  denotes the equilibrium constant for the formation of ion pair aggregates containing  $n$  ion pairs.

Silanolate groups aggregation (cyclic or cage structures) converts active species into dormant centers,<sup>78, 80</sup> greatly reducing the overall polymerization rate. Consequently, kinetic law is affected, leading to the fractional order of reaction with regard to silanolate species (as seen in equation 2.12).<sup>32</sup>

$$\frac{-d[M]}{dt} = \left( \frac{1}{nK_n[SiO^-Cat^+]} \right)^{\frac{1}{n}} \{k_p[M] - k_{dp}\} \quad (2.12)$$

It is interesting to note that the phenomenon of aggregation of ionic pairs is almost independent of the reaction temperature.<sup>79</sup> The rate of A-ROP is directly related to the size of the counterion, increasing dramatically in the order:  $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+ \approx Me_4N^+ \approx Bu_4P^+$ , as concentration of un-aggregated ion pairs increases due to increased bulkiness of counterions, which loosens the ion-ion interactions and therefore the tendency towards aggregation. The additives known as polymerization promoters or activators such as dimethylsulfoxide, DMSO, dimethylformamide, DMF, hexamethylphosphorotriamide, HMPT are frequently used in small amounts to suppress aggregation of silanolate ionic pairs.<sup>10, 81 82 83</sup> Finally, there is the class of highly efficient cationic inclusion complexes (chelating additives) such as crown ethers<sup>84</sup> or macroheterobicyclic ligands (cryptands),<sup>85-88</sup> which act as ion pair separators by “trapping” the cations within their bulky structure, as illustrated in Figure 2.2, Scheme 2.1, and thus accelerate the polymerization reaction. In the latter case, only one type of

very active species was identified during polymerization of D<sub>3</sub> and D<sub>4</sub> initiated by butyl lithium, namely, cryptated ion pairs, and a first order of reaction with respect to silanolate was observed.<sup>85, 87</sup>



Figure 2.2. Separation of metal cations from silanolate anions by the use of crown ethers (A) and cryptates (B).

The structure of cyclic siloxane monomers, i.e., the size of the ring and the structural features of substituents plays very important role in the kinetics of A-ROP.<sup>89</sup> Having the largest ring strain and planar conformation, tricyclosiloxanes show a particularly high reactivity.<sup>90</sup> However, different trends in reactivity of cyclic siloxanes towards silanolate propagation centers with the increase of the ring size were observed depending on the initiator system used for their polymerization.

Due to the simplicity of the dimethylsiloxy-based systems, propagation and depropagation rate constants have been determined for D<sub>3</sub>, D<sub>4</sub>, D<sub>5</sub> and D<sub>6</sub> monomers in polymerizations in toluene, initiated by tert-butyl lithium in the presence of accelerator cryptand ligand [2,1,1].<sup>87, 91, 92</sup> The order of reactivity of D<sub>x</sub> is as follows: D<sub>3</sub> >> D<sub>4</sub> > D<sub>5</sub> > D<sub>6</sub>. The rate constant values for the series are listed in Table 2.2

Table 2.2. Rate constants of propagation and depropagation for polymerizations of cyclic dimethylsiloxanes D<sub>3</sub>, D<sub>4</sub>, D<sub>5</sub> and D<sub>6</sub> in toluene, at 20 °C, initiated by cryptated lithium silanolate active centers.<sup>91, 92</sup>

Cyclic siloxane	$k_p$ , L·mol <sup>-1</sup> ·h <sup>-1</sup>	$k_{dp}$ , h <sup>-1</sup>
D <sub>3</sub>	4700	0
D <sub>4</sub>	17	4
D <sub>5</sub>	6.5	0.9
D <sub>6</sub>	1.1	0.05

In contrast to this, significant increasing trend in reactivity was observed for unstrained dimethylcyclosiloxanes series: D<sub>4</sub> < D<sub>5</sub> < D<sub>6</sub> < D<sub>7</sub> < D<sub>8</sub>, when ROP was initiated by alkali metal silanolates in bulk or in non-polar solvents, as illustrated in Table 2.3.<sup>84, 93</sup>

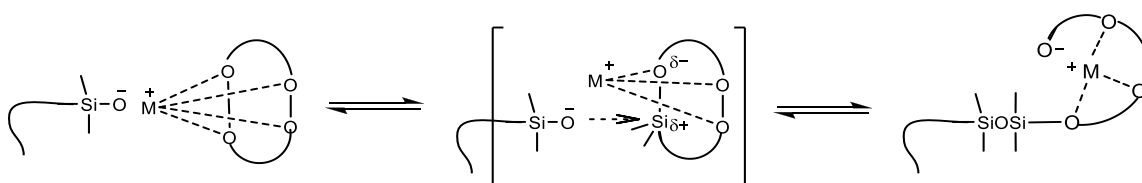
Table 2.3. Rate constants of propagation for polymerizations of cyclic dimethylsiloxanes D<sub>3</sub>, D<sub>4</sub>, D<sub>5</sub>, D<sub>6</sub>, D<sub>7</sub>, D<sub>8</sub> and D<sub>9</sub> in heptane/dioxane, at 30 °C, initiated by potassium phenyldimethylsilanolate.<sup>84</sup>

Cyclic siloxane	$k_p$ , 10 <sup>3</sup> s <sup>-1</sup>
D <sub>3</sub>	2.9
D <sub>4</sub>	0.033
D <sub>5</sub>	0.035
D <sub>6</sub>	0.39
D <sub>7</sub>	5.3
D <sub>8</sub>	6.0
D <sub>9</sub>	4.1

A similar increasing trend in the rate of breaking siloxane bond was observed for a series of linear, trimethylsiloxy-terminated oligodimethylsiloxanes Me<sub>3</sub>Si(OSiMe<sub>2</sub>)<sub>n</sub>OSiMe<sub>3</sub> (n=1-10), under the same reaction conditions.<sup>84</sup> These phenomena are explained by a mechanism involving multifunctional interaction of cyclic or linear siloxanes with the metal counterion - multidentate interaction.<sup>89, 94</sup> By increasing the polarity of the Si-O bond, this multidentate interaction, illustrated in Reaction

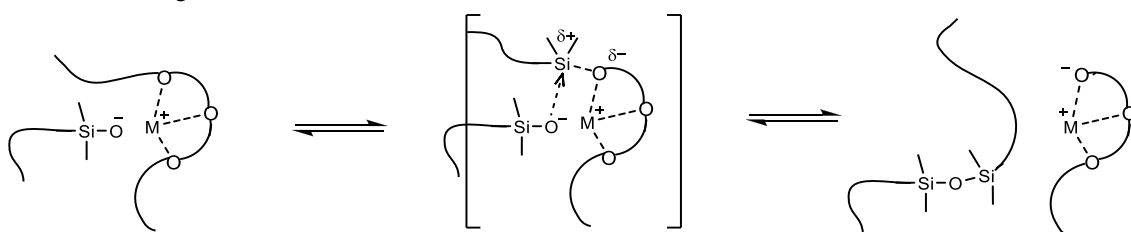
Schemes 2.2 and 2.3, effectively decreases the energy barrier to its cleavage, promoting equilibration processes of back-biting and chain scrambling (redistribution). Larger rings not only open faster but are also formed faster in a reversible depropagation process (back-biting). The chain scrambling processes, leading to broadening of molecular weight distribution (MWD) of the resulting polysiloxane, are also effectively accelerated by multidentate interaction. These interactions are highly undesirable for kinetically controlled polymerizations and can be suppressed either by stronger interaction with another nucleophile or by using bulkier counterions.

Propagation-depropagation



Reaction Scheme 2.2. Multidentate interaction of cyclic siloxane with the alkali metal counterion.

Chain scrambling



Reaction Scheme 2.3. Multidentate interaction of linear siloxane with the alkali metal counterion.

The use of non-ionic phosphazene superbases has also proven to be exceptionally effective way for initiation of A-ROP of  $D_4$  and  $D_3$ .<sup>95-98</sup> The imino-oligophosphazene uncharged bases such as  $t\text{-BuP}_4\text{Me}_{18}$  (Figure 2.3) require the use of a co-initiator, which is a proton donor such as an alcohol. This activation results in formation of a silanolate with a very bulky phosphazanium cation, having a delocalized positive charge, capable of inducing almost instantaneous polymerization of  $D_4$ .<sup>95</sup> The use of phosphazene base  $\text{P}_2\text{-Et}$  (Figure 2.3) as a promoter of A-ROP of  $D_3$  or  $D_3^{\text{Et}2}$  monomer initiated by lithium

silanolate lead to polymers of very narrow distribution of molecular weight ( $PDI < 1.1$ ) at very high conversions of monomers (ca. 70 %).<sup>96</sup>

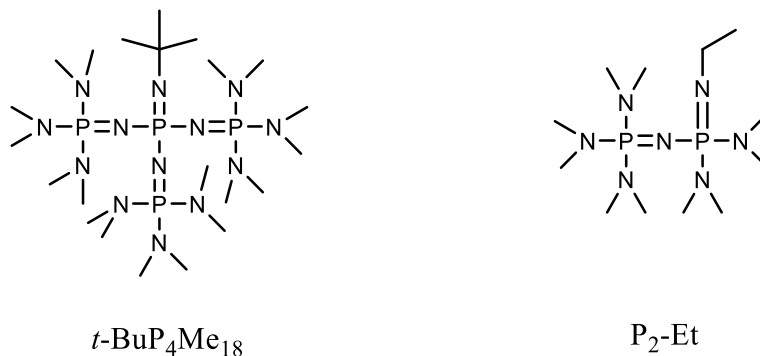


Figure 2.3. Structural formulas of iminooligophosphazene superbases  $t\text{-BuP}_4\text{Me}_{18}$  and  $\text{P}_2\text{-Et}$ .

The advanced class of initiators from the same family are amino-substituted oligophosphazenum hydroxides, for example hexapyrollidinediphosphazenum hydroxide,  $\text{P}_2\text{Pyr}_6^+\text{OH}^-$ , shown in Figure 2.4, which do not require any co-activation.<sup>98</sup> They were found to be very efficient and selective initiators of the A-ROP of cyclosiloxanes ( $\text{D}_3$  and  $\text{D}_4$ ), with the first order of reactions both in monomer and in initiator. A simple mechanism for the polymerization involves a fast initiation in which the diphosphazenum hydroxide is transformed into diphosphazenum silanolate, followed by the propagation step in which silanolate anion, loosely bonded to bulky diphosphazenum cation, opens the monomer ring and extends the polymer chain.

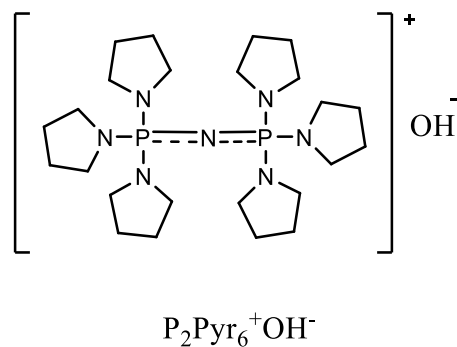


Figure 2.4. Structural formula of hexapyrollidinediphosphazenum hydroxide,  $\text{P}_2\text{Pyr}_6^+\text{OH}^-$ .

The rate of A-ROP of cyclosiloxanes is considerably affected by the nature of organic substituents on silicon.<sup>32, 80</sup> While electron-withdrawing substituents increase reactivity of cyclic siloxane by making the silicon atom to which they are attached more electrophilic, this diminished electron density, on the other side, lowers basicity of formed silanolate anion making it less active. Additionally, the effectiveness of the interaction of siloxy oxygen of monomer with counter-ion is lowered. In an attempt to determine the effect of polarity of substituents on polymerizability in the series of substituted tetracyclosiloxanes of general formula (RMeSiO)<sub>4</sub>, where R = Me, Et, Vi, Ph, C<sub>6</sub>H<sub>4</sub>Cl, it was found that introduction of electron-donating substituents, such as ethyl group, caused reduction in reactivity of cyclic siloxane in polymerization initiated by KOH, while introduction of electron-withdrawing substituents increases their reactivity.<sup>99</sup> Comparison of the rate constants of propagation of studied systems revealed that the contribution of substituent to the reactivity of tetracyclosiloxane in A-ROP increased in the order Et < Me < Vi < C<sub>6</sub>H<sub>4</sub>Cl < Ph. Notable changes in reactivities of tricyclosiloxanes and tetracyclosiloxanes were observed when the methyl groups are, partially or completely, replaced by longer alkyl chains.<sup>86</sup> The kinetics of A-ROP of ethyl- and propyl-substituted tricyclosiloxanes, D<sub>3</sub><sup>Et2</sup> and D<sub>3</sub><sup>Pr2</sup>, have been studied in toluene at 20 °C, by using *sec*-butylLi + cryptand [2.1.1] initiating system. The reactivity of D<sub>3</sub><sup>Et2</sup> and D<sub>3</sub><sup>Pr2</sup> is much lower than that of D<sub>3</sub> ( $k_p = 4,700, 40$  and  $25 \text{ L mol}^{-1} \text{ h}^{-1}$  at 20 °C for D<sub>3</sub>, D<sub>3</sub><sup>Et2</sup> and D<sub>3</sub><sup>Pr2</sup>, respectively).<sup>86</sup> From the kinetic data of the A-ROP of the methylvinyl cyclosiloxane series D<sub>3</sub><sup>MeVi</sup>, D<sub>4</sub><sup>MeVi</sup>, D<sub>5</sub><sup>MeVi</sup> and D<sub>6</sub><sup>MeVi</sup>, obtained under the same conditions, it was concluded that the reactivity of D<sub>4</sub><sup>MeVi</sup> and D<sub>5</sub><sup>MeVi</sup> is almost the same as that of D<sub>3</sub>, while D<sub>3</sub><sup>MeVi</sup> is about 20 times more reactive than D<sub>3</sub>.<sup>54, 85</sup> Identical order of reactivities (D<sub>4</sub><sup>MeVi</sup> ~ D<sub>3</sub> > D<sub>4</sub>) also applies for heterogeneous polymerizations catalyzed by ammonium hydroxide resins.<sup>100</sup> Kinetically controlled A-ROP of tricyclosiloxanes had proven to be a superior approach to synthesis of copolymers containing electron-donating substituents, such as organophosphorous groups of general formula -(CH<sub>2</sub>)<sub>n</sub>P(X)Ph<sub>2</sub>, where X denotes lone pair, O or S.<sup>101</sup> Compared to thermodynamically-controlled homo- or copolymerization of nucleophile-substituted cyclosiloxanes, kinetically controlled process results not only in better polymer yield, but also narrower molecular weight distribution. The kinetically controlled A-ROP of cyclic siloxanes is used when the formation of linear polymers, such as polydiphenylsiloxane<sup>102-105</sup>,

polytrifluoropropylmethylsiloxane<sup>106</sup> or polymethylphenylsiloxane<sup>107</sup> is thermodynamically disfavored.

The kinetically controlled polymerization of asymmetrical cyclosiloxane monomers, i.e., monomers with mixed siloxy units, leads to copolymers of functional siloxane and dimethylsiloxane units of highly regular structure. If regioselectivity of the ROP is provided, that is, if asymmetrical cyclosiloxane is opened exclusively at one site, and if the propagation is not accompanied by inter- and intramolecular side reactions, the monomer enters the chain undivided, providing uniform distribution of functional units in the resulting polymer.<sup>32</sup> The regioselectivity in the A-ROP of these mixed cyclosiloxanes is closely related to the nature of the substituent and to the experimental conditions, as can be seen from selected examples listed in Table 2.4.

The attempts to obtain copolymers of uniform structure using A-ROP of functionalized tetracyclosiloxanes have been less successful. Due to lower reactivity of cyclic tetramers it is necessary to use highly efficient initiating systems such as non-ionic superbases. A-ROP of both 2,2,4,4,6,6-hexamethyl-8,8-divinylcyclotetrasiloxane<sup>108</sup> and 2,2,4,4,6,6-hexamethyl-8,8-diphenylcyclotetrasiloxane<sup>109</sup>, initiated by *t*-BuP<sub>4</sub>Me<sub>18</sub> superbase and performed at 80 °C, led to polydisperse copolymers with random microstructure and a series of monomeric mixed tetra-, penta-, and hexacyclosiloxanes.

Table 2.4. Examples of highly regioselective A-ROP of tricyclosiloxanes  
R<sub>1</sub>R<sub>2</sub>SiO(Me<sub>2</sub>SiO)<sub>2</sub>.

R <sub>1</sub>	R <sub>2</sub>	Conditions	Reference
H	CH <sub>3</sub>	Ph <sub>2</sub> Si(OLi) <sub>2</sub> , THF, -78 °C	110
Vi	Vi	n-BuLi, THF, -30 °C	111
Vi	Vi	Me <sub>3</sub> SiOLi, THF, -30 °C	112
Vi	Vi	Ph <sub>2</sub> Si(OLi) <sub>2</sub> , THF, HMPA, 0 °C	113
C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>4</sub> CF <sub>3</sub>	Ph <sub>2</sub> Si(OLi) <sub>2</sub> , THF, HMPA, 0 °C	114
H	OSiMe <sub>3</sub>	Ph <sub>2</sub> Si(OLi) <sub>2</sub> , THF, -50 °C	115

Kinetically controlled A-ROP of different symmetrical cyclosiloxanes can also produce highly regular copolysiloxanes, although with different distribution of units along the



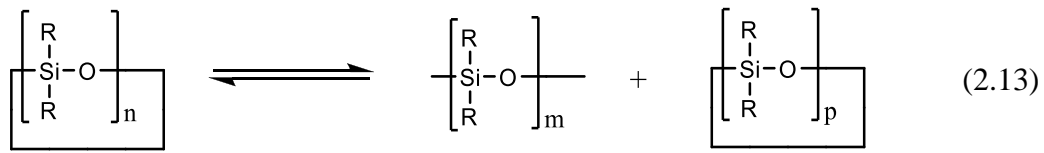
chains compared to copolymers obtained by ROP of cyclosiloxanes with mixed units. The fact that, the more reactive cyclic monomer preferentially enters the chain at the beginning of propagation and that its incorporation slows down as its availability in the feed decreases, is used for preparation of copolysiloxanes with a gradient distribution of repeat units along the copolymer chain.<sup>111, 116</sup>

On the other side, sequential copolymerization of cyclosiloxanes is particularly suitable for the synthesis of well-defined diblock (AB) and triblock (ABA) copolymers. In principle, it is recommended that the less reactive monomer be polymerized first, so that the cross-propagation with residual monomer (leading to randomization) in the second step is avoided. The use of monofunctional initiator leads to diblock copolymers, while triblock copolymers are formed with bifunctional initiators. The sequential copolymerization of dimethylsiloxy and diphenylsiloxy cyclic monomers leading to AB or ABA block copolymers was extensively studied.<sup>117-121</sup> Usually, randomization to some extent occurs during the second step of these processes, due to harsh conditions required for the ROP of the phenyl substituted cyclic monomers.

### **2.5.3 Siloxane Redistribution (Equilibration): Thermodynamic Control**

Ring opening polymerization is thermodynamically controlled in the cases when it is allowed to reach the equilibrium state. The equilibration route is of particular importance for preparation of mixed linear and cyclic siloxanes which are difficult to prepare otherwise, as well as for readjustment of molecular weight distribution of polysiloxanes. An example of preparation of mixed siloxanes is equilibration of mixtures of symmetrical disiloxanes, hexamethyldisiloxane and diphenyltetramethyldisiloxane initiated by potassium hydroxide.<sup>122</sup> Equilibration has been conveniently used as a route for preparation of random copolysiloxanes. Good redistribution of comonomers units along the polymer chains is crucial for achieving desired improvements of properties, for example, for suppression of low temperature crystallization.<sup>13, 123</sup>

A polysiloxane polymerization system at equilibrium consists of two homologue series of species, linear and cyclic, each having continuous distribution of molecular sizes as described by equation 2.13.



The equilibrium state is independent of the initiator used and of the size of cyclic monomer and it can be reached by both anionic and cationic route. The yield, molecular weight and molecular weight distribution of polymer fraction at equilibrium are controlled by thermodynamics of polymerization and completely unrelated to its kinetics. With the cyclic siloxanes produced by equilibration being predominantly oligomers, the polymer yield is directly determined from the equilibrium between open chains and cyclics. Equilibrium molar constant for the formation of cyclic n-mer from linear polymer,  $K_{cn}$ , is in most cases considered approximately equal to equilibrium concentration of that cyclic (equation 2.14).<sup>11, 50, 124</sup>

$$K_{cn} = \frac{\left[ \left( \begin{array}{c} \text{R}_2\text{SiO} \\ | \\ \text{---} \end{array} \right)_n \right]_e}{p^n} \sim \left[ \left( \begin{array}{c} \text{R}_2\text{SiO} \\ | \\ \text{---} \end{array} \right)_n \right]_e \quad (2.14)$$

where  $\left[ \left( \begin{array}{c} \text{R}_2\text{SiO} \\ | \\ \text{---} \end{array} \right)_n \right]_e$  denotes equilibrium molar concentration of cyclic n-mer,  $p=1-1/\bar{x}$ , with  $\bar{x}$  being the average number of siloxy units in linear fraction. Consequently, the overall equilibrium cyclization constant can be considered equal to the molar concentration of siloxy units contained in equilibrium fraction of cyclics and independent of the initial concentration of cyclic monomer. Considering that the smallest cyclic consists of three siloxy units, this relationship can be described as follows (equation 2.15.):

$$K_c = \sum_{n=3}^{\infty} n \left[ \left( \begin{array}{c} \text{R}_2\text{SiO} \\ | \\ \text{---} \end{array} \right)_n \right]_e \quad (2.15)$$

Unlike the equilibrium concentration of cyclic oligomers, the yield of linear fraction at equilibrium is strongly dependent on initial concentration of cyclic monomer as described by equation 2.16.

$$w_p = 1 - w_c = 1 - K_c / [R_2SiO]_{tot} \quad (2.16)$$

in which  $w_p$  and  $w_c$  denote equilibrium weight fractions of the polymer and cyclics, respectively, and  $[R_2SiO]_{tot}$  represent total molar concentration of siloxy units in the polymerization system, that is, the initial concentration of cyclic monomer. Therefore, in order for polymer to be formed during equilibration reaction the total concentration of siloxy units must exceed the value for the overall equilibrium cyclization constant:  $[R_2SiO]_{tot} \geq K_c$ . The dilution of equilibration polymerization system decreases the polymer yield.<sup>51, 124</sup> If the concentration of siloxy units in the system is reduced by dilution with solvent, the concentration of cyclics remains the same at the expense of linear polymer. The weight fraction of the cyclics in the equilibrated polysiloxane system increases with dilution up to a critical point beyond which polymer cannot be formed in the thermodynamically driven process. Dilution of the siloxane equilibration system can also arise as a consequence of the volume occupied by substituents. For example, the equilibrium concentration of total cyclic oligomers in bulk significantly increases with polarity and bulkiness of the substituents, as illustrated in Table 2.5. Consequently, the effective siloxane equilibration can be performed to produce polymer in high yield, only in bulk or in concentrated solutions using cyclosiloxanes with small, nonpolar substituents.

Table 2.5. The yield of linear polymer [-RR'SiO-] in bulk siloxane equilibrates.<sup>49, 51</sup>

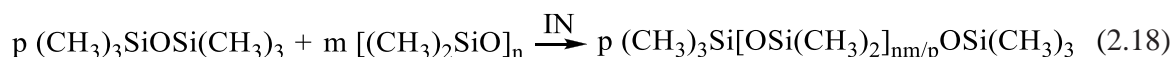
R	R'	Polymer Yield, %
CH <sub>3</sub>	H	88
CH <sub>3</sub>	CH <sub>3</sub>	82
CH <sub>3</sub>	CH <sub>3</sub> CH <sub>2</sub>	74
CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	70
CH <sub>3</sub>	CF <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub>	17
C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	0

The enthalpy change ( $\Delta H$ ) of siloxane equilibration is exclusively related to the strain energy of cyclic species, since the number of siloxy bonds does not change during the polymerization. In contrast to cyclic trisiloxanes, for which there is considerable ring strain, and their presence at equilibrium is mostly negligible, larger cyclics are practically strain-free, so there is also no enthalpic contribution from the cleavage of the rings. The entropy of siloxane equilibration, on the other hand, is affected by two competing contributions. Conformational entropy gain is the driving force for ROP since there is more conformational mobility to open chains than to the cyclics, but contrary to this, cyclization is entropically favored (particularly towards formation of smaller rings) because it results in the increase of the number of molecules in the system. As a consequence, the balance between these two entropic effects determines the composition of the siloxane system at equilibrium.

The equilibria between linear species determine average molecular weight and molecular weight distribution of the polymer. The number-average molecular weight of polymer at equilibrium is related to the number of end groups (equation 2.17), which are introduced by the initiator, or more commonly, by the end-blocker, when more precise control of molecular weight is required.

$$M_n = \frac{2[\text{R}_2\text{SiO}]_{\text{eq}}M_0}{[\text{end-group}]} \quad (2.17)$$

where  $M_0$  is the molecular weight of siloxy repeat unit and  $[\text{R}_2\text{SiO}]_{\text{eq}}$  is the equilibrium concentration of siloxy units in the open chains. The most frequently used end-blockers are triorganosiloxy-terminated oligosiloxanes, such as hexamethyldisiloxane,  $(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_3$ , as shown in equation 2.18. Besides the chain length regulation, this mode of termination also results blocking the chain ends with non-reactive groups thus providing a high thermal and chemical stability to the resulting product(s).<sup>1, 32, 52</sup>



End-blockers containing carbofunctional or silicon-functional groups are broadly used for preparation of reactive telechelic polymers, utilized as intermediates for preparation of block copolymers.<sup>125-127</sup> Also, vinyl-silyl functional groups are commonly introduced at the polysiloxanes chain-ends using end-blockers such as 1,3-divinyltetramethyldisiloxane

or dimethyl vinyl-terminated oligosiloxanes. Such vinyl groups provide crosslinking sites for preparation of siloxane-based elastomers.

Since the state of equilibrium is attained through random processes involving breaking and reforming of siloxane bond, it is expected that the polymer's molecular weights distribution be in agreement with the Flory normal distribution function, which predicts polydispersity index (PDI) of equilibrated polymer to be  $PDI = M_w/M_n = 2$ .<sup>128, 129</sup> Sometimes, however, association phenomena related to end groups may lead to the broadening of molecular weight of linear polysiloxane.<sup>130</sup> The distribution of sizes of cyclic oligomers at equilibrium is monotonically decreasing function of the ring size, as predicted by Jacobson-Stockmayer macrocyclization theory, which is based on the premise that the proportion of cyclic species in equilibrium with linear species is related to the probability of successful collisions of terminal groups of the  $x$  units long linear molecules.<sup>131</sup> For the dimethylsiloxane cyclics series at equilibrium with high molecular weight polymer in bulk, the following composition was determined: 10 wt. % D<sub>3</sub> to D<sub>5</sub>, 3.6 wt. % D<sub>6</sub> to D<sub>18</sub> and 4.7 wt. % D<sub>19</sub> and higher cyclic oligomers.<sup>51</sup>

#### **2.5.4 Transient Initiators for Anionic Ring Opening Polymerization of Cyclic Siloxanes**

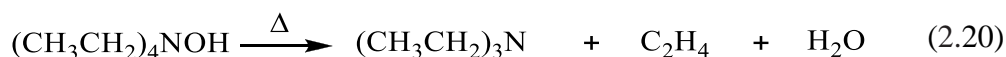
A wide range of initiators is available for A-ROP of cyclic siloxane with equilibration, SER.<sup>1, 10</sup> Representative initiators include strong bases such as alkali metal hydroxides, silanolates, alkoxides, phenolates, as well as quaternary ammonium and phosphonium hydroxides and their silanolates. The latter group of thermally labile compounds, often termed *transient initiators*, offers advantages over commonly used alkali metal bases, removal of which requires tedious, time-consuming procedures of washing, neutralization, deactivation and filtration. Unless quantitatively removed or deactivated, the base initiators remain active causing depolymerization at elevated temperature and hydrolytic degradation at room temperature.<sup>82</sup> For example, polydimethylsiloxane containing 0.01 % of KOH will lose 99 % of its weight within 20 hours at 250 °C, while the same concentration of RbOH will cause the same level of degradation within only 2 hours.<sup>82</sup> In contrast to this, with the use of transient initiators, the issues related to thermal and hydrolytic stability are completely eliminated: they are sufficiently active to initiate

polymerization at lower temperatures (70-120 °C) but when heated above 130 °C, they decompose and become inactive.

The most representative example of a transient initiator is tetramethylammonium hydroxide, which decomposes thermally giving trimethylamine and methanol, according to equation 2.19.

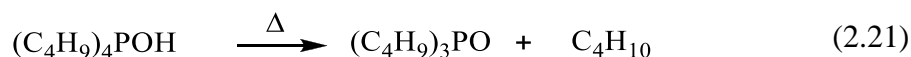


Higher alkylammonium hydroxides such as tetraethylammonium hydroxide,  $(\text{CH}_3\text{CH}_2)_4\text{OH}$ , and tetra *n*-propylammonium hydroxide,  $(n\text{-C}_3\text{H}_7)_4\text{OH}$ , decompose into amine, olefin and water, as shown in equation 2.20.



This type of decomposition, however, occurs readily at lower temperatures than decomposition of their tetramethylammonium analogue. This indicates that for quaternary ammonium initiator to be effective, the alkyl substituents on nitrogen should not contain  $\beta$  hydrogen atoms.

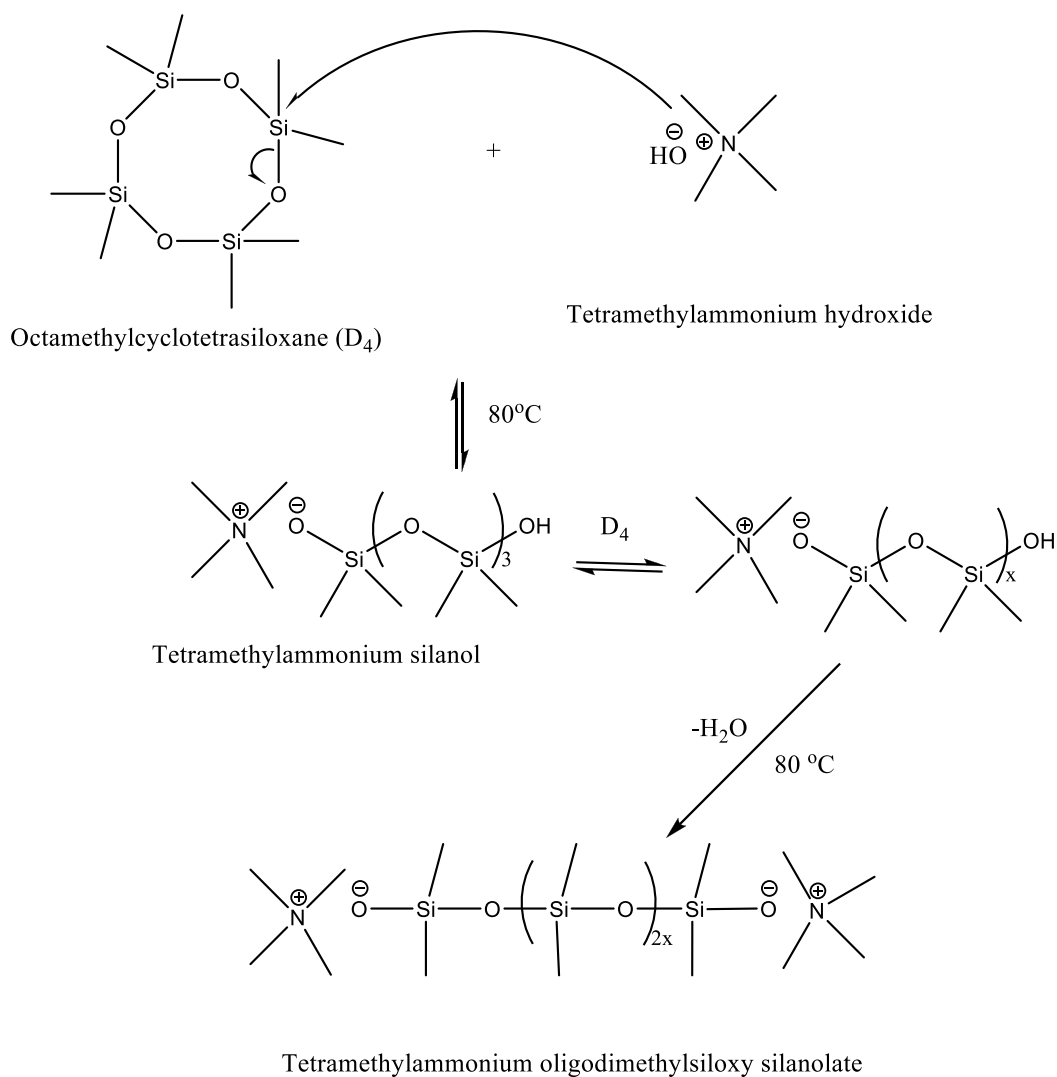
Equally effective transient siloxane equilibration initiators are quaternary phosphonium bases, which thermally decompose in a different manner than their tetraalkylammonium analogues, as shown in equation 2.21 for the example of decomposition of tetra *n*-butylphosphonium hydroxide, which decomposes into tributylphosphine oxide and butane.



Although described transient initiators are quite effective for siloxane equilibration, they are available only as crystallohydrates (tetramethylammonium hydroxide pentahydrate) or aqueous solution (tetrabutylphosphonium hydroxide). Because the presence of water may not only complicate the kinetics of polymerization process, but also alter molecular weights of polysiloxanes produced and introduce undesired changes into the polymer structures, recommended approach is to use instead well-defined silanolate salts of these bases and in that way eliminate interference of water.<sup>132</sup> Not only that a water-free

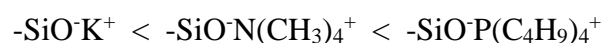
initiator will produce polymer with controlled and reproducible molecular weights,<sup>82</sup> but also another advantage of using transient initiators in the form of silanolate is the fact that they are, unlike hydroxides, readily soluble in the siloxane media from the very start of the polymerization process.

Very convenient approach,<sup>132</sup> applied in the work presented in this dissertation, is to prepare telechelic oligodimethylsiloxy disilanolate, by reacting transient hydroxide with octamethylcyclotrisiloxane, D<sub>4</sub>, as illustrated in Reaction Scheme 2.4 for an example of preparation of *bis*-tetramethylammonium oligodimethylsiloxy silanolate. Using the same technique, starting with linear instead of cyclic siloxanes, monofunctional tetramethylammonium silanolate active initiator species can also be prepared.<sup>133</sup>



Reaction Scheme 2.4. Preparation of *bis*-tetramethylammonium oligodimethylsiloxy silanolate (TMAS).

The efficiency of two transient initiators, tetramethylammonium- and tetrabutylphosphonium silanolate, was evaluated in anionic equilibrium polymerization of D<sub>4</sub> in the presence of amino-functional disiloxane end-blocker, and compared with that of potassium silanolate.<sup>132</sup> Significant differences in reaction rates were observed as the counterion of the silanolate initiating species varied. The rate of disappearance of cyclic monomer (D<sub>4</sub>) and end-blocker in the presence of these initiators increased in the following order:



The enhanced activity of transient initiators relative to potassium silanolate is attributed to higher degree of dissociation of ion pairs and possible improved solubility of their cations in the reaction medium. Similar trends in reactivity of these initiators were observed for the equilibration systems with non-functional end-blockers.<sup>134</sup>

### 2.5.5 Cationic Ring Opening Polymerization of Cyclic Siloxanes

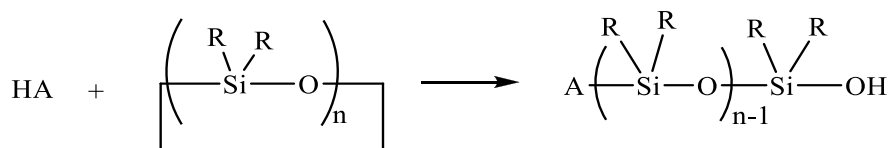
Cyclic siloxanes also polymerize readily in the presence of strong protic or Lewis acids.<sup>1, 32, 52</sup> While the cationic ring opening process, C-ROP, is the preferred route to linear polymers containing substituents which are sensitive to the presence of bases, such as SiH,<sup>135</sup> and while it may offer convenience of taking place at suitable rate at room temperature, it's main drawback is pronounced tendency to formation of cyclic oligomers from the early stages of the reaction,<sup>52</sup> which limits its application to the kinetically controlled synthesis. Most of kinetic studies have been performed either on the polymerization of D<sub>3</sub> or D<sub>4</sub>, using trifluoromethanesulfonic acid, CF<sub>3</sub>SO<sub>3</sub>H, as initiator. The reactivity of siloxane bond in dimethylcyclosiloxane towards acids decrease in the order D<sub>3</sub> > D<sub>7</sub> > D<sub>6</sub> > D<sub>5</sub> > D<sub>4</sub>,<sup>136</sup> and similar trend was observed in methylhydridocyclosiloxanes.<sup>135</sup>

C-ROP of cyclic siloxanes leads to simultaneous formation of the linear polymer fraction and a series of cyclic and macrocyclic polysiloxanes.<sup>137-139</sup> The complex mechanism of the cationic polymerization of cyclic siloxanes was controversial for a long time; it was postulated to follow either a) direct addition polymerization pathway in which the cyclic monomer is opened directly by an active center,<sup>140, 141</sup> or b) the acidolytic polymerization pathway, in which the cyclic monomer is opened by the acid and the



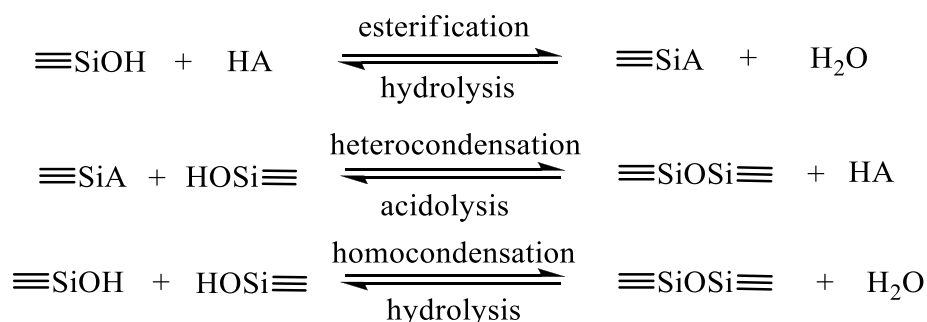
polymer is formed by polycondensation reaction.<sup>142-144</sup> This controversy was reconciled after the results on the polymerization of D<sub>3</sub> initiated by trifluoromethanesulfonic acid indicated that both mechanisms played significant roles.<sup>145</sup> Since the time when trisiloxonium ions were detected and proved to initiate polymerization of cyclosiloxanes, their role as active propagating species was widely accepted in considerations of the C-ROP mechanism.<sup>146</sup>

The initiation step involves acidolytic splitting of siloxy bonds of a cyclosiloxane as schematically described in Reaction Scheme 2.5.



Reaction Scheme 2.5. Initiation of C-ROP of cyclic siloxanes.

The equilibrium concentration of silanol (SiOH), silyl ester groups (SiA) and initiator (HA) present in the system are determined by fast reversible reactions shown in Reaction Scheme 2.6.

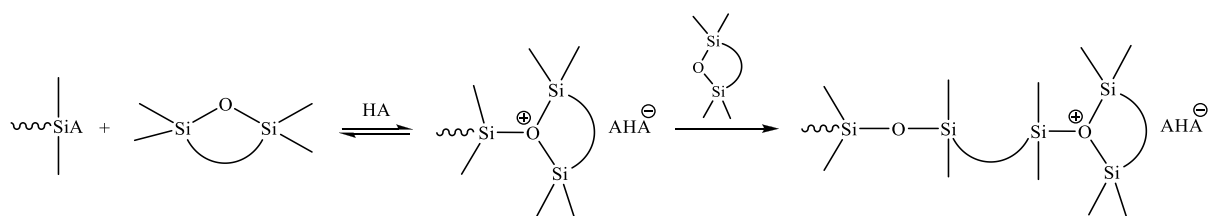


Reaction Scheme 2.6. Reversible condensation reactions occurring during C-ROP of cyclic siloxanes.

Reactions of hetero- and homocondensation directly participate in the formation of polymer. If they occur intermolecularly, condensations lead to chain extension;

intramolecular condensations result in formation of cyclic products thus contributing to a large proportion of cyclic oligomers occurring during C-ROP of cyclic siloxane from the early stage of reaction. Reactions of acidolysis or hydrolysis of the siloxane bonds lead to chain scrambling of linear chains and ring opening of cyclic siloxanes. The esterification-hydrolysis reactions are distinctly faster than condensation reactions, as shown in the kinetic study of  $D_3$  initiated by trifluoroacetic acid. These equilibria were found to be strongly affected by association through secondary bonds (hydrogen bonding).<sup>147</sup>

The propagation step of C-ROP consists of direct addition of cyclic siloxane to the active center at the end of a growing chain. Propagation in the presence of protic acid and without additional water occurs at siloxonium ion, as proven in the study with  $D_3$ ,  $D_4$  and tricyclosiloxanes containing vinyl and trifluoropropyl groups, where polymers with rather high polydispersity (1.8-3.3) were obtained in 70-85 % yields.<sup>148</sup> When no additional water or silanol is present, the activation of silyl-ester end group by acid leads to the formation of the active propagation center. Siloxonium ion is formed in the reaction between monomer and acid-activated silyl ester, as shown in Reaction Scheme 2.7.<sup>149</sup>

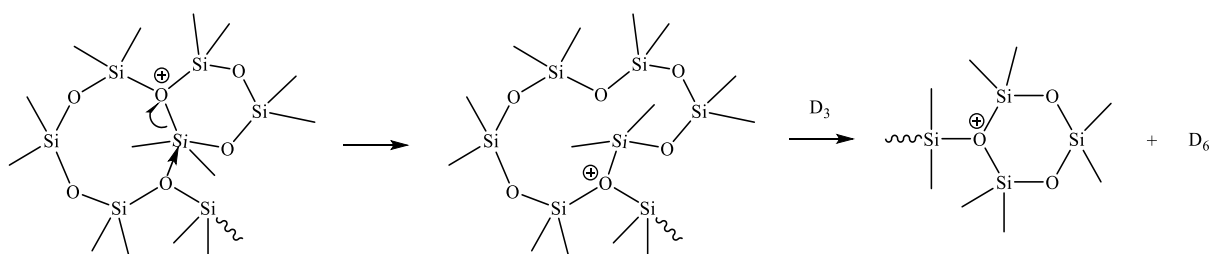


Reaction Scheme 2.7. Formation of siloxonium ion during the propagation step of C-ROP of cyclic siloxanes.

Since silanol and ester groups are continually interchanged, the chain growth proceeds bidirectionally. The silanols can also condense, not only with themselves, but also with ester groups and with oxonium active centers. The formation of active propagation centers is reversible process in which equilibrium is positioned towards the dormant species, which explain linear increase in polymer molecular weight.<sup>149</sup>

The molecular weight distribution of polymer formed in C-ROP is rather broad (1.6-2) due to several factors: continuous initiation along the process, various condensation reactions, backbiting and chain transfer. The compounds capable of breaking siloxane bonds and terminating polymer chains (water, alcohols, acids and their esters and anhydrides) reduce polymer molecular weight.<sup>52</sup>

A very specific size distribution of cyclic oligomers formed during the C-ROP was observed when there was a considerable excess of cyclics whose size was a multiple of the monomer, i.e., for the most explored system based on hexamethylcyclotrisiloxane, ( $D_3$ ),  $m = 6, 9, 12, \dots = 3n$ .<sup>137-139</sup> This feature excludes the back-biting mechanism of the cyclization, typical for kinetically controlled polymerization of  $D_3$  and points to the end-to-end closure condensation mechanism.<sup>52, 137</sup> The ratio of cyclic and linear fraction in C-ROP systems depends on the type of initiating system, presence of water and other additives.<sup>138, 150, 151</sup> The kinetics of formation of  $D_6$  during C-ROP of  $D_3$  monomer is different from that of other cyclic oligomers. The proposed mechanism<sup>150</sup> of  $D_6$  formation in C-ROP of  $D_3$  suggests the special kind of interconversion of rings involving siloxonium ion intermediate as shown in Reaction Scheme 2.8.



Reaction Scheme 2.8. The mechanism of  $D_6$  formation during C-ROP of  $D_3$ .

In industry, the C-ROP process is usually performed as equilibration of cyclic siloxanes in the presence of various end blockers, used not only for regulation of the molecular weights, but also for introduction of desired functional groups to the chain ends.<sup>152-154</sup> Heterogeneous catalysis of these equilibrations, where acidic active centers are attached to various supports (silicates, clays, crosslinked polystyrene resins), offer many practical advantages over homogeneous catalysis, which usually requires tedious, time-consuming post-polymerization workup including initiator deactivation, neutralization and

separation. Utilizing the advantages of heterogeneously catalyzed equilibration of cyclosiloxanes, various  $\alpha, \omega$ -telechelic oligosiloxanes, terminated with vinyl dimethylsiloxy, trimethylsiloxy, dimethylsiloxy or carboxypropyldimethylsiloxy groups were successfully synthesized in the presence of sulfonated crosslinked polystyrene cation exchange resin (CER).<sup>155</sup> This approach enables preparation of wide variety of reactive siloxane oligomers, which can be further used as building blocks for siloxane-siloxane or siloxane-organic block copolymers.<sup>125</sup> Also, C-ROP of cyclosiloxanes in the presence of cation exchange resin was conveniently used in the work described in this dissertation for preparation of model branched star polysiloxanes, as well as for preparation of vinyl dimethylsiloxy-terminated oligodimethylsiloxy end-blockers described in Sections 3.5, 3.7, 3.8. and 4.2.1.

## 2.6 Crystallization of Polysiloxanes

Polydimethylsiloxane (PDMS) is the most widely used polysiloxane with countless commercial applications resulting from its excellent combination of thermal and oxidative stability, low temperature elasticity, surface and rheological properties, as well as semipermeability to gasses and non-immunogenic character. Due the pronounced ability of PDMS molecules to change their spatial arrangements by rotations around the skeletal bonds, i.e., dynamic flexibility, PDMS is one of the most flexible polymers known, having the glass transition at approximately  $-125$  °C. However, its features of unusually long Si-O skeletal bonds, high molecular symmetry, small side groups on silicon, the absence of side groups at oxygen and wide and very deformable angles of Si-O-Si links, also contribute to the ability to readily crystallize, owing to its high flexibility at rather low temperatures, around  $-90$  °C. There are typically two melting peaks occurring in DSC thermograms of linear and cyclic PDMSs of high molecular weight, as shown in Figure 2.5.

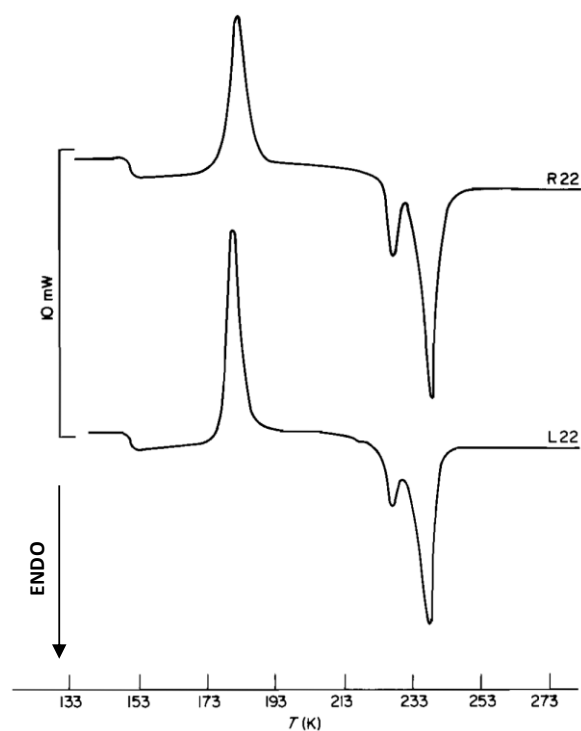


Figure 2.5. Typical DSC thermograms of cyclic (top) and linear (bottom) PDMS of  $M_n=25,000$  g/mol.<sup>156</sup>

The possible causes for this phenomenon are differences in crystallite size distribution, melting-recrystallization (cold crystallization) of the original crystallites and their subsequent melting, and the presence of different crystalline forms.<sup>123</sup> During the heating run, the PDMS chains recover enough mobility to rearrange and crystallize. The position and size of cold crystallization peaks depend on the rate of the previous cooling history: the faster the sample is cooled, the higher the temperature of cold crystallization and the larger the area under the peak of this exothermic, transition.<sup>156-159</sup> In a classic comprehensive study of supercooling of PDMS, Helmer and Polmanteer<sup>158</sup> reported that, by increasing the cooling rates, PDMS can be supercooled and the area of the cold crystallization peak increased accordingly. While at their highest controlled cooling rate of 52 °C/s 85 % of the crystallization took place during the heating cycle, the cold crystallization was completely suppressed at cooling rates as low as 1.6 °C/s. After observing changes in the relative magnitude of the two melting peaks, which occurred at different cooling rates, the same authors proposed that the two endotherm DSC peaks correspond to melting of different types of crystals. The endothermic peak at higher

temperature is assigned to melting of more perfect crystals and its relative magnitude increases with the decrease of cooling rate.

Investigation of the effect of molecular weight on low-T features of PDMS<sup>157</sup> revealed that the exothermic cold crystallization peak shifts towards lower temperatures as molecular weight of polymer decreases. The same (decreasing) trend was observed for the ratio of magnitudes of cold crystallization and melting peaks. It was also reported, in a study with essentially monodisperse samples that increase in molecular weight of PDMS results in the increase in relative area of lower melting peak.<sup>156</sup>

The first attempt to deduce the crystalline structure of linear PDMS chain by X-ray diffraction was that of Damaschun,<sup>160</sup> who proposed monoclinic unit cell with helical conformation and six repeat units (twelve SiO bonds), as illustrated in Figure 2.6. The measured crystallographic parameters of Damaschun's model cell are  $a \times b \times c = 13.0 \text{ \AA} \times 8.3 \text{ \AA} \times 7.75 \text{ \AA}$ .

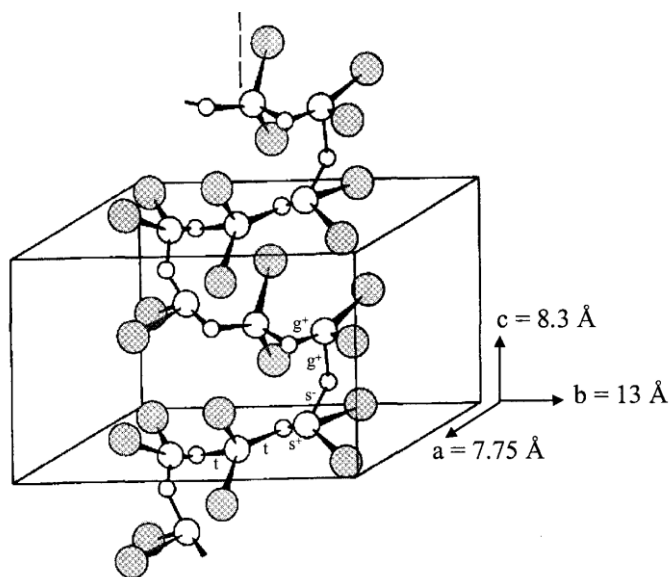


Figure 2.6. Crystalline PDMS helix conformation with the sequence of 6 repeat units in the unit cell as proposed by Damaschun.<sup>160</sup>

While the monoclinic unit cell model was soon supported by Andrianov et al.,<sup>161</sup> another model was proposed more recently by Albouy.<sup>162</sup> Using X-ray diffraction, the author showed that basic crystalline structure belongs to a tetragonal system with eight

siloxo units per cell and a four-fold extended helical configuration of the polymer chain (Figure 2. 7).

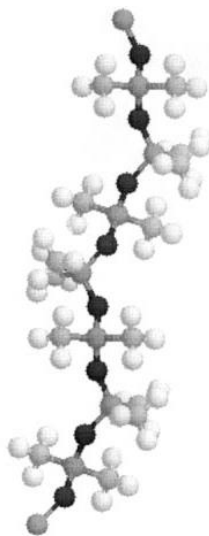


Figure 2.7. A four-fold extended helical conformation of a model of PDMS chain in crystalline state, as proposed by Albouy.<sup>162</sup>

Unlike PDMS, which on heating from crystalline state transforms directly into isotropic melt, all other alkyl disubstituted polysiloxanes pass through a thermotropic liquid crystalline, LC, mesophase before isotropization. The most explored polysiloxane with regard to LC mesophase behavior is polydiethylsiloxane, PDES. Besides its ability to exist in the mesomorphic state, a characteristic feature of linear PDES is also an endothermic transition in the crystalline state occurring between approximately  $-80$  and  $-50$  °C.<sup>163-167</sup> As in the case of linear PDMS, variations in the melting behavior of PDES result from different thermal histories. The overall degree of crystallinity depends significantly on whether the sample was annealed in the mesophase at  $7$  °C or quenched from the melt: the former procedure resulting in crystallinities that were near 100 % and total absence of glass transition, while the latter, rapid quenching to  $-195$  °C from the melt, showed distinct glass transition at  $T_g = -134$  °C.<sup>165</sup> Comparison of melting and isotropization temperatures for polysiloxanes with varying lengths of alkyl substituents suggested the linear increase of these characteristic temperatures with the increase in number of methylene ( $\text{CH}_2$ ) groups in the side chains.<sup>168</sup> In a study on the molecular weight dependence of thermal transitions of PDES, Molenberg and Moller<sup>169</sup> observed that the molecular weight dependence of isotropization temperature is very strong, even

at the highest molecular weights. They also found that mesophase is not formed below a critical molecular weight of  $M_n = 28,000$  g/mol. This MW-dependent destabilization of mesophase is related to the occurrence of another crystal modification, denoted as  $\gamma$ -PDES, which emerges right below the melting to mesophase transition and which is formed directly from isotropic melt.

The molecular organization of the mesophase of LC polydialkylsiloxanes such as PDES, PD-*n*PrS and PD-*n*BS was described as parallel columnar mesophase, in which the molecules are positionally and orientationally ordered in a two-dimensional hexagonal lattice, with no positional order along the chains<sup>86, 170</sup> (Figure 2.8).

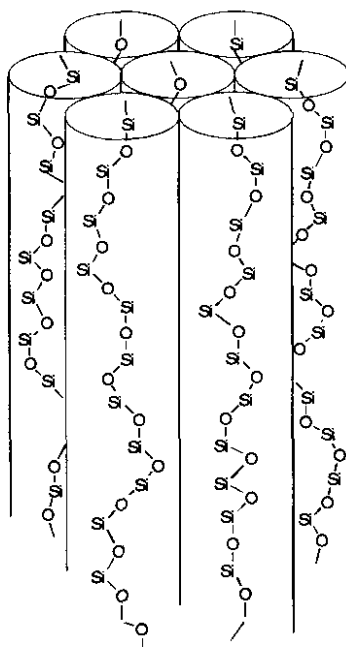


Figure 2.8 Columnar LC packing of poly(di *n*-alkylsiloxane) molecules.<sup>86</sup>

Polysiloxanes disubstituted with a variety of aromatic substituents such as phenyl, *p*-tolyl, *m*-tolyl, *p*-methoxyphenyl or *p*-propyl phenyl were shown to all undergo through mesophase state on melting.<sup>104, 171</sup> As expected, the temperatures of these transitions were higher than those of their aliphatic analogues. In contrast to the crystalline and LC character of polymers with all aryl-type substituents, the replacement of a single phenyl group by a methyl group in the triad of diphenyl repeat units is sufficient to destroy both the crystalline and LC character of the polymer.



### 2.6.1 Suppression of Crystallization

Pronounced propensity to crystallize at low temperatures markedly narrows the temperature span of usefulness of PDMS elastomers. While crystallization of PDMS occurs at approximately  $-90\text{ }^{\circ}\text{C}$ , elasticity of the polymer begins to dramatically deteriorate at  $-50$  to  $-40\text{ }^{\circ}\text{C}$ .<sup>161</sup> Therefore, in order to reduce or completely eliminate the low temperature crystallization, PDMS has to be modified by copolymerization with small amounts of other siloxane units bearing bulky substituents such as methylphenylsiloxane, diphenylsiloxane, 3,3,3-trifluoropropylmethylsiloxane, etc. Also, structural modification of linear PDMS chains, i.e., introduction of branching units (T-units, Q-units) was reported to effectively suppress crystallization of PDMS.<sup>115, 172</sup> These methods can effectively restrict PDMS from crystallization, forcing it to remain elastic in lower temperature region.

Random copolymers of dimethylsiloxane and phenyl substituted siloxanes were extensively studied with the purpose to relate their structure to low temperature behavior. It is well-known and not surprising that polydiphenylsiloxane (PDPS), another member of the polysiloxane family, possesses higher thermal and oxidative stability than its alkyl-substituted counterparts,<sup>13, 104, 105</sup> as well as mechanical properties that are measurably different from those of PDMS. Furthermore, aromatic side groups are also quite effective in increasing polymer's radiation stability.<sup>173, 174</sup>

In one of the early studies, the low-temperature characteristics of copolymers with dimethylsiloxane (DiMeS) and methylphenylsiloxane (MePhS) repeat units were investigated with respect to copolymer composition,<sup>175</sup> where MePhS molar concentration was varied from 0 to 99.9 mol %. It was found (based on Gehman cold-flex, dilatometric and stress-temperature measurements), that only copolymers containing MePhS units in the range from 7.5 to 15 mol % did not exhibit crystallization.

An analysis of crystallizability of linear and branched PDMS, random copolymers of DiMeS and MePhS, as well as random copolymers of DiMeS and methylethyl- $\beta$ -adamantylsiloxane, suggests that, in order for thermodynamically stable folded PDMS crystals to be formed, the average length of DiMeS sequence must amount to no less than 30 siloxane bonds (or 15 siloxy repeat units).<sup>176</sup> For non-crystallizing copolymers of DiMeS and heterounits such as MePhS and T-branch unit, the size of which is not

dramatically greater than DiMeS, this corresponds to at least 6-6.5 mol % of these crystallization disruptors, given that there is their random distribution along polymer chains. More effective suppression of crystallization took place in random copolymers of DiMeS and methylethyl- $\beta$ -adamantylsiloxane, containing at least 4.8 mol % of the latter, and it was explained by bulkiness of ethyl- $\beta$ -adamantyl substituents being able to disrupt the folding of longer PDMS sequences.

Suppression of low-temperature crystallization was also extensively studied on copolymers with DiMeS and DiPhS repeat units. Analyzing a series of such copolymers with DiPhS content varying from 2 to 80 mol % by X-ray diffraction, calorimetry and optical microscopy, Andrianov and coworkers<sup>177</sup> determined that random DiPhS-containing copolymers stop undergoing crystallization when DiPhS content exceeds 4 mol %.

It was also reported that other aromatic substituents, such as naphthyl, benzyl and phenylethyl may bring improvement to the low-temperature flexibility of PDMS. In the series of copolysiloxanes containing 2.5 mol % of such substituents their effectiveness was as follows:  $\alpha$ -naphthyl > benzyl >  $\beta$ -phenyl-ethyl > phenyl >  $\alpha$ -phenyl ethyl.<sup>178</sup>

The effect of bulky substituents in various siloxane comonomer repeat units: diphenylsiloxane (DiPhS), trifluoropropylmethylsiloxane (TFPMeS), ethylphenylsiloxane (EtPhS) and methylphenylsiloxane (MePhS), on low-temperature transitions of polydiethylsiloxane (PDES) was studied by DSC, <sup>29</sup>Si NMR and DMA.<sup>179</sup>  
<sup>180</sup> All comonomers were found effective in lowering both melting and crystal-crystal transitions with respect to DiEtS homopolymers, ultimately leading to completely amorphous random copolymers. Compared to PDMS, for which as little as 4 mol % of DiPhS units is enough to inhibit crystallinity, the PDES homologue requires approximately 8 mol % of random incorporation of the same comonomer to achieve the same effect. Incorporation of the less bulky EtPhS, MePhS or TFPMeS comonomers resulted in smaller disruption of crystalline structure of PDES, requiring the critical molar contents of these disruptors of crystallinity to be higher than in the case of DiPhS: 16.4, 19.6 and 15 mol % for EtPhS, MePhS and TFPMeS, respectively. In spite of the relatively high contents of the crystallization disruptors, the extremely low glass transition temperatures observed for these copolymers (– 122 to –128 °C, equivalent to those of

PDMS), are among the lowest published for completely amorphous polymers. In a similar study, Liu et al<sup>181</sup> reported on the synthesis and characterization of highly randomized, non-crystalline DiMeS-DiEtS copolysiloxanes, which at DiEtS level of 50 mol % exhibited only glass transition at extremely low temperature of  $-137\text{ }^{\circ}\text{C}$ . In view of relative thermo-oxidative instability of ethyl-substituted polysiloxanes, the potential applications of these polymers lie in the low-temperature elastomer area.

## 2.7 <sup>29</sup>Si NMR Spectroscopy: A Powerful Tool for Structural Analysis of Polysiloxanes

High resolution <sup>29</sup>Si NMR is a powerful method for structural analysis of siloxane polymers, able to provide detailed information on the surrounding of a given silicon atom in a complex atomic framework.<sup>182</sup> The main differences between various siloxy units arise from different organic substituents and the number of oxygen atoms connected to a silicon atom. Depending on the number of siloxy bonds connected to a given Si atom, the basic units of methyl substituted polysiloxanes can be divided into four main groups which are in silicone literature conventionally denoted by symbols M, D, T and Q, referring to  $\text{Me}_3\text{SiO}_{0.5}$ ,  $\text{Me}_2\text{Si}(\text{O}_{0.5})_2$ ,  $\text{MeSi}(\text{O}_{0.5})_3$  and  $\text{Si}(\text{O}_{0.5})_4$  units, respectively. In the latter, subscript 0.5 to O indicates that each oxygen atom is shared by two adjacent Si atoms, while, in the former, the substitution of one or more methyl groups at the Si atom by other substituents (X) is indicated by a superscript. For example,  $\text{M}^{\text{X}}$ ,  $\text{M}^{\text{X}2}$ ,  $\text{D}^{\text{X}}$ ,  $\text{D}^{\text{X}2}$  and  $\text{T}^{\text{X}}$  denote  $\text{Me}_2\text{XSiO}_{0.5}$ ,  $\text{MeX}_2\text{SiO}_{0.5}$ ,  $\text{MeXSi}(\text{O}_{0.5})_2$ ,  $\text{X}_2\text{Si}(\text{O}_{0.5})_2$  and  $\text{XSi}(\text{O}_{0.5})_3$ , respectively, where X is often Et, Ph, Vi, H, etc.

From the ratio of intensities of <sup>29</sup>Si NMR signals assigned to terminal, M, and internal, D, monomer units, the length of the main polysiloxane chain can be estimated. Similarly, the degree of branching can be also evaluated from the relative intensities of signals assigned to Si atoms from linear and branched units. This is of particular practical importance when linear precursors for elastomers are considered, where branches, often with non-functional chain ends, may introduce irregularities into the elastomer networks in the form of elastically inactive imperfections (dangling chains) which limit the resulting mechanical properties.

Typical  $^{29}\text{Si}$  NMR chemical shift ranges for M, D, T and Q are summarized in Figure 2.9, together with selected X-substituent groups commonly used in silicone polymers (X: Ph, H, OH, OMe). It can be seen from Figure 2.9, that these ranges are well separated (non-overlapping), allowing for accurate qualitative and quantitative structural analysis. Within the ranges, systematic shift differences, caused by neighboring groups effects, reveal important information about that polymer microstructure. Hence, specific chemical shift of any given Si atom in a copolysiloxane consisting of D and  $\text{D}^{\text{X}}$  units is affected by the type of the nearest neighbor groups, causing the characteristic triplet splitting of the signal. On top of this, the second neighboring group can cause further triplet splitting (of each triad signal) providing even finer fingerprint of the corresponding fine structure and deeper insight into the distribution of comonomer units (pentad structure).

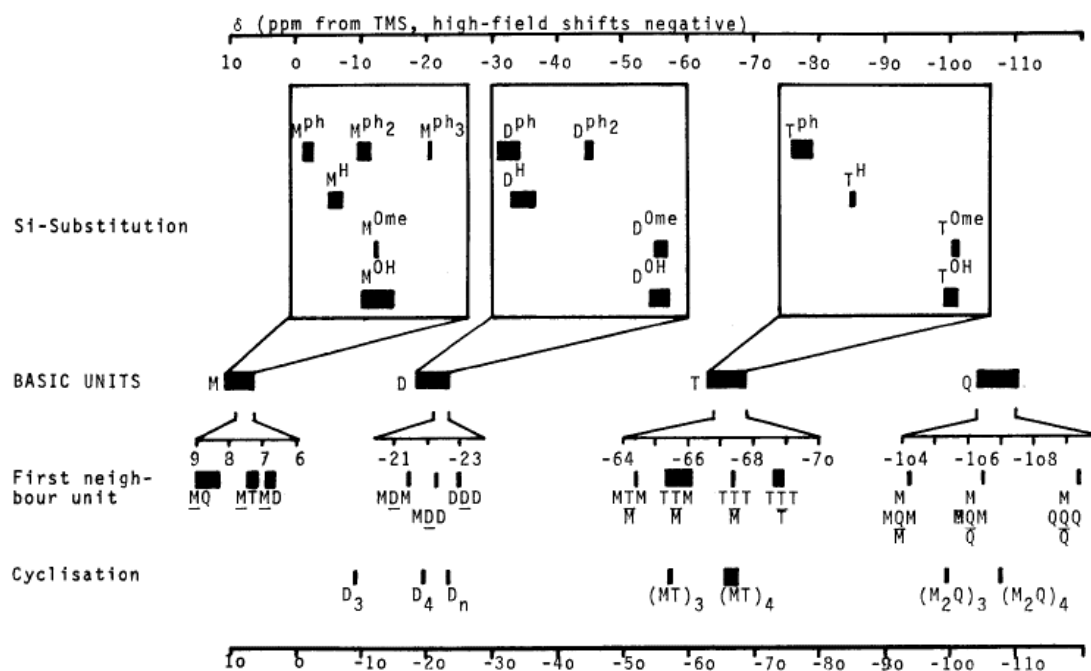


Figure 2.9. Structural correlations of  $^{29}\text{Si}$  NMR chemical shifts.<sup>183</sup>

Microstructure or sequence distribution of repeat units in copolysiloxanes, crucial in determining both their properties and applications, can be conveniently determined from their  $^{29}\text{Si}$  NMR spectra by relatively simple linkage probabilities.<sup>184</sup> These are calculated

from relative intensities of signals from various triad sequences and are expressed in terms of run numbers, sequence length, or simply probability.<sup>183-185</sup>

Run number (R), is defined as the average number of monomer sequences (runs) occurring in a copolymer per 100 monomer units. It can be related to any measurable feature of copolymer microstructure using simple stoichiometric and statistical considerations. The mathematical formalism for determination of sequence distribution utilizes relative areas of different <sup>29</sup>Si NMR signals resonances so that for a copolymer consisting of repeat units A and B the average run number for species A can be determined from equation 2.22:

$$R_{\text{exp}} = k_A A_M \quad (2.22)$$

where  $A_M$  denotes molar percent of repeat units A and  $k_A$  is the variable containing information about the ratio of triad signal intensities:

$$k_A = 2 - 2 \sqrt{\frac{F_0}{\sum_{i=0}^2 F_i}} \quad (2.23)$$

with  $F_i$  being the integral of the  $i$ -th signal of the triad,  $i$  being the number of the nearest neighbor monomer units of the second species, and  $F_0$  being the integral of the signal for dominant triad.

An example of the high resolution <sup>29</sup>Si NMR spectrum of a copolysiloxane consisting of DiMeS and DiPhS repeat units, obtained by a silanolate-initiated A-ROP of D<sub>4</sub> and D<sub>4</sub><sup>Ph2</sup> cyclic siloxanes (of Section 4.2),<sup>186</sup> is shown in Figure 2.10. Two major resonances observed at  $\delta \sim 21.6$  ppm and  $\delta \sim 47.4$  ppm correspond to DiMeS and DiPhS silicons, respectively. Closer inspection of the DiMeS spectral region shows fine structure assigned to indicated configurations resulting from the presence of DiPhS species in the nearest and the next-nearest neighbor positions. Integration of these signals reflects the relative abundance of different Si species. It is worth noting that in cases like this, where relative content of one type of units (DiPhS) is quite low (only 3.6 mol %), only one spectral region (DiMeS) is often useful for microstructural analysis, since integration of signals in the other is rather difficult and not precise enough.

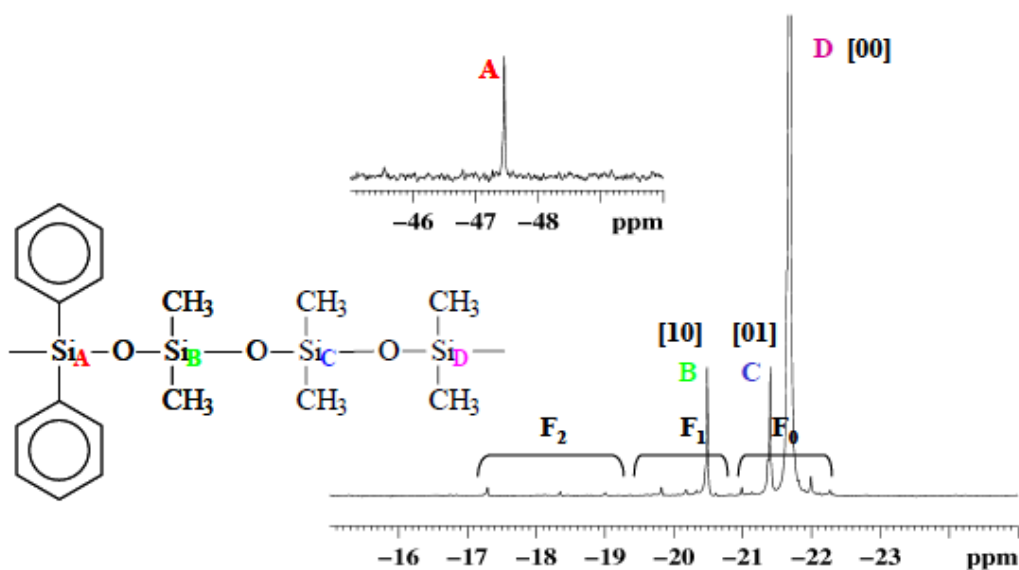


Figure 2.10. High resolution  $^{29}\text{Si}$  NMR spectrum of DiMeS-DiPhS copolysiloxane containing 3.6 mol % DiPhS units (see Section 4.2) in  $\text{CDCl}_3$ , at  $60^\circ\text{C}$ .<sup>186</sup>

The average run number for a statistically random polymer (such as the copolysiloxanes of this work), is given by:<sup>184</sup>

$$R_{\text{random}} = \frac{A_M B_M}{50} \quad (2.24)$$

Generally, if  $R_{\text{exp}} > R_{\text{random}}$ , the microstructure of the copolymer is alternating in monomer units, if  $R_{\text{exp}} = R_{\text{random}}$ , the microstructure is random (i.e., statistical), and if  $R_{\text{exp}} < R_{\text{random}}$ , the microstructure consists of sequences of blocks of A and blocks of B monomer units.

Determination of the number-average run number also allows for calculation of the average sequence length of a given monomer type,  $l_A$  or  $l_B$ , which is simply the mol % of the given type of monomer unit divided by the number of runs of that type present ( $R_{\text{exp}}/2$ ):

$$l_A = \frac{2A_M}{R_{\text{exp}}} \quad (2.25)$$

$$l_B = \frac{2B_M}{R_{exp}} \quad (2.26)$$

For example, studies of silanolate-initiated copolymerizations of D<sub>4</sub> with D<sub>4</sub><sup>Ph<sup>2</sup></sup> or D<sub>4</sub><sup>MeVi</sup>,<sup>187, 188</sup> (by analysis of signal intensities of pentad and triad sequences in high-resolution <sup>29</sup>Si NMR), showed that the polymers obtained at equilibrium were entirely random in structure, and that such sequence distribution persisted over a broad range of comonomers composition: 10-70 mol % of MeViS units in (D<sub>4</sub> + D<sub>4</sub><sup>MeVi</sup>) system and 9-52 mol % DiPhS units in (D<sub>4</sub> + D<sub>4</sub><sup>Ph<sup>2</sup></sup>) system. For the former system, it was also found that the randomness of microstructure was independent of temperature. The experimental values for run numbers *R*, obtained from relative intensities of triad signals in <sup>29</sup>Si NMR spectra, were constant over a 130 °C range and in a close agreement with calculated value of *R*<sub>random</sub> for a given composition.<sup>188</sup> The same study also showed that composition of the cyclosiloxane fraction at equilibrium, and the sequencing of their comonomer units matched exactly those of the copolymer chains.

<sup>29</sup>Si NMR technique was extensively used throughout the experimental part of this dissertation, not only for evaluation of the structure of synthesized copolysiloxanes, but also as a powerful tool for monitoring of the dynamics of their copolymerization reactions.<sup>189, 190</sup>

## 2.8 Size Exclusion Chromatography

Another technique that was extensively used in this work for both polymer analysis and synthetic processes monitoring was size exclusion chromatography (SEC), also known as gel permeation chromatography (GPC). Performed in combination with light scattering and viscometry, SEC has almost completely replaced traditional methods for determination of polymer molecular weights, such as osmometry, dilute solution viscometry and ultracentrifugation. Besides relative simplicity, versatility, high speed of measurements and small sample demand, the main advantage of SEC also includes its ability to provide entire molecular weight distribution function and not only average values of molecular weights. Furthermore, combined with multi angle light scattering (MALS) and viscometry (VIS) detection capabilities, SEC is also able to provide the

distributions of root mean square radii of gyration (RMS), intrinsic viscosities, detection of aggregation, as well as information on molecular conformation and polymer branching.

For example, SEC separation coupled with VIS and MALS detection allows for direct determination of extremely useful Mark-Houwink-Sakurada (MHS) equation (equation 2.27), which relates intrinsic viscosity and viscosity average molecular weight of polymer<sup>191, 192</sup>:

$$[\eta] = KM^a \quad (2.27)$$

through important constants  $K$  and  $a$  (for a given polymer, solvent and temperature), where exponent  $a$  bears information about polymer conformation. Generally, for flexible polymer molecules in thermodynamically good solvents it ranges from about 0.65 to about 0.75, in theta solvent it equals 0.5. Values for  $a$  equaling or even exceeding unity can be found for less flexible rodlike macromolecules, such as some polysaccharides or polyelectrolytes, while increasing compactness of macromolecular chains results in decreasing  $a$ , which in the ultimate case of compact spheres equals zero and intrinsic viscosity becomes independent of the molecular weight. The decrease of the exponent  $a$  is also observed for branched polymers that often show an evenly decreasing slope of MHS plot with increasing molar mass to  $a$  values approaching and even extending below 0.5.<sup>193, 194</sup> These characteristics of MHS relationship regarding the increase in compactness of macromolecules due to branching is illustrated in Figure 2.11 for examples of linear and branched polylactic acid.



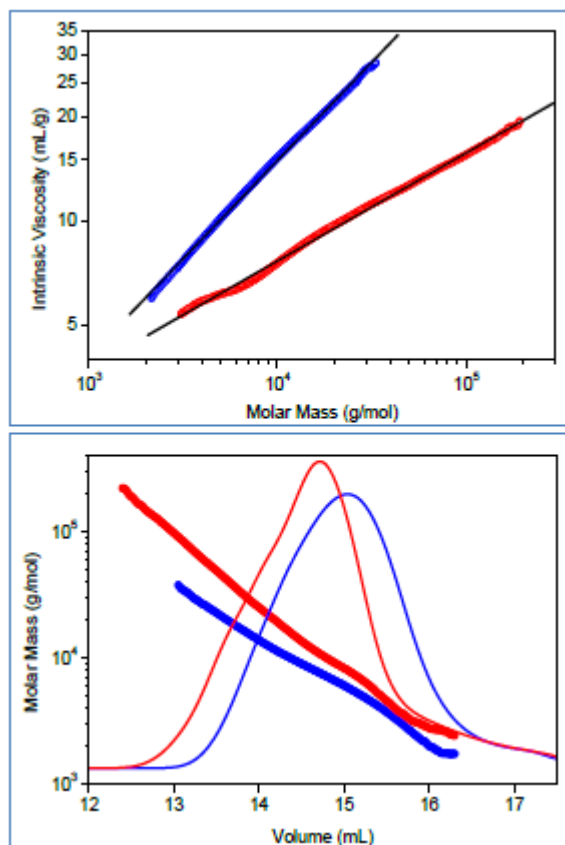


Figure 2.11. Top: Mark-Houwink-Sakurada plots of linear (blue) and branched (red) polyactic acid. The slopes for linear and branched samples equal 0.56 and 0.31, respectively. Bottom: Plots of molar mass versus elution volume for the same set of samples, overlaid with respective RI chromatograms.<sup>195</sup>

Long chain branching in polymers can also be identified from the shape of SEC chromatograms. Distinct increase in molecular weight due to branching is typically expressed by the appearance of shoulders on the low retention times (high MW) side of the respective chromatograms.

### 3. EXPERIMENTAL

#### 3.1 Materials

Octamethylcyclotetrasiloxane ( $D_4$ ), octaphenylcyclotetrasiloxane ( $D_4^{Ph2}$ ), 1,3,5,7-tetramethyl-1,3,5,7-tetravinyl-cyclotetrasiloxane ( $D_4^{MeVi}$ ), hexaethylcyclotrisiloxane ( $D_3^{Et2}$ ), octaethylcyclotetrasiloxane ( $D_4^{Et2}$ ), mixture of cyclic and linear diethylsiloxanes (DiEt-“hydrolyzate”), 1,3-divinyl tetramethyldisiloxane, phenyltris(trimethylsiloxy)silane, *tetrakis*(trimethylsiloxy)silane and polydimethylsiloxane, trimethylsiloxy-terminated, DMS-T05, were obtained from Gelest (Morrisville, PA). With the exception of solid  $D_4^{Ph2}$ , which was dried at 110 °C for 2 hours prior to use, all reagents were used as received. Cyclohexane, toluene, methylene chloride, tetrahydrofuran, isopropanol, and methanol were purchased from Fisher Scientific (Pittsburgh, PA). Tetramethylammonium hydroxide pentahydrate was purchased from Sigma Aldrich (St. Louis, MO). Ion exchange resin Amberlyst® 15(H) was supplied from Alfa Aesar (Ward Hill, MA) and was used as received. NMR solvents: chloroform-*d*, dimethyl sulfoxide-*d*<sub>6</sub> and acetone-*d*<sub>6</sub>, as well as relaxation agent chromium(III) acetylacetonate, Cr(acac)<sub>3</sub>, were all purchased from Acros Organics (Morris Plains, NJ).

#### 3.2 Characterization Methods

SEC analyses using toluene as an eluent at 30 °C were performed in a SEC/MALS/VIS/RI system consisting of an Agilent 1260 Infinity isocratic pump (Agilent Technologies, Santa Clara, CA), an Agilent 1260 Infinity Thermostated Column Compartment with a set of five Phenogel™ 5μm columns from Phenomenex (Torrance, CA) covering a MW range of 100 to 5·10<sup>5</sup>. An Agilent 1260 Infinity autosampler, a DAWN HELEOS-II, multiangle (18 angles from 22.5° to 147°) laser-light scattering (MALS) detector with the He-Ne light wavelength at 658.0 nm, a ViscoStar-II online viscosity detector, and an Optilab T-rEX differential refractometer (all three detectors from Wyatt Technology Corp., Santa Barbara, CA) were used. The flow rate was kept at

1.0 mL/min and data were collected and processed using ASTRA 6 software from Wyatt Technology.

SEC analyses using THF as an eluent were performed on a system consisting of a Waters 515 HPLC pump (Waters Corp, Milford, MA, USA), a set of four 300 x 7.8 mm Phenogel™ 5 µm columns (50, 10<sup>2</sup>, 10<sup>3</sup> and 10<sup>4</sup> Å) (Phenomenex, Torrance, CA); 2410 differential refractometer operating at 40 °C (Waters Corp, Milford, MA, USA); autosampler (SIL-20A/20AC, Shimadzu); on-line degasser JMDG-4 (JM Science, Grand Island, NY, USA) and Millenium software. The flow rate was 0.5 mL/min at 30 °C.

NMR analyses were performed using BRUKER DPX 300 instrument with 5 mm multinuclear probe at resonance frequency of 59.62 MHz and 300.13 MHz for <sup>29</sup>Si and <sup>1</sup>H nuclei, respectively. In a typical procedure, approximately 300 mg of the sample was dissolved in 0.6 mL of CDCl<sub>3</sub>. In case of <sup>29</sup>Si NMR, 6 mg of relaxation agent Cr(acac)<sub>3</sub> was added. <sup>1</sup>H NMR spectra were acquired using 16 scans, π/2 pulse (10 µs) and 10 s relaxation delay. Basic <sup>29</sup>Si NMR screening was done using 1,000 scans, π/12 pulse and 2 s relaxation delay. For quantitative analysis, <sup>29</sup>Si NMR spectra were obtained using π/2 pulse (8 µs) with 120 s relaxation delay and 1,024 scans, and gated <sup>1</sup>H decoupling. External calibration was performed using TMS/CDCl<sub>3</sub> 25 vol. % solution. All tests were carried out at room temperature.

A differential scanning calorimeter (DSC) model Q100, from TA Instruments, New Castle, DE, was used for studying polymer melting transitions. Measurements were performed at a heating rate of 10 °C/min, from –80 to 50 °C.

TA Instruments thermogravimetric analyzer, (TGA), model Q50, was used for dynamic thermogravimetric analyses of reaction mixture samples in nitrogen atmosphere at a heating rate of 10 °C/min from room temperature to 700 °C.

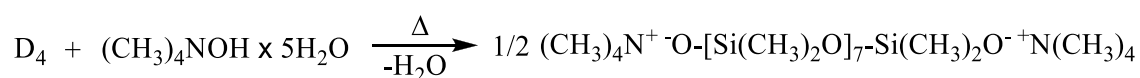
Viscosity of polymers was measured in a constant shear stress mode (100 Pa) on AR2000 EX Rotational Rheometer (TA Instruments) at 25 °C using cone/plate geometry (plate diameter 40 mm, cone angle 2°).

The content of vinyl groups in the prepared polymers and oligomers was determined by iodine value (IV), using the Hanus method,<sup>196</sup> which is based on reaction of double bonds with the molar excess of iodine monobromide, determination of excess halogen by

addition of KI and titration of the liberated iodine with a standardized sodium thiosulphate solution.

### 3.3 Preparation of $\alpha,\omega$ -bis Tetramethylammonium-Oligodimethylsiloxydisilanolate Initiator (TMAS)

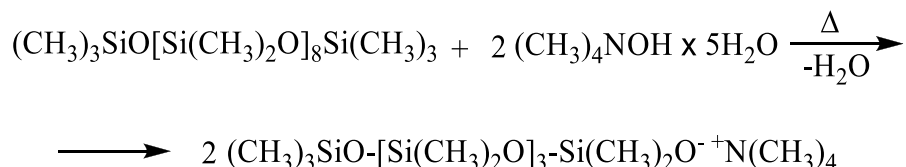
$\alpha,\omega$ -bis tetramethylammonium-oligodimethylsiloxydisilanolate (TMAS) was prepared according to the literature references<sup>82, 132</sup> presented by following equation:



An apparatus consisting of 500 mL three-necked, round bottom glass reactor equipped with Dean-Stark trap with condenser and bubbler, nitrogen inlet, and magnetic stirring bar was used. Tetramethylammonium hydroxide pentahydrate (50 g, 0.28 mol) and equimolar amount of D<sub>4</sub> (83 g, 0.28 mol) were added into the reactor followed by cyclohexane (113 g, 145 mL). The reaction mixture was stirred and heated in a silicone oil bath at 80 °C for 24 h. Continuous strong purge of nitrogen was applied as the reaction proceeded to facilitate elimination of crystalline water and water liberated from the silanol condensation reaction via cyclohexane azeotrope. The progress of the reaction was monitored by recording the amounts of water collected in Dean-Stark trap with time. After quantitative removal of water, the reaction mixture was vigorously stirred and purged with nitrogen for about 1 h at 85 °C to allow the residual cyclohexane to evaporate. The product was transferred to a glass jar and kept under nitrogen prior to use. The TMAS initiator, initially a clear, colorless liquid that very slowly turned into waxy white solid upon cooling, was obtained in a 99 % yield. From relative intensities of <sup>1</sup>H NMR signals (in acetone-*d*<sub>6</sub>) for N-CH<sub>3</sub> protons at 3.4 ppm and Si-CH<sub>3</sub> protons at 0 ppm, number-average molecular weight of TMAS was calculated. For different batches these values ranged from ca 700 (*DP* ca. 9) to 1,250 (*DP* ca. 12).

### 3.4 Preparation of Tetramethylammonium-Oligodimethylsiloxysilanolate Initiator (monoTMAS)

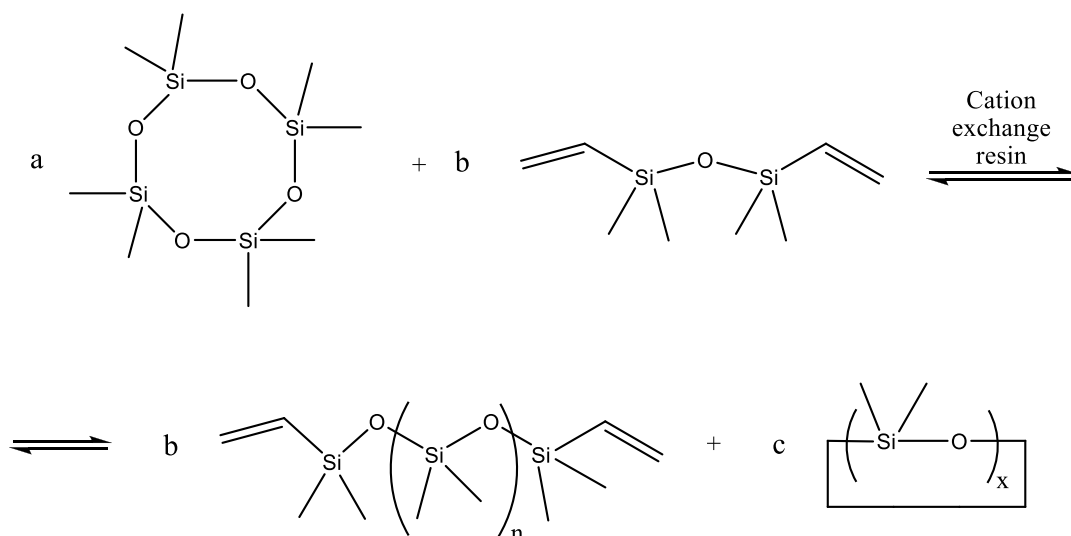
Tetramethylammonium-oligodimethylsiloxysilanolate (monoTMAS) was prepared according to the literature references<sup>82, 132, 133</sup> using the following chemistry:



Tetramethylammonium hydroxide pentahydrate (40 g, 0.22 mol) and trimethylsiloxy-terminated oligodimethylsiloxane (89 g, 0.11 mol) were added into the 500 mL three-necked, round bottom glass reactor equipped with Dean-Stark trap with condenser and bubbler, nitrogen inlet, and magnetic stirring bar, followed by the addition of cyclohexane (110 g, 141 mL). The reaction mixture was stirred and heated in a silicone oil bath at 80 °C for 24 h. The elimination of water via cyclohexane azeotrope was facilitated by continuously flushing of the reactor content with nitrogen. The progress of the reaction was monitored by recording the amounts of water collected in Dean-Stark trap with time. After quantitative removal of water (40 h), the reaction mixture was vigorously stirred and purged with nitrogen for about 1 h at 85 °C to allow the residual cyclohexane to evaporate. The product was transferred to a glass jar and kept under nitrogen prior to use. The monoTMAS initiator was dark yellow liquid obtained in a 72 % yield. From relative intensities of <sup>1</sup>H NMR signals (in acetone-*d*<sub>6</sub>) for N-CH<sub>3</sub> protons at 3.4 ppm and Si-CH<sub>3</sub> protons at 0 ppm, number-average molecular weight of monoTMAS was calculated to be ca.700 (*DP* ca. 8).

### 3.5 Preparation of $\alpha,\omega$ -Telechelic Dimethylvinylsiloxy End-Blocker (DiViEB)

$\alpha,\omega$ -Dimethylvinylsiloxy end-blocker (DiViEB) was synthesized by an equilibration reaction of D<sub>4</sub> with 1,3-divinyltetramethyldisiloxane, [CH<sub>2</sub>=CHSi(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>O, according to the literature reference<sup>155</sup> using the following chemistry:

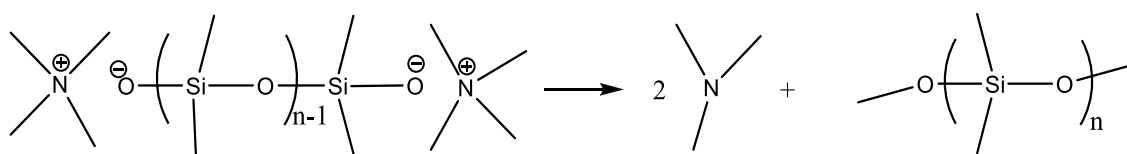


The reaction was carried out in a 250 mL three-necked, round-bottom flask, which was equipped with thermometer and magnetic Teflon<sup>®</sup> stirring bar and immersed in a paraffin oil bath at constant temperature of 40 °C. A mixture of D<sub>4</sub> (100 g, 0.34 mol) and 1,3-divinyltetramethyldisiloxane (41.9 g, 0.22 mol) and strongly acidic cation exchange resin Amberlyst<sup>®</sup>15(H) (3 g, 2 wt. % of the reactants mass) was placed in the reactor and vigorously stirred at 40 °C for 24 h. After the completion of the reaction, Amberlyst<sup>®</sup>15(H) was conveniently separated from the product by vacuum filtration. DiViEB was low-viscosity clear colorless liquid with typical number average molecular weight ( $M_n$ ) of DiViEB was 650, as determined by iodometry (Iodine Value IV = 78 gI<sub>2</sub>/100g (theoretical IV=79 gI<sub>2</sub>/100g)). Viscosity ( $\eta$ ) of DiViEB at 25 °C was 3 mPas, and acid value AV = 0.2 mg KOH/g.

### 3.6 Ring Opening Polymerization of Cyclic Siloxanes (ROP): Preparation of Vinyl-Terminated Terpolysiloxanes

Compositions of the reaction mixtures used for preparations of polymers of this work are shown in Tables 3.1, 3.2 and 3.3. General reaction scheme describing these preparations is shown in Reaction Scheme 4.1. The following was a typical procedure used.

Predetermined amounts of D<sub>4</sub>, "comonomer" (D<sub>4</sub><sup>Ph2</sup>, or D<sub>3</sub><sup>Et2</sup>, or D<sub>4</sub><sup>Et2</sup>, or DiEtS "hydrolyzate", or D<sub>4</sub><sup>MePh</sup>), D<sub>4</sub><sup>MeVi</sup> and DiViEB were placed in a 250-mL three-necked, round-bottom flask equipped with a mechanical stirrer, thermometer and nitrogen inlet. A small amount of D<sub>4</sub> (1-2 mL) was reserved for quantitative transfer of initiator. The reaction mixture was heated to 105 °C in a silicone oil bath and polymerization was initiated by the addition by Pasteur pipette of a 50 % solution of TMAS in THF. To provide quantitative transfer of the initiator, a vial in which TMAS solution was prepared was rinsed with the reserved amount of D<sub>4</sub>. The reaction was allowed to proceed for 24 hours at 105 °C with strong mechanical stirring, following which TMAS was thermally decomposed by heating the vigorously stirred reactor content at 135 °C for additional two hours (see the following reaction):



The low molecular weight fraction (cyclic products) was partially removed from the system by nitrogen purge at 170 °C, and the remaining cyclics were then separated from the polymer product by repeated precipitation from a 10 wt. % methylene chloride solution into a 6-fold volume of methanol. Traces of solvents in isolated polymer were removed by drying under vacuum at 80 °C for two hours.

Table 3.1. Compositions of reaction mixtures and targeted molecular weights of the prepared DiPhS- and DiEtS-containing terpolymers<sup>a</sup>.

Polymer ID number	D <sub>4</sub> , g (mmol)	D <sub>4</sub> <sup>Ph2</sup> , g (mmol)	D <sub>3</sub> <sup>Et2</sup> , g (mmol)	D <sub>4</sub> <sup>Et2</sup> , g (mmol)	D <sub>4</sub> <sup>MeVi</sup> , g (mmol)	DiViEB, g (mmol)	TMAS, g (mmol)	M <sub>t</sub> <sup>b</sup> , g/mol	DP <sub>t</sub> <sup>b</sup>	[DiViEB] <sup>c</sup>	[TMAS] <sup>d,e</sup>
Group A with D <sub>4</sub> <sup>Ph2</sup>											
1	40 (132)	4.0 (4.9)			0.14 (0.38)	4.5 (6.9)	2.4 (3.4)	7,200	80	12.1	6.25
2	40 (132)	4.0 (4.9)			0.14 (0.38)	2.3 (3.4)	1.2 (1.7)	13,500	160	6.3	3.15
3	50 (165)	5.0 (6.2)			0.17 (0.48)	0.93 (1.4)	0.90 (0.72)	39,000	480	2.1	1.05
4	50 (165)	5.0 (6.2)			0.17 (0.48)	0.75 (1.1)	0.72 (0.57)	48,400	600	1.7	0.85
Group B with D <sub>3</sub> <sup>Et2</sup>											
5	30 (99)		2.1 (7.0)		0.10 (0.28)	1.4 (2.1)	1.3 (1.05)	16,300	200	5.0	2.5
6	30 (99)		2.1 (7.0)		0.10 (0.28)	1.2 (1.7)	1.1 (0.87)	19,400	240	4.2	2.1
7	30 (99)		2.1 (7.0)		0.10 (0.28)	0.58 (0.87)	0.55 (0.44)	37,500	480	2.1	1.05
8	30 (99)		2.1 (7.0)		0.10 (0.28)	0.46 (0.70)	0.44 (0.35)	46,600	600	1.7	0.85
8a	30 (99)		1.5 (4.9)		0.10 (0.28)	0.46 (0.70)	0.43 (0.34)	46,300	600	1.7	0.85
Group C with D <sub>4</sub> <sup>Et2</sup>											
9	30 (99)			2.1 (5.2)	0.11 (0.29)	1.39 (2.09)	1.31 (1.05)	16,300	200	5.0	2.5
10	30 (99)			2.1 (5.2)	0.11 (0.29)	1.16 (1.7)	1.09 (0.87)	19,400	240	4.2	2.1
11	30 (99)			2.1 (5.2)	0.11 (0.29)	0.58 (0.87)	0.55 (0.44)	37,500	480	2.1	1.05
12	30 (99)			2.1 (5.2)	0.11 (0.29)	0.46 (0.70)	0.44 (0.35)	46,600	600	1.7	0.85
Group D with DiEtS "Hydrolyzate"											
13	40 (132)			2.9 (7.0)	0.14 (0.39)	2.30 (3.5)	1.19 (1.7)	13,000	160	6.3	3.15
14	30 (99)			2.1 (5.2)	0.11 (0.29)	1.39 (2.1)	0.72 (1.05)	16,100	200	5.0	2.5
15	30 (99)			2.1 (5.2)	0.11 (0.29)	1.16 (1.7)	0.60 (0.87)	19,100	240	4.2	2.1
16	30 (99)			2.1 (5.2)	0.11 (0.29)	0.87 (1.3)	0.45 (0.65)	25,100	320	3.1	1.55
17	30 (99)			2.1 (5.2)	0.11 (0.29)	0.57 (0.87)	0.30 (0.44)	37,200	480	2.1	1.05
Reference Polymers											
PDMS	30 (99)				0.11 (0.29)	0.44 (0.66)	0.44 (0.33)	45,700	600	1.7	0.85
PDES			30 (97.8)		0.08 (0.22)	0.30 (0.49)	0.30 (0.25)	62,500	600	1.7	0.85

<sup>a</sup> MeViS content in all polymers was 0.3 mol %. DiMeS content was 96.1 mol % in DiPhS-containing polymers and 94.7 mol % in DiEtS-containing polymers.

<sup>b</sup> M<sub>t</sub>: targeted molecular weight; DP<sub>t</sub>: targeted degree of polymerization.

<sup>c</sup> [DiViEB]: mmol DiViEB/mol(SiR<sub>2</sub>O); SiR<sub>2</sub>O: sum of all -SiR<sub>2</sub>O- units introduced with cyclic monomers.

<sup>d</sup> [TMAS]: (mmol SiO/mol(SiR<sub>2</sub>O))/2; SiR<sub>2</sub>O: as in c.

<sup>e</sup> [DiViEB]/[TMAS]=2



Table 3.2. Compositions of reaction mixtures for the series of DiPhS-containing polymers of targeted DP=160 prepared with different concentrations of TMAS initiator.<sup>a</sup>

Polymer ID number	D <sub>4</sub> , g (mmol)	D <sub>4</sub> <sup>Ph<sub>2</sub></sup> , g (mmol)	D <sub>4</sub> <sup>MeVi</sup> , g (mmol)	DiViEB, g (mmol)	TMAS, g (mmol)	M <sub>t</sub> <sup>b</sup> , g/mol	DP <sub>t</sub> <sup>b</sup>	[DiViEB] <sup>c</sup>	[TMAS] <sup>d</sup>	[DiViEB]/[TMAS]
2a	50 (165)	5.0 (6.2)	0.17 (0.48)	2.8 (4.3)	0.27 (0.21)	13,290	160	6.3	0.31	20
2b	50 (165)	5.0 (6.2)	0.17 (0.48)	2.8 (4.3)	0.54 (0.43)	13,350	160	6.3	0.63	10
2c	50 (165)	5.0 (6.2)	0.17 (0.48)	2.8 (4.3)	0.78 (0.86)	13,390	160	6.3	1.25	5
2d	50 (165)	5.0 (6.2)	0.17 (0.48)	2.8 (4.3)	1.29 (1.43)	13,500	160	6.3	2.1	3
2	40 (132)	4.0 (4.9)	0.14 (0.38)	2.3 (3.4)	1.18 (1.72)	13,530	160	6.3	3.15	2
2e	40 (132)	4.0 (4.9)	0.14 (0.38)	2.3 (3.4)	2.35 (3.44)	13,810	160	6.3	6.3	1

<sup>a</sup> MeViS content in all polymers was 0.3 mol %. DiMeS content was 96.1 mol % in DiPhS-containing polymers.

<sup>b</sup> M<sub>t</sub>: targeted molecular weight; DP<sub>t</sub>: targeted degree of polymerization.

<sup>c</sup> [DiViEB]: mmol DiViEB/mol(SiR<sub>2</sub>O); SiR<sub>2</sub>O: sum of all -SiR<sub>2</sub>O- units introduced with cyclic monomers.

<sup>d</sup> [TMAS]: (mmol SiO<sup>-</sup>/mol(SiR<sub>2</sub>O))/2; SiR<sub>2</sub>O: as in c.

Table 3.3. Compositions of reaction mixtures and targeted molecular weights for preparation of MePhS-containing polymers<sup>a</sup>.

Polymer ID number	D <sub>4</sub> , g (mmol)	D <sub>4</sub> <sup>MePh</sup> , <sup>b</sup> g (mmol)	D <sub>4</sub> <sup>MeVi</sup> , g (mmol)	DiViEB, g (mmol)	TMAS, g (mmol)	M <sub>t</sub> <sup>c</sup> , g/mol	DP <sub>t</sub> <sup>c</sup>	[DiViEB] <sup>d</sup>	[TMAS] <sup>e,f</sup>
18	30 (99.1)	2.1 (3.83)	0.10 (0.29)	0.13 (0.7)	0.06 (0.07)	46,100	600	1.7	0.17
19	30 (99.1)	4.4 (7.96)	0.11 (0.30)	0.13 (0.7)	0.06 (0.07)	47,400	600	1.7	0.17

<sup>a</sup> MeViS content for both polymers 18 and 19 was 0.3 mol %. MePhS content was 3.6 mol % and 7.2 mol % for polymers 18 and 19, respectively.

<sup>b</sup> Cyclic source of MePhS units used was D<sub>x</sub><sup>MePh</sup>, a commercially available mixture of x = 3, 4, 5 derivatives. Calculations of reaction composition are performed assuming x = 4.

<sup>c</sup> M<sub>t</sub>: targeted molecular weight; DP<sub>t</sub>: targeted degree of polymerization.

<sup>d</sup> [DiViEB]: mmol DiViEB/mol (SiR<sub>2</sub>O); SiR<sub>2</sub>O: sum of all -SiR<sub>2</sub>O- units introduced with cyclic monomers.

<sup>e</sup> [TMAS]: (mmol SiO<sup>-</sup>/mol (SiR<sub>2</sub>O))/2; SiR<sub>2</sub>O: as in d.

<sup>f</sup> [DiViEB]/[TMAS]=10

### 3.7 Preparation of Model Phenyl-*tris*(Polydimethylsiloxane) (Ph-T-PDMS) 3-Armed Star Polymer

Ph-T-PDMS model star polymer of Reaction Scheme 4.3, was prepared by equilibration of D<sub>4</sub> with phenyl-*tris*(trimethylsiloxy)silane, added in the molar ratio of 7.5:1, respectively, to yield an average of 10 dimethylsiloxy repeat units per arm. The composition of the reaction mixture for this polymerization is given in Table 3.4.

Table 3.4. Composition of reaction mixture for the preparation of model phenyl-*tris*(polydimethylsiloxane) (Ph-T-PDMS) 3-armed star polymer.

Polymer ID	D <sub>4</sub> , g (mmol)	Phenyl tris(trimethylsiloxy) silane, g (mmol)	Amberlyst <sup>®</sup> 15, g	M <sub>t</sub> <sup>a</sup>	DP <sub>t</sub> <sup>a</sup>
Ph-T-PDMS	50 (165)	8.4 (22)	1.2	2,600	30

<sup>a</sup> M<sub>t</sub>: targeted molecular weight; DP<sub>t</sub>: targeted degree of polymerization.

This reaction was conducted in a 125 mL three-necked, round-bottom flask, equipped with thermometer and magnetic Teflon<sup>®</sup>-coated stirring bar and immersed in a paraffin oil bath at constant temperature of 40 °C. D<sub>4</sub> (50 g, 0.17 mol) and phenyl-*tris*(trimethylsiloxy)silane (8.4 g, 0.022 mol) and strongly acidic cation exchange resin Amberlyst<sup>®</sup>15(H) (1.2 g, 2 wt. % of the total mass) were placed in the reactor and vigorously stirred at 40 °C for 24 hours. After the reaction was completed, the catalyst was separated from the product by vacuum filtration. Removal of cyclic oligomers was accomplished by vacuum distillation at 130 °C for 3 hours followed by multiple (6 times) precipitation from 10 wt. % polymer solution in toluene into a three-fold volume excess of methanol until all low-MW species were removed. Progress of this removal was monitored by SEC in toluene, and Ph-T-PDMS was isolated in 42 % yield. <sup>29</sup>Si NMR (CDCl<sub>3</sub>): δ (ppm) -80.8 to -78.8 (Ph-Si-[OSi(CH<sub>3</sub>)<sub>2</sub>]<sub>3</sub>-), -22.6 to -21.0 (-[Si(CH<sub>3</sub>)<sub>2</sub>O]-), 7.2 to 9.1 ((CH<sub>3</sub>)<sub>3</sub>SiO-). SEC-MALS (toluene): M<sub>w</sub>=5,060 g/mol, M<sub>n</sub>=3,500 g/mol, PDI = 1.45. Viscosity at 25 °C = 47 mPas.

### 3.8 Preparation of Model *tetrakis*(Polydimethylsiloxane) (Q-PDMS) 4-Armed Star Polymer

Q-PDMS model star polymer of Reaction Scheme 4.4, was prepared by equilibration of D<sub>4</sub> with *tetrakis*(trimethylsiloxy)silane, added in the molar ratio of 10:1, respectively, to yield an average of 10 dimethylsiloxy repeat units per arm. The composition of the reaction mixture for this preparation is given in Table 3.5.

Table 3.5. Composition of reaction mixture for the preparation of model *tetrakis*(polydimethylsiloxane) (Q-PDMS) 4-armed star polymer

Polymer ID	D <sub>4</sub> , g (mmol)	Tetrakis (trimethylsiloxy) silane, g (mmol)	Amberlyst <sup>®</sup> 15, g	M <sub>t</sub> <sup>a</sup>	DP <sub>t</sub> <sup>a</sup>
Q-PDMS	50 (165)	6.5 (17)	1.2	3,350	40

<sup>a</sup> M<sub>t</sub>: targeted molecular weight; DP<sub>t</sub>: targeted degree of polymerization.

This reaction was conducted in the same way as the preparation of model phenyl-*tris*(polydimethylsiloxane) (Ph-T-PDMS) 3-armed star polymer described in Section 3.7. Q-PDMS was clear colorless liquid and was isolated in 48 % yield. <sup>29</sup>Si NMR (CDCl<sub>3</sub>): δ (ppm) -105.0 to -110.0 (-[Si(CH<sub>3</sub>)<sub>2</sub>O]<sub>4</sub>-Si), -22.6 to -21.0 (-[Si(CH<sub>3</sub>)<sub>2</sub>O]-), 7.2 to 9.1 ((CH<sub>3</sub>)<sub>3</sub>SiO-). SEC-MALS (toluene): M<sub>w</sub> = 8,157 g/mol, M<sub>n</sub> = 4,958 g/mol, PDI = 1.6. Viscosity at 25 °C = 70 mPas.

### 3.9 Attempted Desilylation of Model Phenyl-*tris*(PDMS) 3-Armed Star Polymer with Monofunctional TMS to obtain *tetrakis*(PDMS) 4-Armed Star Polymer (Q-PDMS)

5 g of model phenyl-*tris*(polydimethylsiloxane) of Section 3.7 was placed in a 125-mL three-necked, round-bottom flask equipped with a magnetic Teflon<sup>®</sup>-coated stirring bar, thermometer and nitrogen inlet. The polymer was heated to 105 °C in a silicone oil bath and 0.87 g of monofunctional TMS was added as a 50 % solution in THF. The composition of this reaction mixture is given in Table 3.6.

Table 3.6. Composition of reaction mixture for the attempted desilylation of model phenyl-*tris*(PDMS) 3-armed star polymer with monofunctional TMS.

Polymer ID	Ph-T-PDMS, g (mmol)	monoTMS, g (mmol)	[monoTMS] <sup>a</sup>
Q-PDMS	5 (1.9)	0.87 (5.8)	100

<sup>a</sup> [monoTMS]: (mmol silanolate/mol(Si(CH<sub>3</sub>)<sub>2</sub>O))

Reaction was allowed to proceed for 24 hours at 105 °C with strong mechanical stirring. Following this, TMS was thermally decomposed by heating the vigorously stirred reaction mixture at 135 °C for additional two hours. The low molecular weight fraction

(cyclic products) was removed from the system by nitrogen purge at 160 °C for 4 hours. The product, semitransparent, brown, low-viscosity liquid, was isolated in 68 % yield.

$^{29}\text{Si}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm)  $-80.8$  to  $-78.8$  ( $\text{Ph-Si-}[\text{OSi}(\text{CH}_3)_2]_3-$ ),  $-22.6$  to  $-21.0$  ( $-\text{Si}(\text{CH}_3)_2\text{O}-$ ),  $7.2$  to  $9.1$  ( $(\text{CH}_3)_3\text{SiO}-$ ). SEC-MALS (toluene):  $M_w = 12,390$  g/mol,  $M_n = 4,230$  g/mol, PDI = 2.93.

The absence of signals at  $-105.0$  to  $-110.0$  ppm, characteristic for Q-branched silicons,  $-\text{Si}(\text{CH}_3)_2\text{O}-\text{Si}$ , in the  $^{29}\text{Si}$  NMR spectrum of the obtained product indicated that desilylation of Si-C<sub>Ar</sub> bonds from phenyl-T- units of model phenyl-*tris*(PDMS) did not occur.

### 3.10 Preparation of Samples for Monitoring of the Course of the Silanolate-Initiated Polymerization of Cyclic Siloxanes

Compositions of all reaction mixtures used for preparations performed in this portion of the work are shown in Table 3.7. The following was a typical procedure used.

Table 3.7. Compositions of reaction mixtures of Systems A - D and targeted molecular weights of the resulting polymers. <sup>a</sup> For description of the “Systems” see Sections 4.4 and 4.5.

Polymerization System	D <sub>4</sub> , g (mmol)	D <sub>4</sub> <sup>Ph2</sup> , g (mmol)	D <sub>3</sub> <sup>Et2</sup> , g (mmol)	D <sub>4</sub> <sup>MePh</sup> , g (mmol)	D <sub>4</sub> <sup>MeVi</sup> , g (mmol)	DiViEB, g (mmol)	TMAS, g (mmol)	$M_t^b$	$DP_t^b$	[DiViEB] <sup>c</sup>	[TMAS] <sup>d, e</sup>
<b>A</b> D <sub>4</sub> + D <sub>4</sub> <sup>Ph2</sup>	60 (198)	6.0 (7.4)			0.21 (0.58)	0.26 (1.37)	0.17 (0.14)	47,500	600	1.7	0.17
<b>B</b> D <sub>4</sub> + D <sub>3</sub> <sup>Et2</sup>	60 (198)		4.3 (14.0)		0.21 (0.58)	0.26 (1.37)	0.13 (0.14)	45,900	600	1.7	0.17
<b>C</b> D <sub>4</sub>	50 (165)					0.22 (1.1)	0.14 (0.11)	44,800	600	1.7	0.17
<b>D</b> D <sub>4</sub> + D <sub>4</sub> <sup>MePh</sup>	60 (198)			8.9 (15.9)	0.22 (0.60)	0.27 (1.4)	0.14 (0.14)	47,500	600	1.7	0.17

<sup>a</sup> MeViS content in all terpolymers was 0.3 mol %. DiMeS content was 96.1 mol % in DiPhS-containing polymer, 94.7 mol % in DiEtS-containing polymer and 92.5 mol % in MePhS-containing polymer.

<sup>b</sup>  $M_t$ : targeted molecular weight;  $DP_t$ : targeted degree of polymerization.

<sup>c</sup> [DiViEB]: mmol DiViEB/mol (SiR<sub>2</sub>O); SiR<sub>2</sub>O: sum of all  $-\text{SiR}_2\text{O}-$  units introduced with cyclic monomers.

<sup>d</sup> [TMAS]: (mmol SiO<sup>-</sup>/mol (SiR<sub>2</sub>O))/2; SiR<sub>2</sub>O: as in c.

<sup>e</sup> [DiViEB]/[TMAS]=10

Predetermined amounts (as shown in Table 3.7) of D<sub>4</sub>, D<sub>4</sub><sup>Ph2</sup> or D<sub>3</sub><sup>Et2</sup> or D<sub>4</sub><sup>MePh</sup>, D<sub>4</sub><sup>MeVi</sup> and DiViEB were placed in a 250-mL three-necked, round-bottom flask equipped with a

mechanical stirrer, thermometer and nitrogen inlet. The reaction mixture was heated to 105 °C in a silicone oil bath and polymerization was initiated by the addition of a 50 wt. % solution of TMAS in THF via Pasteur pipet. Samples of the reaction mixtures of approximately 3 g were taken during the polymerizations using a plastic pipet. Each sample was immediately quenched in liquid nitrogen and stored under nitrogen in a freezer at -20 °C to prevent further reaction progress. Frozen samples were used for SEC/MALS/Vis, TGA and <sup>29</sup>Si NMR analyses.

In experiment in which SEC monitoring was performed in THF as an eluent, all samples of the reaction mixtures were dissolved immediately in THF in exactly the same concentrations of 0.30 g/mL THF to enable acquisition of meaningful monitoring results.

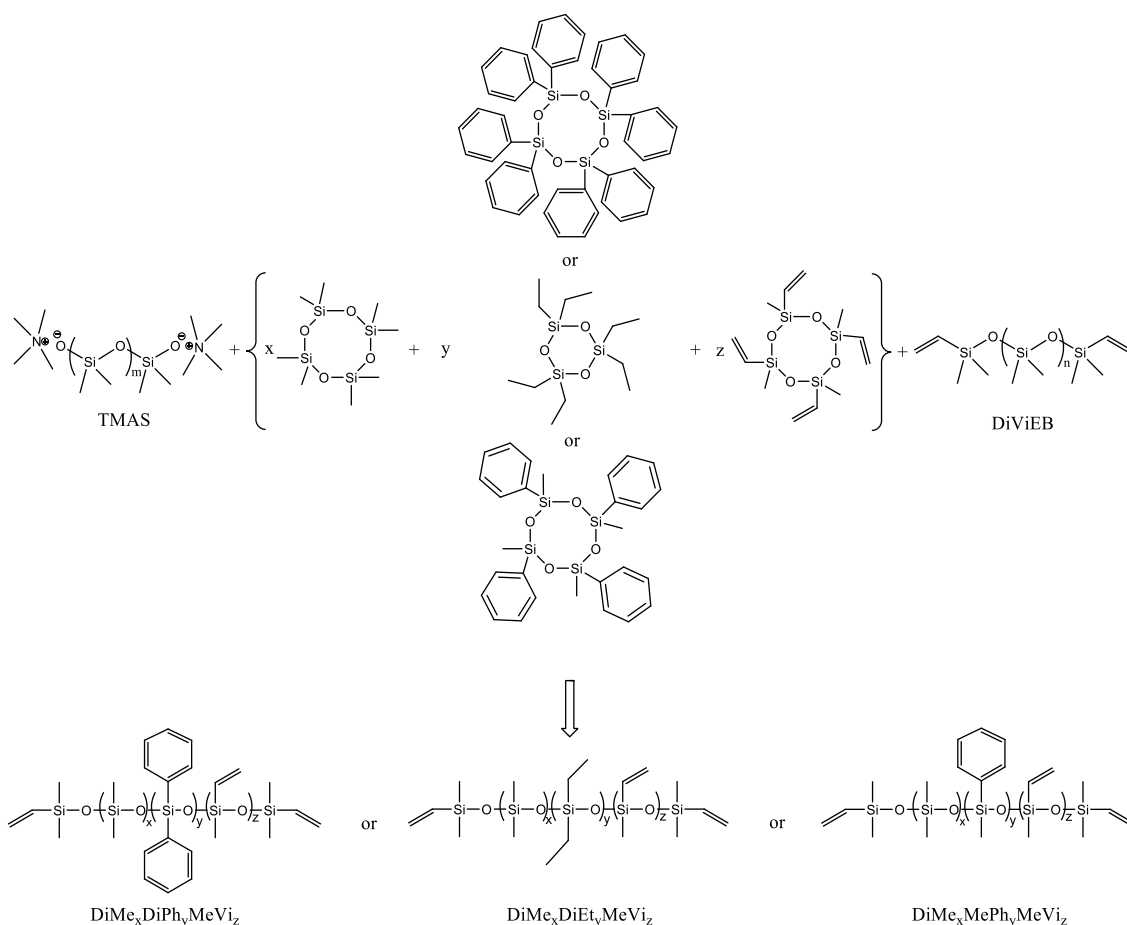
## 4. RESULTS AND DISCUSSION

Two main goals of this research program were: (a) to evaluate and better understand the silanolate-initiated ring opening polymerization (ROP) of selected cyclic siloxanes, and (b) to develop novel vinylsilyl-terminated  $\alpha,\omega$ -telechelic terpolysiloxanes, which will be completely amorphous and have strictly linear molecular chain configuration. Such polymers are expected to be excellent candidates for 3D printing of objects built from custom-made elastomers for extreme temperature applications.

### 4.1 Overview of Synthesized Vinylsilyl-Terminated $\alpha,\omega$ -Telechelic Terpolysiloxanes

In order to accomplish the above stated goals, three families (series) of  $\alpha,\omega$ -telechelic dimethylvinylsiloxy-,  $\text{CH}_2=\text{CH}-\text{Si}(\text{CH}_3)_2-\text{O}-$ , terminated terpolysiloxanes containing different relative amounts of Me, Ph, Et and Vi side groups (as listed in Tables 3.1-3.3) were synthesized, using the TMAS-initiated anionic ROP, shown in Reaction Scheme 4.1.

Mixture of cyclosiloxanes



Reaction Scheme 4.1. Synthesis of vinyl-functional DiPhS-, DiEtS- and MePhS-containing terpolysiloxanes.

These reactions were complex systems of ROPs of different mixtures of cyclic siloxanes and siloxane equilibration reactions to which polysiloxanes are prone in the presence of strongly nucleophilic species, such as dimethylsilanolate anions. The monomer mixtures predominantly contained  $D_4$  (> 95 mol %), but also small amounts (< 5 mol %) of crystallization disruptors ( $D_4^{\text{Ph}2}$ ;  $D_3^{\text{Et}2}$  or  $D_4^{\text{Et}2}$ ,  $D_4^{\text{MePh}}$ ) and traces of  $D_4^{\text{MeVi}}$  to introduce even smaller amounts of pendant vinyl groups for complete subsequent crosslinking of the polymers obtained. Tetramethylammonium disilanolate, TMAS, was used as a transient ROP initiator, since it could be easily destroyed after the completion of the polymerizations (by simple and convenient increase in the reaction temperature, by about 20 °C, for about two extra hours), and thus removed from the finished polymer product,

where, if remaining, initiators can subsequently cause potential problems. Divinyl end-blocker, DiViEB, was used as a molecular chain weight regulator, and also as an introducer of dimethylvinylsiloxy-end-groups to the resulting polymers, for subsequent crosslinking reactions.

The polymer nomenclature used in this work is illustrated in Reaction Scheme 4.1. All polymers were  $\alpha,\omega$ -telechelic vinylsiloxy-terpolysiloxanes (in the following text: terpolymers), characterized by their variable content of crystallization-disrupting repeat units, which are named as follows: DiPhS for diphenylsiloxy-, DiEtS for diethylsiloxy-, and MePhS for methylphenylsiloxy-. DiMeS is used for dimethylsiloxy- repeat units. Subscripts x, y and z represent molar percentiles of the respective repeat units, as targeted for each polymer sample.

In the first, DiPhS-containing series,  $\text{DiMe}_x\text{DiPh}_y\text{MeVi}_z$ , (Group A of Table 3.1), all prepared polymers were targeted to contain  $y = 3.6$  mol % of DiPhS units,  $z = 0.3$  mol % of MeViS units and  $x = 96.1$  mol % of DiMeS units, respectively, and degrees of polymerization (DP) in the range from 80 to 600. For the targeted DP of 160, a sub-series of DiPhS-containing polymers was prepared within which the concentration of the TMAS initiator was varied, as shown in Table 3.2. The composition of DiPhS-containing polymers was determined from relative intensities of  $^1\text{H}$  NMR signals assigned to protons from methyl (-0.1 – 0.2 ppm) and phenyl (7.3 – 7.7 ppm) side groups.<sup>182</sup> In the second, DiEtS-containing series, the DiPhS repeat units were replaced with  $y = 5$  mol % DiEtS units (using different sources of DiEtS units for the three subgroups) while keeping the MeViS content at the  $z = 0.3$  mol % level, DiMeS at  $x = 94.7$  mol %, and targeting similar DP values. The content of DiEtS repeat units incorporated into these polymers was determined from the ratios of signals assigned to protons from methyl (-0.1 – 0.2 ppm) and ethyl (0.4 – 1.1 ppm) side groups. The working hypothesis was that replacement of phenyl side groups in these copolymers with large and bulky ethyl groups would equally well suppress crystallization, while at the same time preventing the observed chain branching from happening (see further text) by reducing the electrophilicity of the Ph-bearing silicons and their susceptibility to nucleophilic attacks by silanolate anions. In the third series of terpolymers (Table 3.3), MePhS units were incorporated in place of DiPhS and DiEtS ones at two different levels ( $y = 3.6$  and  $7.2$  mol %), to serve as the third type of crystallization disruptors.



Characterization of obtained terpolymers by iodometry, SEC-MALS-VIS, rheometry and  $^1\text{H}$  NMR gave results presented in Tables 4.1, 4.2. and 4.3.

Refractive index increment,  $dn/dc$ , represents the key parameter for translating refractive index (RI) detector output to exact sample concentration and therefore enabling the calculation of important molecular parameters from the multi-angle light scattering (MALS) and viscosity (VIS) detector's signals. As it can be seen from Tables 4.1, 4.2. and 4.3, the values of  $dn/dc$  parameter for all synthesized polysiloxanes fall in the typical range between 0.05 and 0.20 mL/g providing reliable determination of absolute molecular weights, molecular weight distributions, intrinsic viscosities, and other molecular properties of terpolysiloxanes.

The hydrodynamic radius,  $R_h$ , or radius of hydrodynamically equivalent sphere, i.e., a hypothetical sphere that would have the same intrinsic viscosity as the actual polymer molecule, is the quantity derived from intrinsic viscosity,  $[\eta]$ , and expressed as:<sup>193</sup>

$$R_h = \left( \frac{3[\eta]M}{10 \pi N_A} \right)^{1/3} \quad (4.1)$$

where  $M$  is the molecular weight and  $N_A$  is Avogadro's number. The average values of hydrodynamic radii for studied polysiloxanes vary in the range 3.7 – 10.2 nm, as shown in Tables 4.1, 4.2. and 4.3.

Table 4.1. Characterization of DiPhS- and DiEtS-containing terpolysiloxanes obtained from reaction systems described in Table 3.1.

Polymer ID number	SEC-MALS-VIS											DiPhS or DiEtS content				
	$M_t^a$ , g/mol	$DP_t^a$	$IV_t^b$ , gI <sub>2</sub> /100g	$IV_{exp}^b$ , gI <sub>2</sub> /100g	dn/dc <sup>c</sup> , mL/g	$M_w$ , g/mol	$M_n$ , g/mol	$M_p$ , g/mol	PDI <sup>d</sup>	$[\eta]^e$ , mL/g	$R_h^f$ , nm	MHS parameters		$\eta^g$ at 25 °C, Pa s	Feed, mol %	Polymer (by <sup>1</sup> H NMR), mol %
												$a$	K, mL/g			
Group A with D <sub>4</sub> <sup>Ph2</sup>																
1	7,200	80	7.8	7.4	-0.077	37,200	13,600	15,600	2.74	11.9	3.7	0.474	0.096	0.3	3.6	2.4
2	13,500	160	4.6	5.0	-0.072	89,600	21,400	23,300	4.19	19.0	5.6	0.474	0.108	1.2	3.6	3.1
3	39,000	480	2.2	2.8	-0.068	234,800	50,600	67,300	4.64	35.4	9.3	0.480	0.124	19.5	3.6	3.5
4	48,400	600	2.0	2.4	-0.071	260,500	58,500	71,200	4.45	41.0	10.2	0.481	0.135	15.0	3.6	3.6
Group B with D <sub>3</sub> <sup>Et2</sup>																
5	16,300	200	4.1	4.3	-0.085	24,600	14,900	21,100	1.65	12.8	4.6	0.636	0.0221	0.6	5.0	4.4
6	19,400	240	3.6	3.8	-0.087	27,100	14,400	24,100	1.88	14.0	5.0	0.630	0.0246	0.8	5.0	4.6
7	37,500	480	2.3	2.5	-0.083	54,600	34,600	49,600	1.58	21.9	7.0	0.647	0.0202	3.8	5.0	4.6
8	46,600	600	2.1	2.4	-0.084	59,300	36,100	54,500	1.64	23.8	7.5	0.646	0.0211	5.6	5.0	5.4
8a	46,300	600	2.1	2.2	-0.086	62,800	38,000	56,100	1.65	25.7	7.9	0.644	0.0231	6.7	3.6	3.6
Group C with D <sub>4</sub> <sup>Et2</sup>																
9	16,300	200	4.1	4.3	-0.085	24,500	14,200	21,000	1.73	12.5	4.6	0.633	0.0226	0.58	5.0	4.0
10	19,400	240	3.6	4.0	-0.084	27,400	16,400	23,500	1.68	13.4	4.8	0.638	0.0213	0.70	5.0	3.8
11	37,500	480	2.3	2.6	-0.082	56,400	33,400	51,100	1.69	21.1	7.2	0.643	0.0202	3.50	5.0	3.6
12	46,600	600	2.1	2.4	-0.084	65,300	38,700	57,600	1.69	24.4	8.0	0.653	0.0190	6.01	5.0	3.9
Group D with DiEtS “Hydrolyzate”																
13	13,000	160	4.9	5.0	-0.085	20,700	12,500	19,100	1.66	11.8	4.2	0.664	0.0172	0.47	5.0	4.6
14	16,100	200	4.0	4.0	-0.085	26,300	15,800	22,800	1.67	13.7	4.8	0.661	0.0177	0.55	5.0	5.1
15	19,100	240	3.6	4.0	-0.085	28,600	17,700	26,000	1.61	14.9	5.0	0.666	0.0170	0.7	5.0	5.1
16	25,100	320	3.0	3.5	-0.084	37,500	23,000	35,000	1.63	17.5	5.8	0.668	0.0165	2.8	5.0	5.7
17	37,200	480	2.3	2.5	-0.084	55,600	34,100	52,100	1.63	23.2	7.3	0.662	0.0178	4.4	5.0	4.9
Reference Polymers																
PDMS	45,700	600	2.1	2.2	-0.084	83,000	54,700	70,400	1.52	30.8	7.1	0.635	0.0245	9.1		
PDES	62,500	600	1.7	1.6	-0.045	46,600	32,700	38,200	1.42	20.7	6.3	0.637	0.0231	35.9		

<sup>a</sup>  $M_t$ : targeted molecular weight;  $DP_t$ : targeted degree of polymerization.

<sup>b</sup>  $IV_t$  and  $IV_{exp}$ : iodine values theoretical and experimental, respectively.

<sup>c</sup> dn/dc was determined online, using 100 % mass recovery.

<sup>d</sup> PDI: polydispersity index;  $PDI=M_w/M_n$ .

<sup>e</sup>  $[\eta]$ : intrinsic viscosity as determined by Visco Star II online detector.

<sup>f</sup>  $R_h$ : hydrodynamic radius.

<sup>g</sup>  $\eta$ : dynamic viscosity of isolated polymer samples as determined by cone-and-plate viscometry.

Table 4.2. Characterization of DiPhS-containing terpolymers of targeted DP=160, prepared with different concentrations of TMAS initiator.

					SEC-MALS-VIS									DiPhS content		
Polymer ID number	$M_t^a$	$DP_t^a$	$IV_t^b$ , gI <sub>2</sub> /100g	$IV_{exp}^b$ , gI <sub>2</sub> /100g	dn/dc <sup>c</sup> , mL/g	$M_w$ , g/mol	$M_n$ , g/mol	$M_p$ , g/mol	PDI <sup>d</sup>	$[\eta]^e$ , mL/g	$R_h^f$ , nm	MHS parameters		$\eta^g$ at 25 °C, Pa s	Feed, mol %	Polymer (by <sup>1</sup> H NMR), mol %
												$a$	$K$ , mL/g			
2a	13,290	160	4.7	4.9	-0.073	22,950	15,530	20,670	1.48	13.8	3.6	0.676	0.017	0.6	3.6	3.4
2b	13,350	160	4.7	4.9	-0.072	26,240	15,640	21,320	1.68	14.1	3.7	0.628	0.026	0.7	3.6	3.4
2c	13,390	160	4.7	5.0	-0.076	35,760	18,350	20,680	1.95	16.8	4.3	0.549	0.055	0.8	3.6	3.4
2d	13,500	160	4.6	4.9	-0.072	59,470	21,900	22,580	2.72	17.4	5.0	0.508	0.077	0.9	3.6	3.2
2	13,530	160	4.6	5.0	-0.072	89,600	21,400	23,300	4.19	19.0	5.6	0.474	0.108	1.2	3.6	3.1
2e	13,810	160	4.6	4.9	-0.072	179,436	24,040	18,960	7.46	20.1	6.7	0.444	0.132	1.2	3.6	3.1

<sup>a</sup>  $M_t$ : targeted molecular weight;  $DP_t$ : targeted degree of polymerization.

<sup>b</sup>  $IV_t$  and  $IV_{exp}$ : iodine values theoretical and experimental, respectively.

<sup>c</sup> dn/dc was determined online, using 100 % mass recovery.

<sup>d</sup> PDI: polydispersity index;  $PDI=M_w/M_n$ .

<sup>e</sup>  $[\eta]$ : intrinsic viscosity as determined by Visco Star II online detector.

<sup>f</sup>  $R_h$ : hydrodynamic radius.

<sup>g</sup>  $\eta$ : dynamic viscosity of isolated polymer samples as determined by cone-and-plate viscometry.

Table 4.3. Characterization of MePhS-containing terpolymers of targeted DP=600 prepared with different contents of MePhS units.

					SEC-MALS-VIS									MePhS content		
Polymer ID	$M_t^a$	$DP_t^a$	$IV_t^b$ , gI <sub>2</sub> /100g	$IV_{exp}^b$ , gI <sub>2</sub> /100g	dn/dc <sup>c</sup> , mL/g	$M_w$ , g/mol	$M_n$ , g/mol	$M_p$ , g/mol	PDI <sup>d</sup>	$[\eta]^e$ , mL/g	$R_h^f$ , nm	MHS parameters		$\eta^g$ at 25 °C, Pa s	Feed, mol %	Polymer (by <sup>1</sup> H NMR), mol %
												$a$	$K$ , mL/g			
18	46,100	600	2.1	2.1	-0.083	65,500	40,900	62,200	1.6	34.4	6.8	0.693	0.0165	16	3.6	3.9
19	47,500	600	2.0	2.2	-0.073	72,500	45,100	64,300	1.6	36.5	7.2	0.693	0.0166	19	7.2	7.8

<sup>a</sup>  $M_t$ : targeted molecular weight;  $DP_t$ : targeted degree of polymerization.

<sup>b</sup>  $IV_t$  and  $IV_{exp}$ : iodine values theoretical and experimental, respectively.

<sup>c</sup> dn/dc was determined online, using 100 % mass recovery.

<sup>d</sup> PDI: polydispersity index;  $PDI=M_w/M_n$ .

<sup>e</sup>  $[\eta]$ : intrinsic viscosity as determined by Visco Star II online detector.

<sup>f</sup>  $R_h$ : hydrodynamic radius.

<sup>g</sup>  $\eta$ : dynamic viscosity of isolated polymer samples as determined by cone-and-plate viscometry.

## 4.2 DiPhS-Containing Polymers

As expected,<sup>13, 175, 187</sup> in the series of terpolymers prepared with 3.6 mol % of DiPhS units (Polymers 1-4 of Group A of Table 4.1), crystallization was completely suppressed in all polymers ranging in DP from 80 to 600 (as indicated by DSC thermograms from -80 °C to +50 °C shown in Figure 4.1).

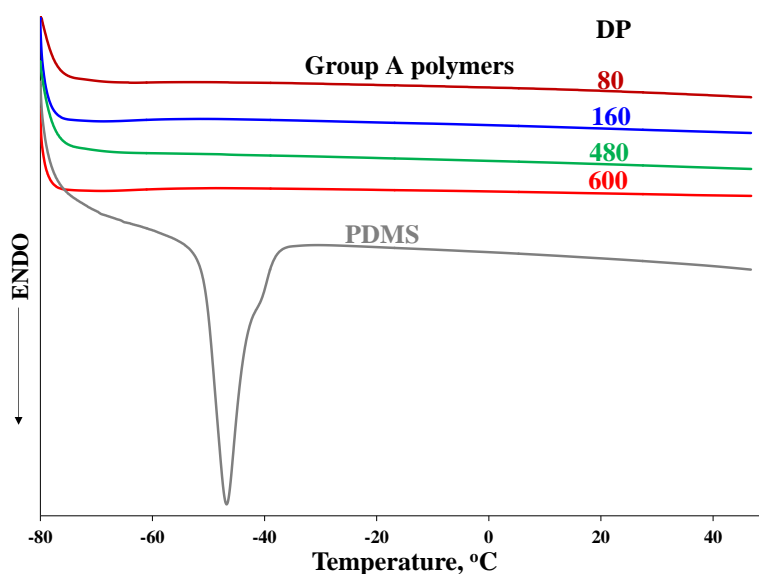


Figure 4.1. DSC thermograms of Group A polymers prepared with 3.6 mol % of DiPhS repeat units and a reference PDMS homopolymer.

Since determination of composition of copolymers by <sup>1</sup>H NMR takes into account protons from DiMeS units introduced with TMS and DiViEB, which are unaccounted for in the targeted compositions of starting mixtures of cyclic siloxanes, the resulting content of DiPhS units in polymers is expectedly lower than targeted. These discrepancies generally increase in DiPhS-containing polymers with the concentration of TMS and DiViEB, as shown in Tables 4.1 and 4.2.

<sup>29</sup>Si NMR spectra of these polymers showed signals for all expected Si atoms, including those from DiMeS units at -22 ppm, DiPhS units at -46 ppm, MeViS units at -35 ppm, terminal DiMeViS end-groups at -4.1 ppm, and dimethylmethoxysilyl- terminal units at

-12 ppm,<sup>197</sup> but also an additional signal at around -80 ppm. By its position, this "additional" signal could be assigned to the trisiloxy-, Ph-Si-[OSi(CH<sub>3</sub>)<sub>2</sub>]<sub>3</sub>-, Ph-T-branches,<sup>183, 198</sup> and in support of such assignment its intensity increased with the decrease in polymer DP caused by increase in concentration of the silanolate initiator used in the corresponding polymerization reactions (see Figure 4.2).

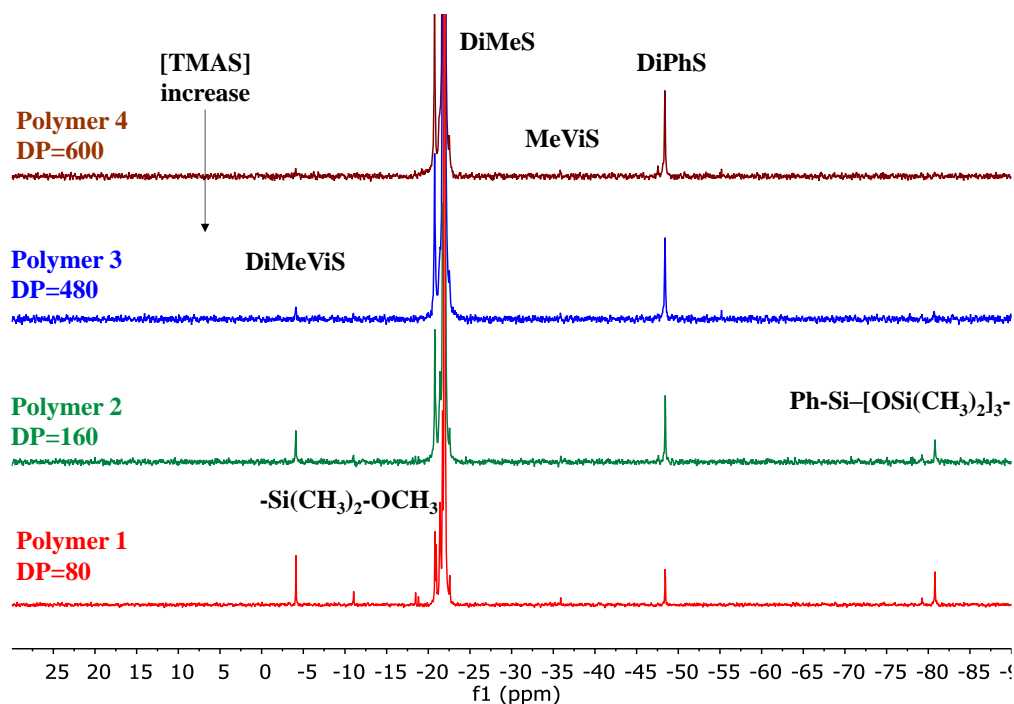


Figure 4.2. <sup>29</sup>Si NMR spectra of group A polymers from Table 4.1 containing 3.6 mol % of DiPhS units.

Comparison of the intensities of <sup>29</sup>Si NMR signals from DiPhS and Ph-T-branch units of polymers of Group A (Table 4.4) showed that, as the concentration of silanolate initiator increased from 2.1 mmol SiO<sup>-</sup>/mol siloxy for Polymer 3, to 6.3 mmol SiO<sup>-</sup>/mol siloxy for Polymer 2, to 12.1 mmol SiO<sup>-</sup>/mol siloxy for Polymer 1, the relative amounts of Ph-T-branches in the sum of all Ph-containing units increased from 6 %, to 27 %, to 61 %, respectively. In the case of Polymer 4, prepared with the lowest concentration of silanolate initiator (1.7 mmol SiO<sup>-</sup>/mol siloxy) the reliable estimation of the concentration of Ph-T-branch units was not possible due to a too low signal to noise ratio.

Table 4.4. Relative abundance of linear, DiPhS, and branched, Ph-Si-[OSi(CH<sub>3</sub>)<sub>2</sub>]<sub>3</sub>-, units in DiPhS-containing terpolymers of Group A.

	Polymer 1	Polymer 2	Polymer 3
Relative intensity of DiPhS signal, %	39	73	94
Relative intensity of Ph-Si-[OSi(CH <sub>3</sub> ) <sub>2</sub> ] <sub>3</sub> - signal, %	61	27	6

<sup>29</sup>Si NMR analysis of the series of six DiPhS-containing terpolymers with targeted DP of 160 (see Table 4.2) and varying concentration of TMAS initiator, gave additional support to the assumption that branching may occur at DiPhS sites during silanolate initiated ROP of cyclic siloxanes (Figure 4.3). Comparison of intensities of <sup>29</sup>Si NMR signals from linear DiPhS units at -48 ppm and Ph-T-branch units at -80 ppm showed (see Table 4.5) that, as the [DiViEB]/[TMAS] ratio increased from 1 for Polymer 2e, to 2 for Polymer 2, to 3 for Polymer 2d, to 5 for polymer 2c, the relative amounts of Ph-T-branches in the sum of all Ph-containing units decreased from 47 %, to 32 %, to 28 %, to 11 %, respectively. The absence of signals at -80 ppm at <sup>29</sup>Si NMR spectra of Polymers 2b and 2a, prepared with the lowest concentrations of silanolate initiator (see Table 3.2), indicated that formation of Ph-T-branch sites might have not occurred at these TMAS levels at all. Based solely on these <sup>29</sup>Si NMR results, summarized in Table 4.5, it appears that, for a given targeted DP of 160, the critical [DiViEB]/[TMAS] ratio, at which branching starts occurring in these DiPhS-containing terpolymers lies in the range of 10/1 to 5/1.

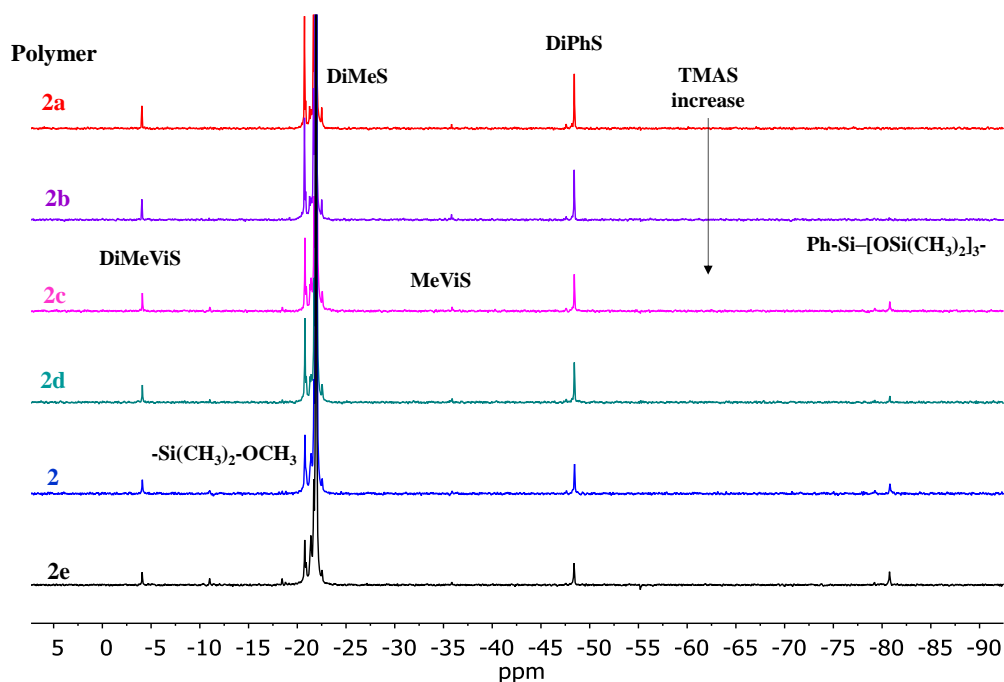


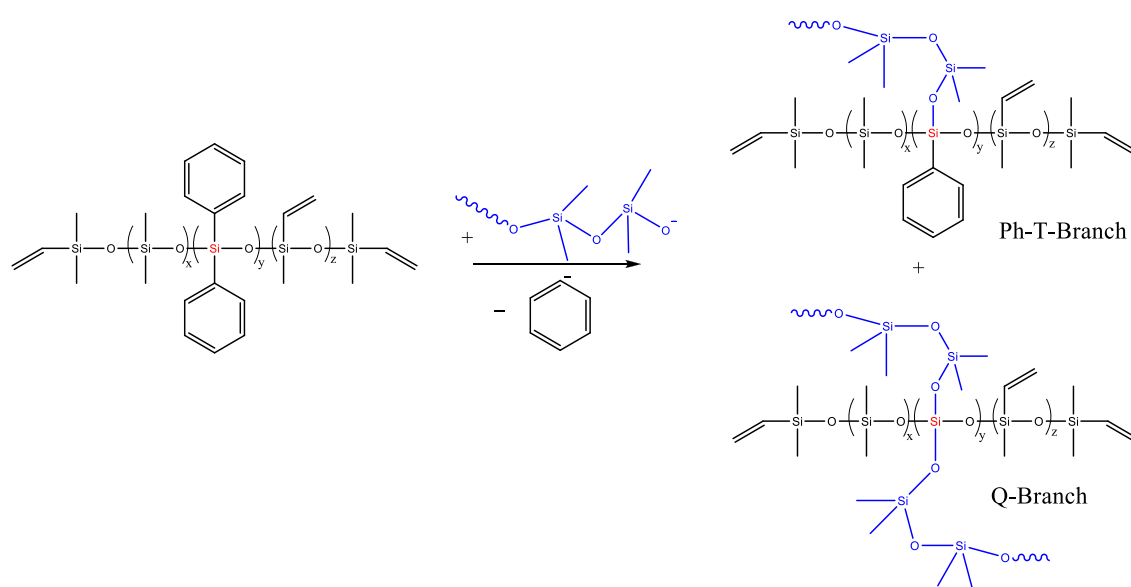
Figure 4.3.  $^{29}\text{Si}$  NMR spectra of the series of terpolymers with targeted DP-160 containing 3.6 mol % of DiPhS units, prepared with different concentrations of TMAS initiator.

Table 4.5. Relative abundance of linear, DiPhS, and Ph-T-branched, Ph-Si-[OSi(CH<sub>3</sub>)<sub>2</sub>]<sub>3</sub>- units in the series of DiPhS-containing terpolymers with targeted DP=160, prepared with different [DiViEB]/[TMAS] ratios.

Polymer ID	2a	2b	2c	2d	2	2e
[DiViEB]/[TMAS]	20	10	5	3	2	1
Relative intensity of DiPhS $^{29}\text{Si}$ NMR signal, %	100	100	89	72	68	53
Relative intensity of Ph-Si-[OSi(CH <sub>3</sub> ) <sub>2</sub> ] <sub>3</sub> - $^{29}\text{Si}$ NMR signal, %	0	0	11	28	32	47

It is known from literature that Si-C<sub>Ar</sub> bonds are quite prone to desilylation in the presence of strong ionic species.<sup>69, 199</sup> Comprehensive study on different silarylene-siloxane elastomers with various aromatic groups incorporated into the polysiloxane main chain backbones reported that splitting of Si-C<sub>Ar</sub> bonds easily occurs even when embedded into the main polymer chains.<sup>69</sup> Furthermore, it was also reported that in

polymerizations of mixed methylarylcyclosiloxanes with various silanolate initiators, chain transfer to another molecule occurred as a result of the scission of the phenyl radicals from Si-Ph side groups.<sup>199</sup> It would be, therefore, reasonable to expect that, in the TMAS-initiated ROPs of cyclic siloxanes of Reaction Scheme 4.1, the side Si-C<sub>Ar</sub> bonds of DiPhS units may also be prone to such desilylation by silanolate anions, leading to the formation of trisiloxy-, Ph-Si-[OSi(CH<sub>3</sub>)<sub>2</sub>]<sub>3</sub>, Ph-T-branches, or even tetrasiloxy-, quarternary, Si-[OSi(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub>-, Q-branches, as illustrated in the Reaction Scheme 4.2. If so, this would explain the formation of observed branching in DiPhS-containing terpolysiloxanes, possible appearance of dangling chains in their subsequently crosslinked networks, and a variety of negative effects that this could have on their resulting mechanical properties.



Reaction Scheme 4.2. Desilylation of Si-C<sub>Ar</sub> side bonds and formation of Ph-T- and Q-branches in DiPhS-containing terpolysiloxanes.

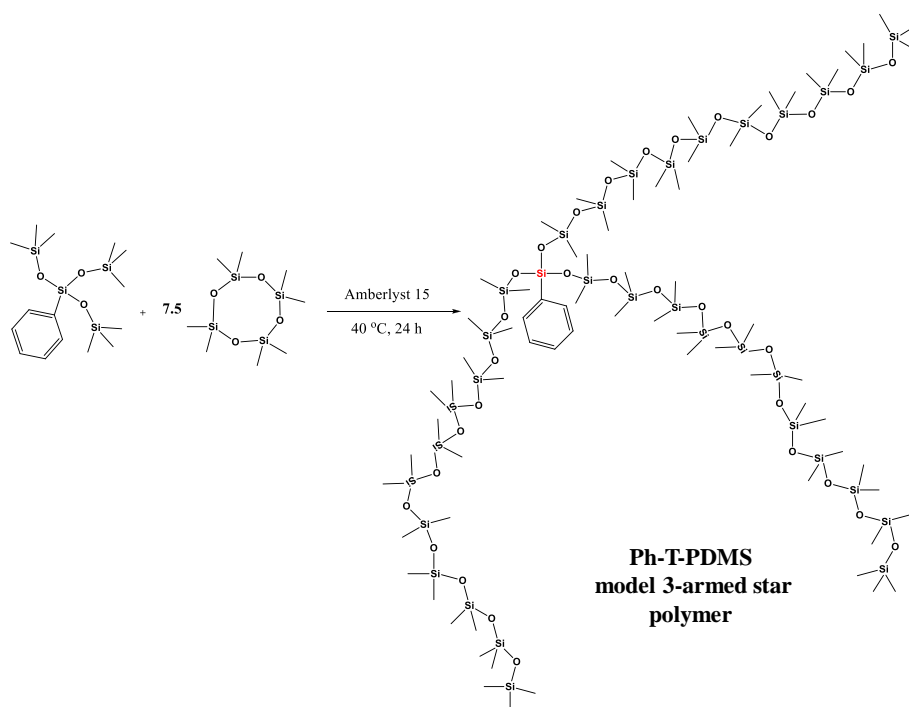
## 4.2.1 Model Branched Polymers

### 4.2.1.1 Model Three-Armed Star Polysiloxane: Trimethylsiloxy-Terminated Phenyl-*tris*(Polydimethylsiloxane)

To verify the Ph-T-branch assignment described in Section 4.2, a model 3-armed PDMS star polymer with a built-in trisiloxy-, Ph-Si-[OSi(CH<sub>3</sub>)<sub>2</sub>]<sub>3</sub>, Ph-T-branch, as a key



structural feature was synthesized as shown in Reaction Scheme 4.3. Its  $^{29}\text{Si}$  NMR was compared with those of DiPhS-containing polymers from Group A of Table 4.1 and a low molecular weight analogue, phenyltris(trimethylsiloxy)silane,  $\text{Ph-Si}[\text{OSi}(\text{CH}_3)_3]_3$ , which was used as a source of Ph-T-branch sites and regulator of chain lengths for 3-armed PDMS star polymer, as shown in Figure 4.4. It can be seen from this figure that spectra of both model compounds contained clearly distinguished signals at around  $-80$  ppm, thus confirming the validity of the assignment for identical signals observed in the DiPhS-containing copolymers of Group A (Figure 4.2 and 4.3).



Reaction Scheme 4.3. Synthesis of model three-armed star polymer: trimethylsiloxy-terminated phenyl-*tris*(polydimethylsiloxane).

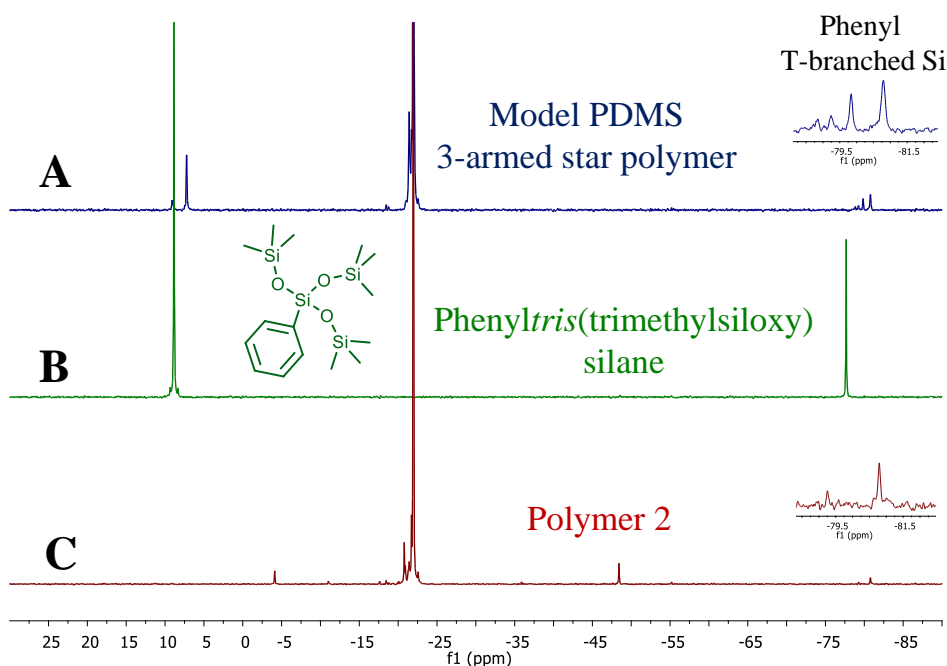
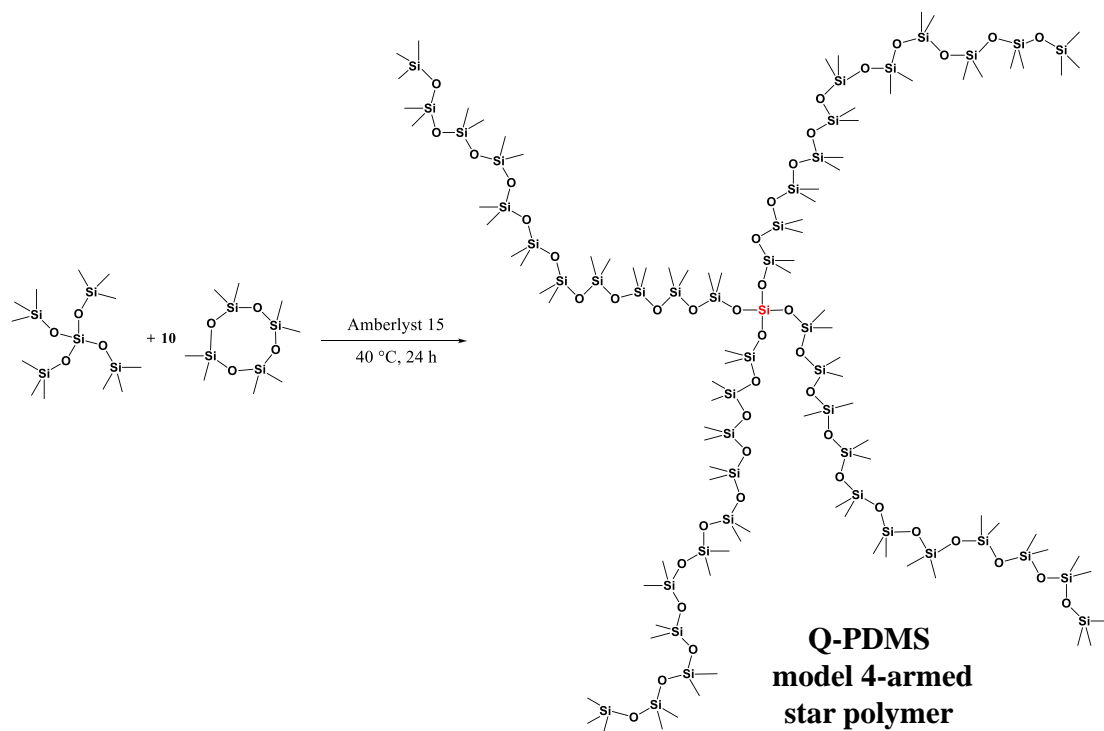


Figure 4.4.  $^{29}\text{Si}$  NMRs of the model phenyltris(PDMS) 3-armed star polymer of Reaction Scheme 4.3 (A), phenyltris(trimethylsiloxy)silane (B) and DiPhS-containing terpolymer, Polymer 2 of Tables 3.1 and 4.1, with DP = 160 (C).

#### 4.2.1.2 Model Four-Armed Star Polysiloxane: Trimethylsiloxy-Terminated *tetrakis*(Polydimethylsiloxane)

Model trimethylsiloxy-terminated *tetrakis*(PDMS), four-armed star polymer containing Q branch structure was synthesized as shown in Reaction Scheme 4.4 using the same strategy as in the case of phenyl-T-branch model compound of Scheme 4.3, only this time starting with *tetrakis*(trimethylsiloxy)silane as a source of Q units.  $^{29}\text{Si}$  NMR spectra of the obtained model Q branch-containing PDMS and of the starting core molecule are shown in Figure 4.5. Magnified traces in inset of Figure 4.5 show that signal from Q branch silicon appears at  $-107$  ppm for model 4-armed star polymer, and at  $-105$  ppm for the low molecular weight *tetrakis*(trimethylsiloxy)silane.



Reaction Scheme 4.4. Synthesis of model four-armed star polymer: trimethylsilyloxy-terminated *tetrakis*(polydimethylsiloxane).

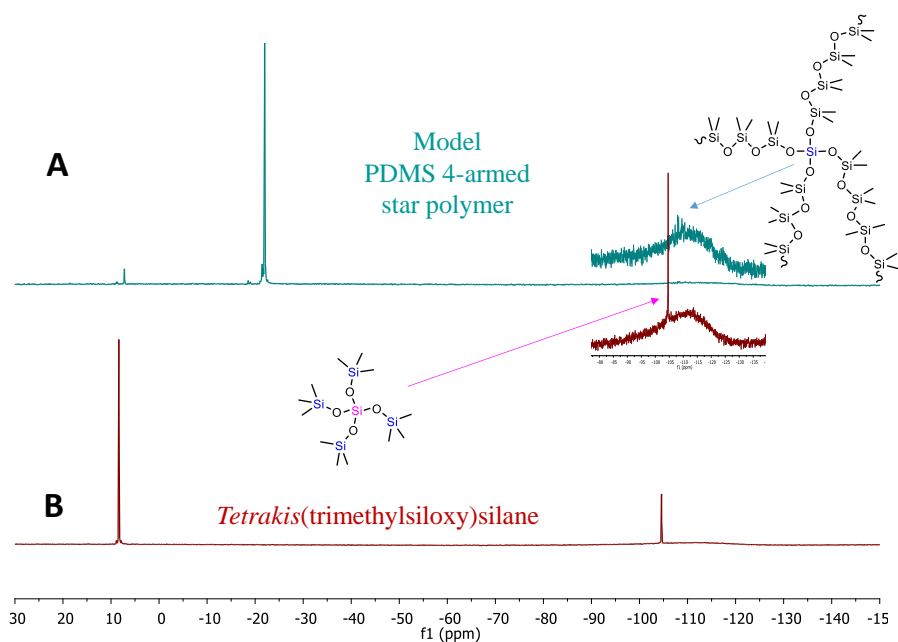
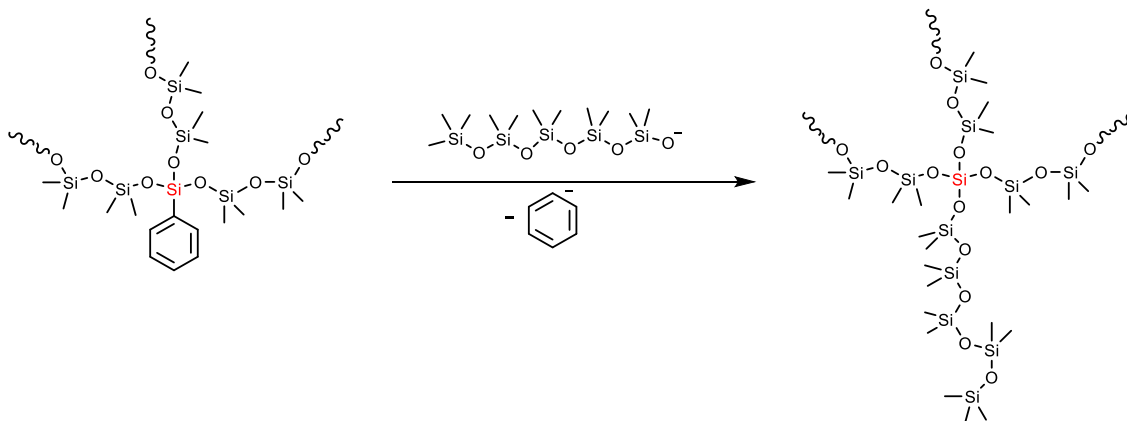


Figure 4.5.  $^{29}\text{Si}$  NMR of model *tetrakis*(PDMS) 4-armed star of Reaction Scheme 4.4 (A), and *tetrakis*(trimethylsilyloxy)silane (B).

No indication of the presence of such Q-branches could be found in  $^{29}\text{Si}$  NMR spectra of DiPhS-containing terpolymers shown in Figures 4.2 and 4.3. Formation of Q-branched structures would occur if total desilylation took place on a single DiPhS repeat unit replacing both phenyl groups with polysiloxane chains.

#### 4.2.1.3 Attempted Desilylation of the Model Phenyl-*tris*(PDMS) 3-Armed Star Polymer

To further evaluate the possibility of the formation of four-functional Q-branch structures in the DiPhS-containing terpolysiloxanes, desilylation of the  $\text{Si-C}_{\text{Ar}}$  bonds of the model polymer phenyl-*tris*(PDMS) was attempted in the reaction with monofunctional tetramethylammonium silanolate, monoTMAS, added in a very high concentration of 100 mmol  $\text{SiO}^-/\text{mol}$  siloxy. The reason for using monofunctional instead of difunctional initiator was to avoid the crosslinking that would occur if silanolate anions from difunctional initiator molecule desilylated  $\text{Si-C}_{\text{Ar}}$  bonds from two different polymer molecules. Schematic representation of this attempted reaction is given in Reaction Scheme 4.5.



Reaction Scheme 4.5. Desilylation of  $\text{Si-C}_{\text{Ar}}$  bonds of the model polymer phenyl-*tris*(polydimethylsiloxane).

However, despite the very high concentration of monoTMAS initiator used in this reaction, as well as long reaction time (24 hours) allowed, desilylation of  $\text{Si-C}_{\text{Ar}}$  bonds from phenyl-T units of model phenyl-*tris*(PDMS) did not take place at all, as confirmed by  $^{29}\text{Si}$  NMR (see Figure 4.6). The absence of  $^{29}\text{Si}$  NMR signal from Q-branched silicons

and the presence of signal from phenyl-T units clearly suggested that silicon atoms from phenyl-T units were less susceptible to nucleophilic attack than the silicon atoms from diphenylsiloxane units. Substitution of one phenyl group in a DiPhS unit by a polydimethylsiloxane branch, seems to stabilize the remaining Si-C<sub>Ar</sub> bond towards further desilylation by decreasing electrophilicity of its silicon atom and thereby its susceptibility to a nucleophilic attack by the silanolate active centers.

The apparent decrease in intensity of <sup>29</sup>Si NMR signal assigned to the Ph-T-branch after attempted desilylation of model phenyl-*tris*(PDMS) was the result of dilution by added initiator – the weight fraction of monoTMAS in the reaction mixture was 0.15.

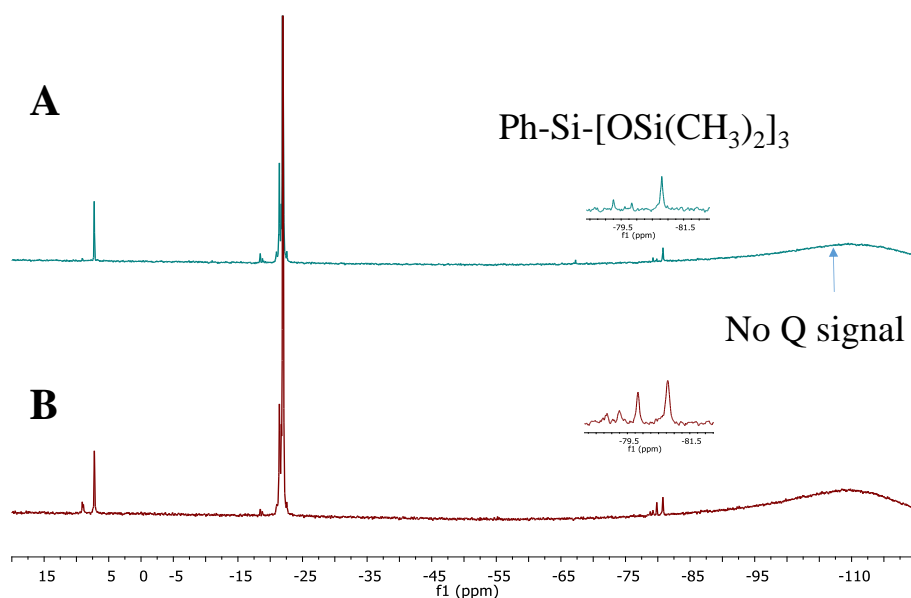


Figure 4.6. <sup>29</sup>Si NMR spectra of the model phenyl-*tris*(PDMS) polymer (B) and the product of the reaction of model phenyl-*tris*(PDMS) with monoTMAS (A).

#### 4.2.2 Molecular Weight Distribution and Conformation of DiPhS-Containing Terpolymers

SEC-MALS-VIS (see Figure 4.7) analysis of DiPhS-containing terpolymers of Table 4.1 showed that in all cases their number-average molecular weights were considerably higher than the targeted values (calculated based on the end-blocker/monomer stoichiometry; see Table 4.1). In addition, all traces had pronounced shoulders at lower

elution times, resulting in significant polydispersities which reached index values of well over 4 in the cases of Polymers 2-4. All of these parameters can be interpreted as indicating branching of polymer chains caused by desilylation of their side Si-C<sub>Ar</sub> bonds and attachment of the long polymer branches from initiator or from growing chains bearing silanolate anions. The lengths of these chains' branches were comparable to those of the terpolymer backbones.<sup>193, 200</sup>

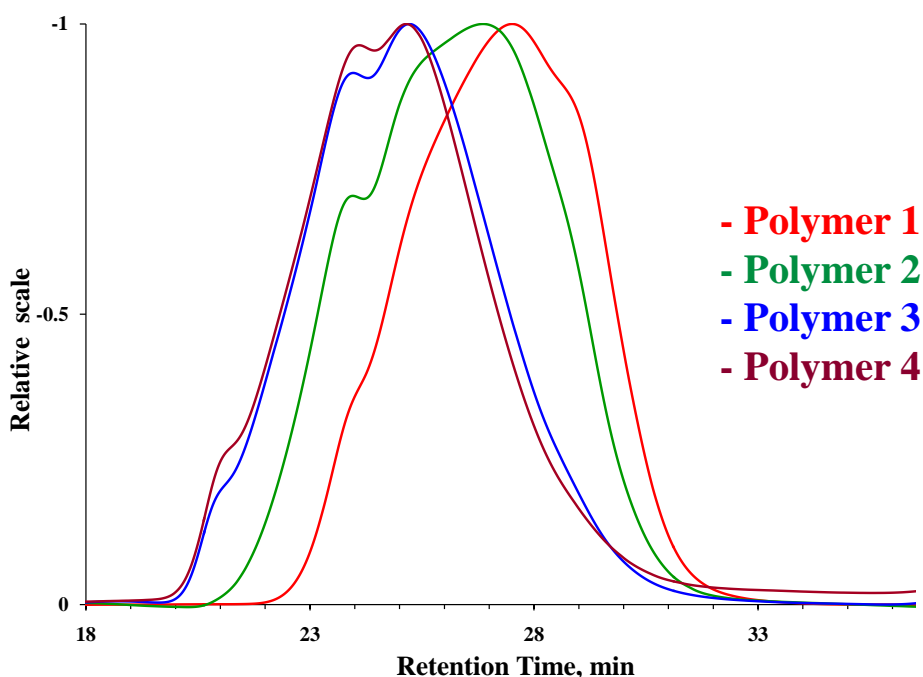


Figure 4.7. SEC-MALS chromatograms (refractive index detector) of DiPhS-containing terpolymers of Group A of Table 4.1, prepared with [TMAS]/[DiViEB]=1/2.

Utilizing multiangle light scattering (MALS) in combination with an online viscometer for SEC detection, the Mark-Houwink-Sakurada (MHS) plots yielding the  $K$  and  $a$  constants of the well-known MHS equation,  $[\eta] = KM^a$ , were obtained, providing further information about these polymers' chain conformations. Generally, the value of the exponent  $a$  is well known to increase with rigidity of polymer chains, and in the ultimate case of rigid rods it equals 2. On the other hand, increasing compactness of polymer molecules, which occurs in cases of chain branching, is usually characterized by decreasing values of exponent  $a$ , reaching zero for the extreme case of compact spheres.

Since the probability of branching also increases with polymer chain length, it is often found that experimental MHS plots of randomly branched polydisperse macromolecules exhibit curvature,<sup>193, 200</sup> i. e., evenly decreasing slopes (exponent  $a$ ) with molecular weight, exactly as it was found in this work for polymers of Group A of Table 4.1 (see Figure 4.8).

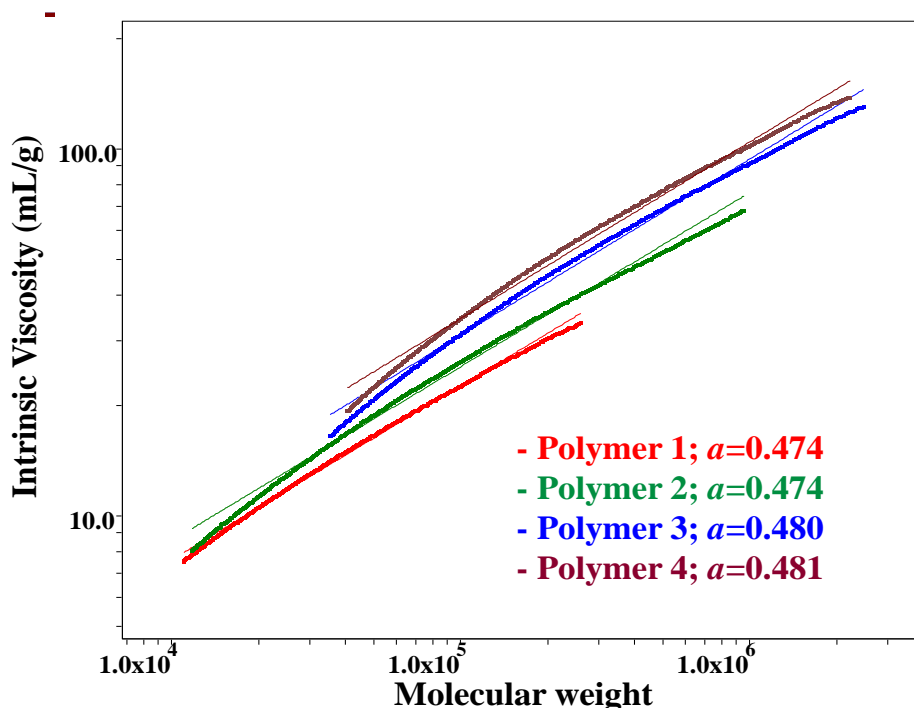


Figure 4.8. Mark-Houwink-Sakurada plots of DiPhS-containing terpolymers of Group A of Table 4.1.

Results of the SEC-MALS-Vis analysis of polymers of targeted  $DP=160$  prepared by varying the [DiViEB]/[TMAS] ratio (see Tables 3.2 and 4.2) further supported the <sup>29</sup>Si NMR findings on the increase of the extent of these polymers' branching occurring with the increase of the silanolate initiator concentration (Figure 4.3, Table 4.4). Gradual appearance and increase in shoulders size at lower retention times (as TMAS concentration increased) on SEC traces representing refractive index detector responses in Figure 4.9, indicate formation of new polymer species of distinctly larger molecular sizes (hydrodynamic volumes). Consequently, molecular weight distribution gradually

broadened from PDI of 1.48 for polymer 2a to 7.46 for polymer 2e, prepared with the lowest and the highest concentration of TMAS, respectively (see Table 4.2). MALS detection, which is more sensitive to the presence of high molecular weight species, showed dramatic shifts of the entire SEC peaks towards lower retention times as branching intensified (Figure 4.10). Most of the  $M_w$  versus retention time curves (displayed in the same figure) decreased monotonically with increasing retention time, in a manner typical for SEC separation. The curve for polymer 2e, however, showed strong upturn at higher retention time, caused by abnormal elution that is typically observed for some highly branched polymers and often called the anchoring effect.<sup>193, 194</sup> This effect occurs when particular parts of large branched molecules start behaving as separate particles/molecules, penetrate pores of SEC columns packing and anchor the entire molecule, delaying its elution to higher retention times than those corresponding to their hydrodynamic volumes. Hence, delayed elution should be expected for highly branched polymer 2e, in which branching occurred at almost every other DiPhS unit, as determined by <sup>29</sup>Si NMR analysis and shown in Table 4.5.

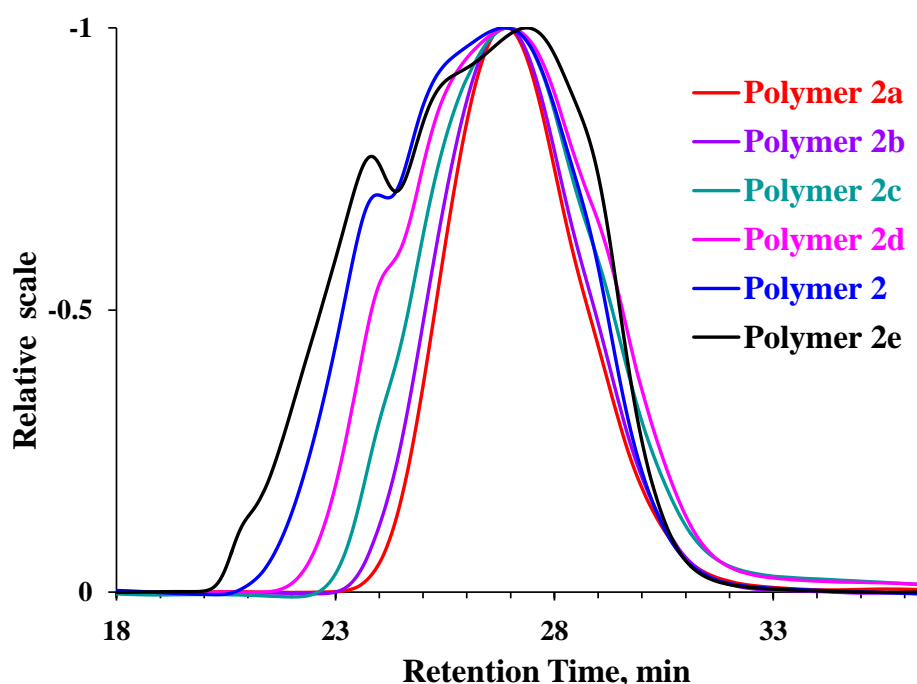


Figure 4.9. SEC-MALS chromatograms (refractive index detector) of DiPhS-containing terpolymers of Table 4.2 (with targeted  $DP=160$ ) as prepared using different concentrations of TMAS initiator.



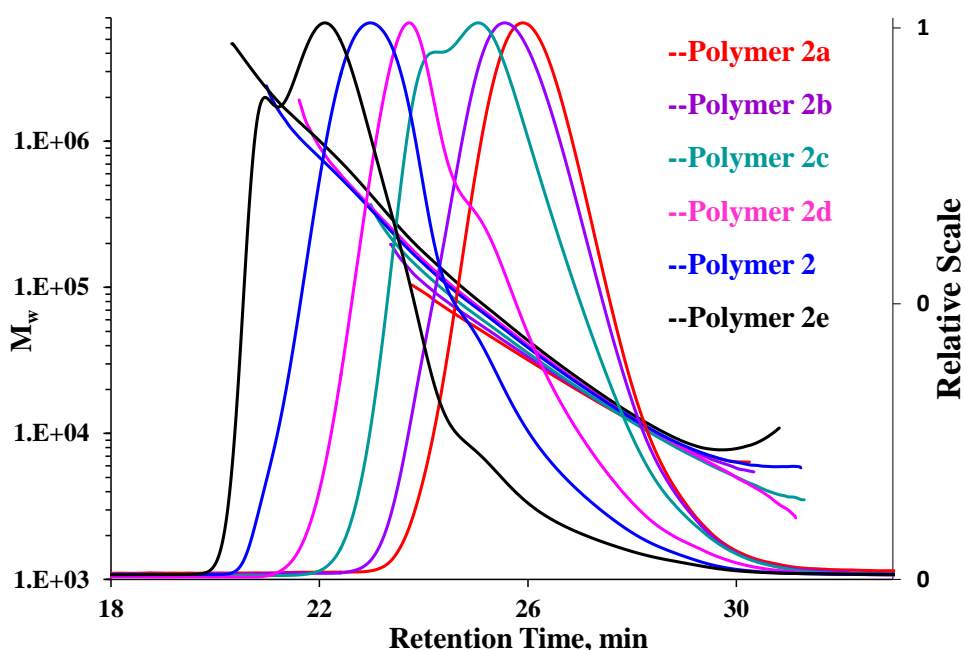


Figure 4.10.  $M_w$  vs. retention time traces superimposed with SEC signals from MALS detector for DiPhS-containing terpolymers of Table 4.2 (targeted  $DP=160$ ) as prepared using different concentrations of TMAS initiator.

MHS plots of this series of DiPhS-containing terpolymers of targeted  $DP=160$  provided further insight into the changes in polymer architecture affected by the silanolate concentration. It can be seen from Figure 4.11 that a 20-fold increase in silanolate initiator concentration (see Table 3.2) for polymer 2e relative to polymer 2a, caused a dramatic drop in the slopes of MHS plots (exponent  $a$  in the MHS equation) from 0.676, characteristic for linear, flexible molecules to 0.444, indicative of increased compactness of polymer molecules due to branching.

The absence of shoulders in SEC traces of polymers 2a and 2b, low polydispersity, as well as the values for the exponent  $a$  of MHS equation are in agreement with the findings of  $^{29}\text{Si}$  NMR analysis that linearity of DiPhS-containing terpolysiloxanes is fully preserved at the low levels of silanolate initiator concentration used for preparation of these two polymers.

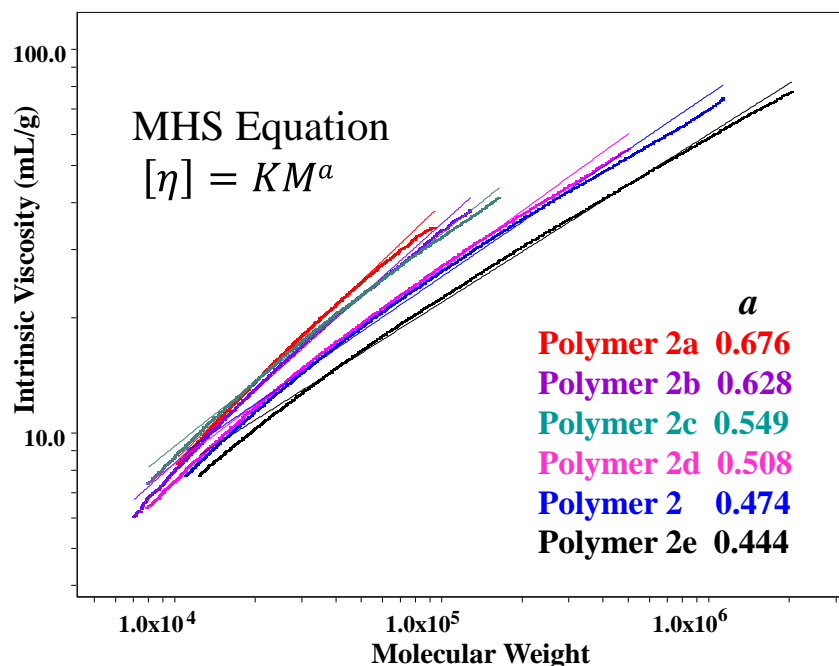


Figure 4.11. Mark-Houwink-Sakurada plots for DiPhS-containing terpolysiloxane series with targeted  $DP=160$  as prepared using different concentrations of TMAS initiator.

### 4.3 DiEtS-Containing Polymers

#### 4.3.1 Evaluation of DiEtS Monomers

Several earlier studies have shown that amorphous polysiloxanes with highly improved low temperature flexibilities can be obtained if diethylsiloxy-, DiEtS, units are incorporated into PDMS chains in relative amounts ranging from rather low (ca. 5 mol %) <sup>201</sup> to very high (ca. 50 mol %). <sup>181</sup> Therefore, three series of DiEtS-containing terpolymers were prepared as shown in Table 3.1, using three different sources of DiEtS units:

- hexaethylcyclotrisiloxane,  $D_3^{Et_2}$ , for Group B polymers
- octaethylcyclotetrasiloxane,  $D_4^{Et_2}$ , for Group C polymers, and
- DiEtS "hydrolyzate", a commercial mixture of  $D_3^{Et_2}$ ,  $D_4^{Et_2}$  and  $D_5^{Et_2}$  cyclic siloxanes, and a linear polydiethylsiloxane, PDES, of a moderately high molecular weight (ca. 17,000), for group D polymers.

Within each group, targeted degrees of polymerization were similar to those for the DiPhS-containing polymers of Group A.

Composition of the commercial DiEtS "hydrolyzate" was determined using  $^{29}\text{Si}$  NMR and SEC in THF, as shown in Figure 4.12. It contained about 30 wt. % of linear fraction with an average degree of polymerization of ca. 170, and about 70 wt. % of cyclics (predominantly  $\text{D}_4^{\text{Et}_2}$ , then  $\text{D}_5^{\text{Et}_2}$  and trace amounts of  $\text{D}_3^{\text{Et}_2}$ ).

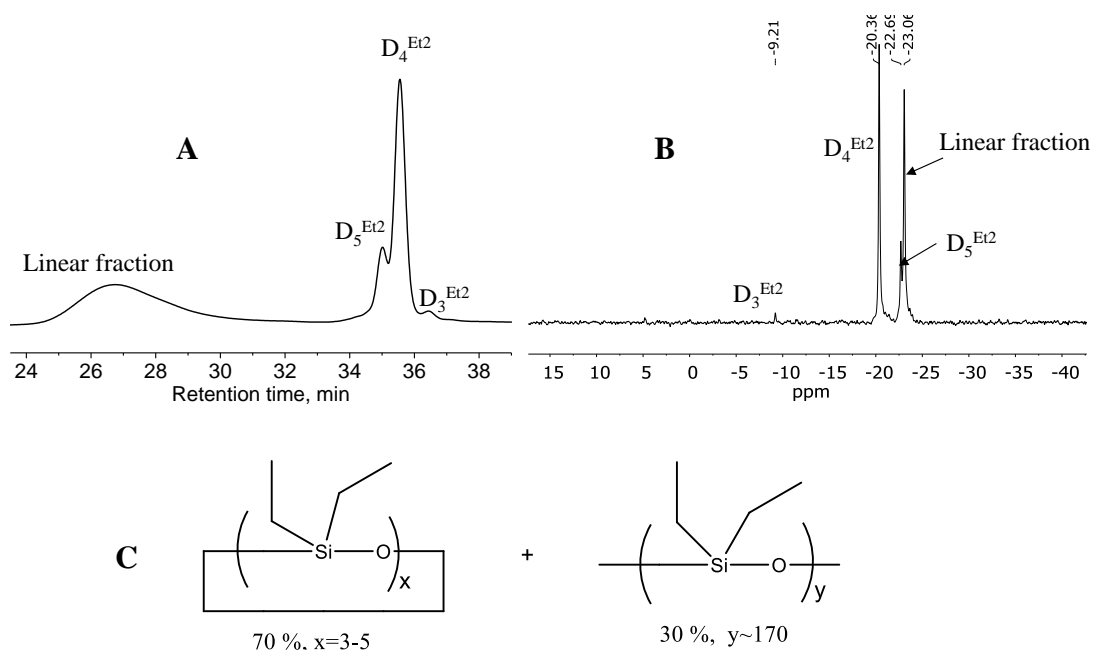


Figure 4.12. SEC chromatogram (A),  $^{29}\text{Si}$  NMR (B) and estimated composition (C) of DiEtS "hydrolyzate" (a name usually given to mixtures of linear and cyclic siloxanes obtained by hydrolysis of the corresponding dichlorosilanes).

### 4.3.2 Suppression of Low-Temperature Crystallization in DiEtS-Containing Polymers

Differential scanning calorimetry, DSC, clearly demonstrated that relative content of DiEtS units was important for suppression of these terpolymers' crystallization, and that its minimum required value was ca. 5 mol %. The use of lower amounts of DiEtS repeat units seemed to affect (i.e., reduce) the extent of these polymers' crystallization and shift the melting temperature to somewhat lower values, as judged by a significantly reduced melting peak observed for the Polymer 8a, prepared with 3.6 mol % of DiEtS units from

$D_3^{Et_2}$  monomer (shown in Figure 4.13). In all cases of Group B and C polymers prepared from pure  $D_3^{Et_2}$  and  $D_4^{Et_2}$  cyclics, respectively, the use of a minimum of 5 mol % of DiEtS units in the mixture of cyclic siloxanes was necessary to completely suppress crystallization in resulting polymers (see Figure 4.14). With this composition, all of these polymers showed no crystallization peaks within the investigated  $DP$  range of 80 to 600, clearly suggesting that DiEtS units were bulky enough and properly distributed along the polymer chains to effectively disrupt their regularity of packing into well ordered crystalline domains.

However, an attempt to prevent crystallization in polymers of Group D by using DiEtS "hydrolyzate" as a reagent failed, in all cases in which the targeted polymer  $DP$  was higher than 200 (see Figure 4.15).

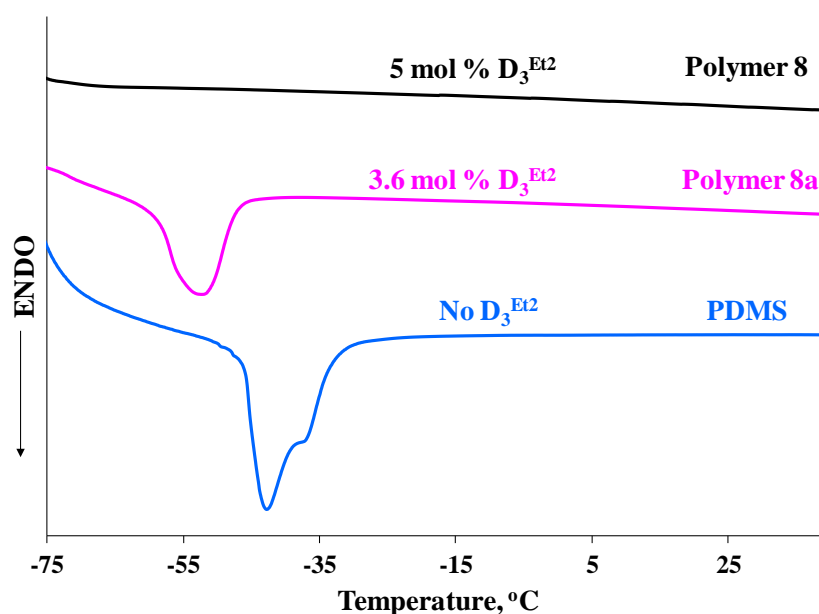


Figure 4.13. DSC thermograms of DiEtS-containing polymers with  $DP = 600$  prepared with indicated amounts of DiEtS units from cyclic trimer,  $D_3^{Et_2}$ .

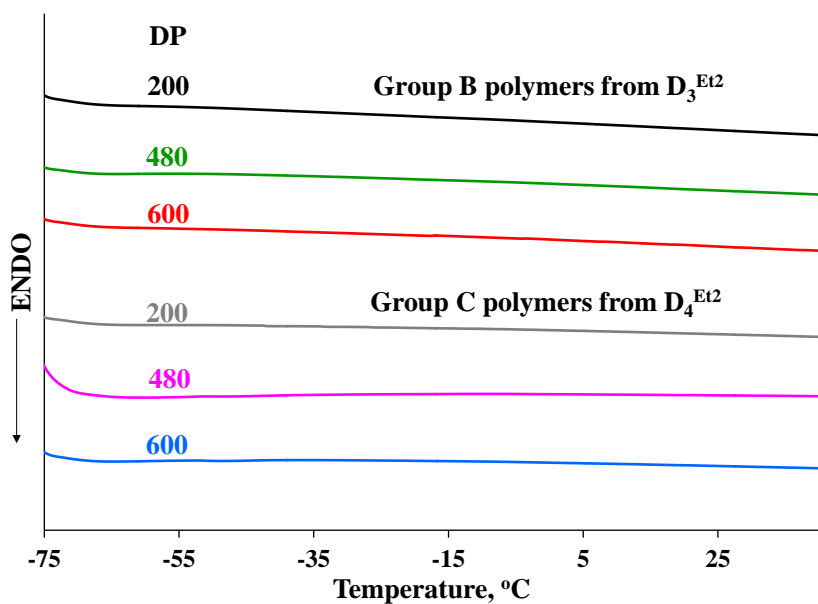


Figure 4.14. DSC thermograms of Group B and C polymers prepared with 5 mol % of DiEtS units.

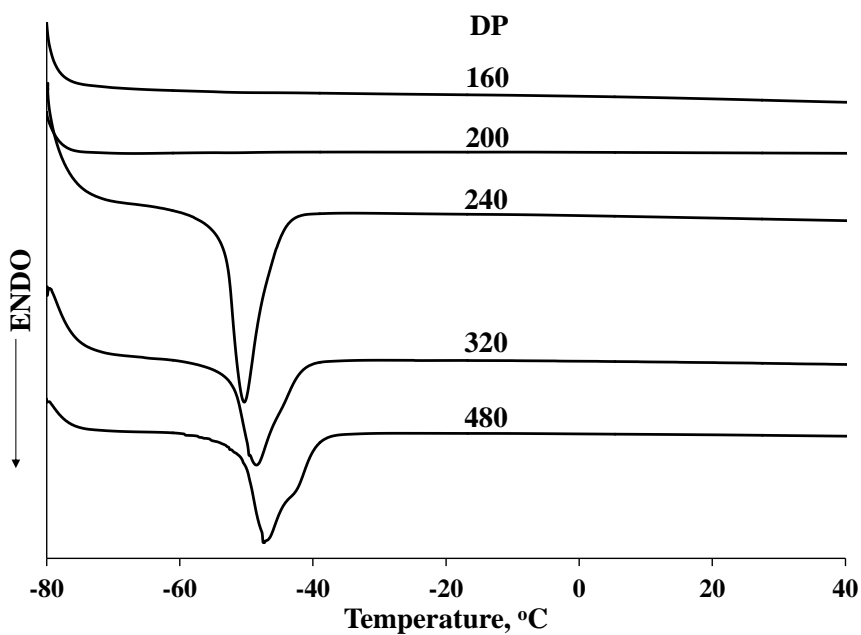


Figure 4.15. DSC thermograms of Group D polymers prepared from DiEtS "hydrolyzate".

$^{29}\text{Si}$  NMR spectra of DiEtS-containing polymers of Groups B and C of Table 4.1 showed a major signal at  $-22$  ppm assigned to silicons from DiMeS units, and, like for polymers of Group A, small signal at  $-4.1$  ppm from silicons from terminal DiMeViS end-groups. Expectedly, the last mentioned signals decreased in intensity with polymer *DP*, as shown in Figure 4.16. It should be particularly noted that there was no indication in  $^{29}\text{Si}$  NMR spectra of any branching in any of the examined samples. Such branching would be expected to show at  $-67$  ppm.

In contrast to this, however,  $^{29}\text{Si}$  NMR of DiEtS-containing terpolymers prepared from DiEtS "hydrolyzate" revealed presence of longer polydiethylsiloxane, PDES, blocks (see Figure 4.17, signals at  $-23$  ppm), indicating that linear PDES fraction of the "hydrolyzate" (see Figure 4.12 C) did not effectively participate in equilibration reactions involving the forming terpolymer chains. This reduced effectiveness of incorporation and random (statistical) distribution of single DiEtS units into the resulting polymer products also reduced the effectiveness of these units in inhibiting the obtained terpolymer crystallization (see Figure 4.15).

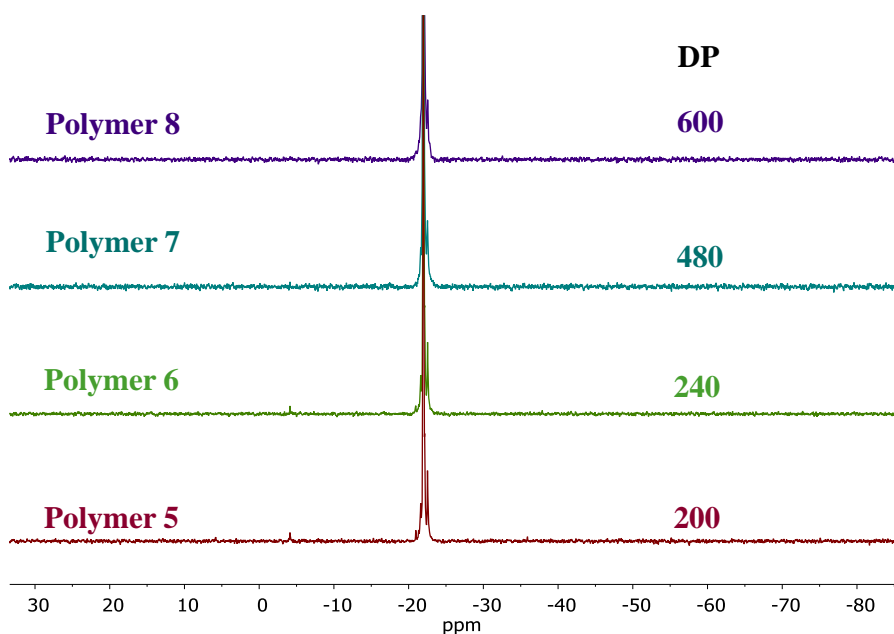


Figure 4.16.  $^{29}\text{Si}$  NMR spectra of Group B terpolymers of indicated DPs.

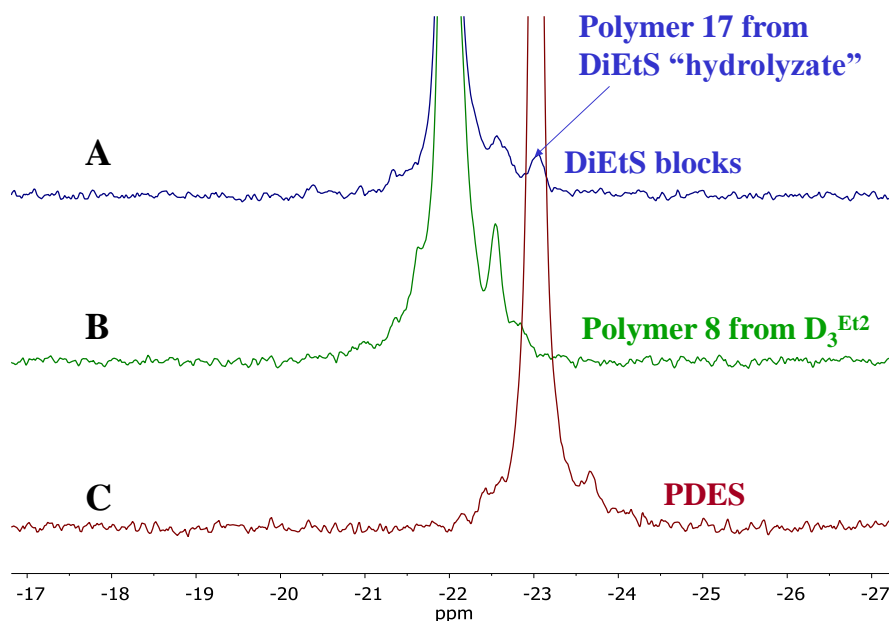


Figure 4.17.  $^{29}\text{Si}$  NMR spectra of DiEtS-containing terpolymers of Table 4.1 prepared from DiEtS "hydrolyzate" (A),  $\text{D}_3^{\text{Et}2}$  (B) and polydiethylsiloxane, PDES, prepared from  $\text{D}_3^{\text{Et}2}$  (C).

### 4.3.3 Molecular Weight Distribution and Conformation of DiEtS-Containing Polymers

SEC-MALS-Vis analysis (see examples for polymers 3, 7, 11 and 17 of Table 4.1 with targeted  $DP$  values of 480, shown in Figure 4.18) indicated that all DiEtS-containing polymers (7, 11 and 17) had simple molecular weight distributions with polydispersity indices ranging between 1.5 and 2, typical for fully equilibrated linear polysiloxanes. SEC traces of all these polymers overlapped almost perfectly with one another, and were free of shoulders at high molecular weight sides (low elution times), in clear contrast to their DiPhS-substituted, branched analogues of Figure 4.7 (with the curve of Polymer 3 shown in Figure 4.18 again, for comparison).

The MHS plots of these DiEtS-containing terpolymers further supported that they were free of branching, having MHS  $a$  values ranging from 0.63 to 0.67 (see Table 4.1), typical for random coils of linear polymers in a thermodynamically good solvent, as shown in Figure 4.19.

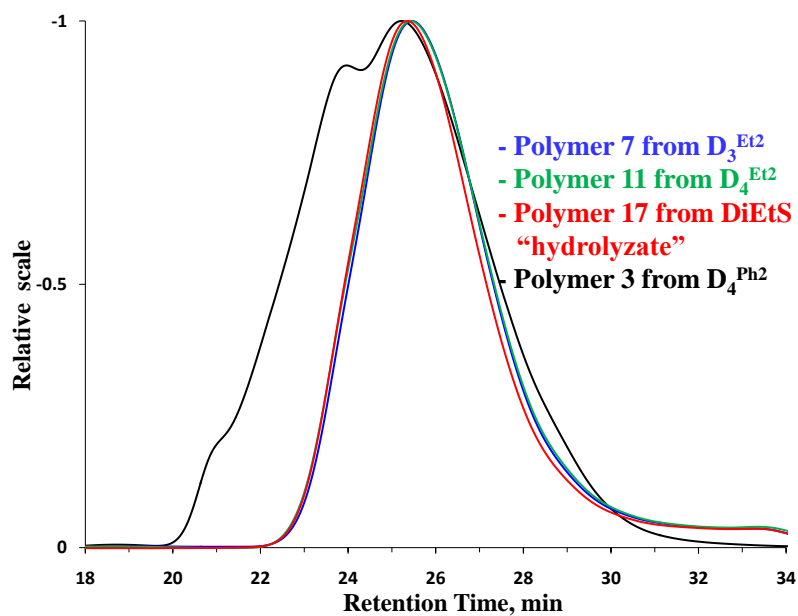


Figure 4.18. SEC-MALS chromatograms (refractive index detector) of DiEtS-containing terpolymers from  $D_3^{Et2}$ ,  $D_4^{Et2}$  and DiEtS "hydrolyzate" targeted for  $DP=480$ , overlaid with SEC chromatogram of the DiPhS-containing analogue 3.

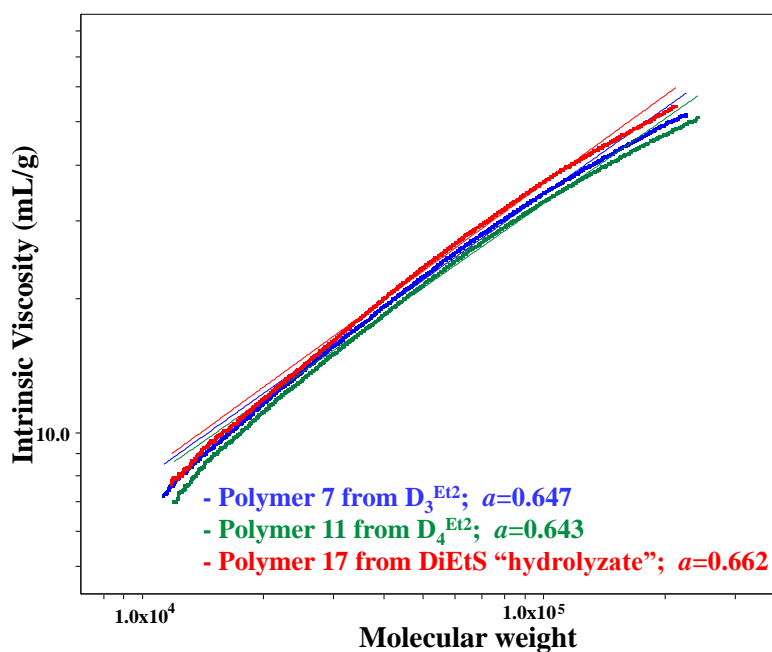


Figure 4.19. Mark-Houwink-Sakurada plots for DiEtS-containing polymers from  $D_3^{Et2}$ ,  $D_4^{Et2}$  and DiEtS "hydrolyzate" targeted for  $DP=480$  of Figure 4.18.



#### **4.4 Monitoring of the Course of the Ring Opening Polymerization of Cyclic Siloxanes during Preparation of Vinylsilyl-Terminated $\alpha,\omega$ -Telechelic Terpolysiloxanes**

In order to better understand the reasons for observed configuration and property changes of terpolysiloxanes described in the preceding sections, the courses of occurrence of their polymerizations were investigated in more details.

##### **4.4.1 Polymerization Systems**

Three polymerization systems: a 3.6 mol % DiPhS-containing terpolymer A, a 5 mol % DiEtS-containing terpolymer B and “pure” PDMS polymer C of Table 3.7, were evaluated for the course of their reaction occurrences. Polymers A and B were selected as representatives of their respective Groups A and B-D of Table 4.1, while PDMS (Polymer C) was used as a standard for comparison. In addition to the two main copolymerizing monomers ( $D_4 + D_4^{\text{Ph}2}$  and  $D_4 + D_3^{\text{Et}2}$ ), Systems A and B also contained  $D_4^{\text{MeVi}}$ , albeit in only very small amounts of 0.3 mol % each, while in the third, System C, pure  $D_4$  was homopolymerized for comparison. In both Systems A and B,  $D_4^{\text{MeVi}}$  did not appear to exert any influence on the course of polymerizations, so for simplicity, it is consciously omitted from the nomenclature used in the following sections, and the following notation was adopted: System A:  $D_4 + D_4^{\text{Ph}2}$ ; System B:  $D_4 + D_3^{\text{Et}2}$ ; and System C: pure  $D_4$ . In all three systems, the targeted degrees of polymerization ( $DP_t$ ) were the same (600).

##### **4.4.2 Monitoring Polymerization Reactions by SEC with Toluene as Eluent**

Polymerizations of Reaction Scheme 4.1 in three investigated systems (A, B and C) were first monitored by SEC, using toluene as eluent, in accordance with standard practices in the chromatography of DiMeS-containing polymers and cyclic monomers, and the results obtained are shown in Table 4.6. and Figure 4.20.

Table 4.6. SEC-MALS-Vis characterization of polymer fraction of samples taken at indicated reaction times during the polymerizations of cyclic siloxanes in Systems A ( $D_4 + D_4^{Ph2}$ ), B ( $D_4 + D_3^{Et2}$ ) and C ( $D_4$ ).

Polymerization System	Reaction time, min	dn/dc <sup>a</sup> , mL/g	$M_w$ , g/mol	$M_n$ , g/mol	$M_p$ <sup>b</sup> , g/mol	PDI <sup>c</sup>	$[\eta]$ <sup>d</sup> , mL/g	$R_h$ <sup>e</sup> , nm	$R_z$ <sup>f</sup> , nm
<b>A</b> $D_4 + D_4^{Ph2}$	30	-0.071	23,100	16,400	22,500	1.40			
	40	-0.066	58,500	38,900	55,100	1.50	29.4	6.2	9.3
	50	-0.066	72,000	46,500	63,000	1.55	29.7	6.8	10.6
	65	-0.066	70,300	40,200	62,200	1.75	29.2	6.6	10.4
	80	-0.066	71,200	41,300	62,500	1.72	29.5	6.6	10.5
	110	-0.065	73,300	43,400	63,200	1.69	29.4	6.7	10.5
	140	-0.066	73,200	41,100	64,400	1.78	29.3	6.7	10.8
	200	-0.067	70,900	41,200	61,100	1.72	29.7	6.7	10.6
<b>B</b> $D_4 + D_3^{Et2}$	5	-0.093	55,900	37,500	55,900	1.49	30.9	6.3	9.6
	12	-0.091	59,900	40,300	59,000	1.49	31.3	6.5	9.8
	20	-0.089	64,600	43,500	62,100	1.49	31.9	6.7	10.1
	30	-0.087	64,700	43,000	63,000	1.50	30.6	6.6	10.1
	45	-0.087	63,700	42,500	62,200	1.50	30.5	6.5	9.7
	60	-0.087	62,400	39,200	62,500	1.59	29.1	6.4	9.9
	90	-0.085	63,200	42,700	62,200	1.48	29.2	6.4	9.6
	120	-0.084	64,600	43,600	63,000	1.48	28.7	6.4	9.3
	300	-0.084	64,900	43,500	63,400	1.49	28.4	6.4	9.5
	420	-0.084	65,100	44,100	62,700	1.48	28.8	6.5	9.4
<b>C</b> $D_4$	5	-0.093	50,600	33,600	50,600	1.51	25.3	5.7	8.4
	20	-0.091	57,500	38,700	55,000	1.49	27.4	6.1	9.2
	30	-0.090	57,200	38,100	55,600	1.50	26.6	6.1	9.1
	45	-0.090	58,200	38,900	56,300	1.50	26.9	6.0	9.1
	60	-0.092	57,100	38,000	54,800	1.50	27.1	6.1	9.1
	90	-0.090	58,300	38,600	56,700	1.51	26.5	6.0	9.0
	120	-0.091	58,400	39,000	56,300	1.50	27.1	6.1	9.3
	200	-0.091	58,700	39,700	56,100	1.48	27.2	6.1	9.2
	300	-0.091	59,100	40,200	56,600	1.47	27.3	6.1	9.2

<sup>a</sup> dn/dc was determined online, using 100 % mass recovery.

<sup>b</sup> $M_p$ : peak molecular weight

<sup>c</sup>PDI: polydispersity index;  $PDI = M_w/M_n$ .

<sup>d</sup>  $[\eta]$ : intrinsic viscosity as determined by Visco Star II online detector.

<sup>e</sup> $R_h$ : hydrodynamic radius.

<sup>f</sup> $R_z$ : root-mean square radius (RMS radius)

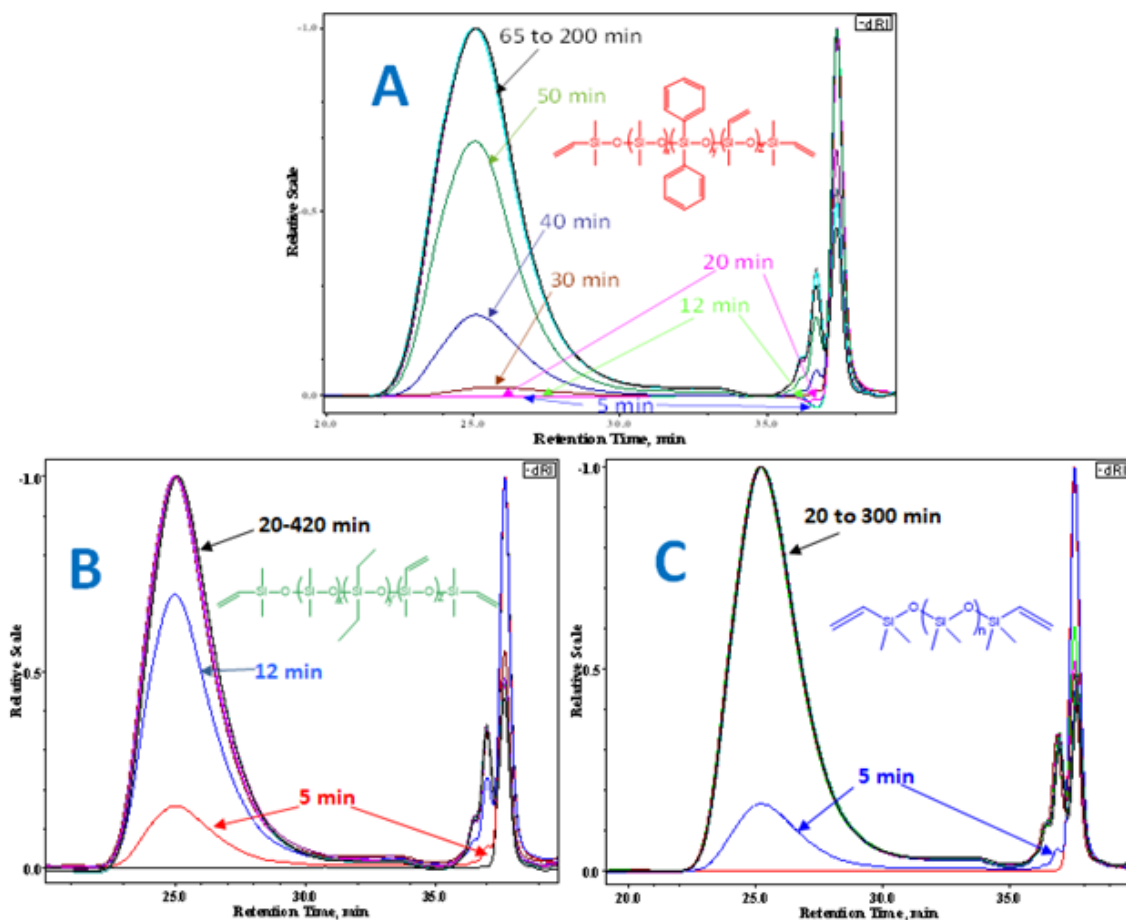


Figure 4.20. SEC chromatograms of samples of polymerization reaction mixtures of Systems A, B and C, at indicated reaction times. Eluent: toluene.

All three systems showed similar main features, as it can be seen from Figure 4.20: very intense, sharp signals from reacting cyclic monomers at 37-38 min retention times, broad and intense signals from growing polymers at 22-30 min retention times, and small multiplet signals from oligomeric cyclic siloxanes that were formed during the course of the reactions at 35.5-38 min retention times. While in the homopolymer System C and in the DiEtS-containing copolymer System B, the first appearance of both polymer signals and the reaction-formed oligomeric cyclics was clearly evident from the very beginning of the reaction process (see chromatograms of the first samples taken after only 5 min of the reaction time), in the DiPhS-containing System A it took about 30 min of the reaction time before these signals evolved and could be clearly seen. In addition, as shown in Figure 4.21, while molecular weights ( $M_w$  and  $M_n$ ) of the polymers formed in Systems B

and C quickly reached targeted values and subsequently did not change throughout the remaining courses of the respective reactions, it took over 50 min of the reaction time for the same to happen in System A.

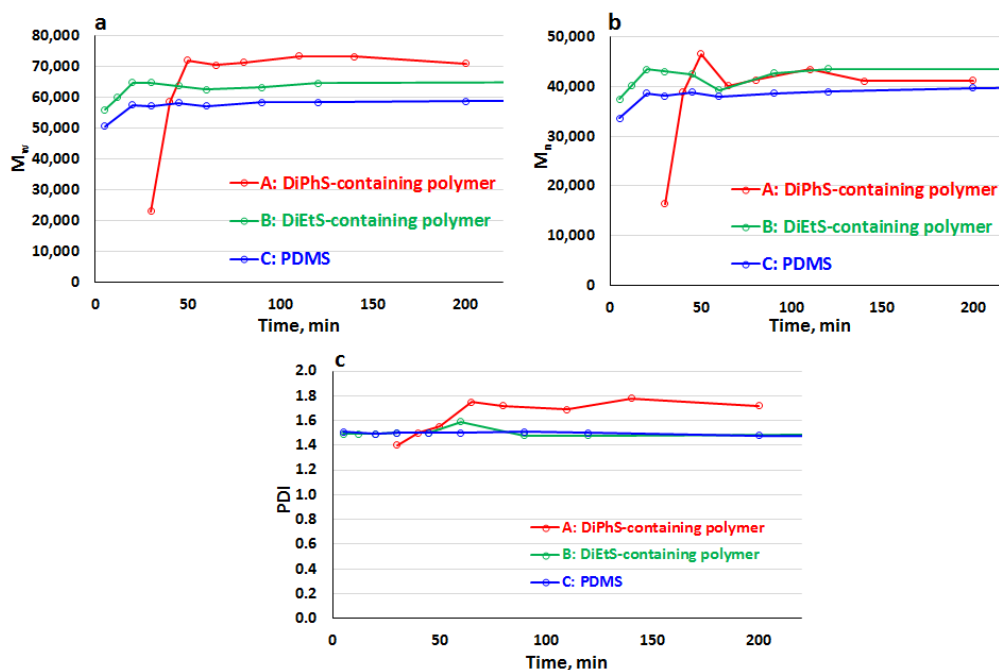


Figure 4.21. Weight-average (a), number-average (b), molecular weights and polydispersity index, PDI (c) of polymers formed in the three examined polymerization systems, as a function of the reaction time.

Comparison of  $M_w$  vs. reaction time plots for three polymerization systems of Figure 4.21a showed that plateau (equilibrium) values of  $M_w$ s had expected trend – the increase from PDMS to DiPhS-containing polymer, as comonomers with bulkier side groups were introduced into the polymer chains. On the other hand,  $M_n$  vs. reaction time plot for DiPhS-containing polymer in Figure 4.21b seemed to deviate from this trend in the plateau region by reaching the  $M_n$  values similar to those of DiEtS-containing polymer of System B. Equilibrated DiPhS-containing polymer of System A had broader molecular weight distribution (PDI around 1.75) than polymers of Systems B and C (PDI around 1.50) as shown in Figure 4.21c. The broadening of the MWD of polymer of System A relative to those of the other two systems could be a consequence of the occurrence of

chain branching through desilylation, described in detail in the previous sections of this dissertation. Additional possible source of polydispersity increase of DiPhS-containing polymer could be a slight enhancement of the rate of randomization (chain transfer) during which dimethylsilylanolate active centers easily attack electrophilic Si atoms on DiPhS sites, splitting the polymer chains.<sup>32</sup>

#### 4.4.3 Monitoring Polymerization Reactions by TGA

While TGA is a widely used analytical tool for characterization of polymer thermal and thermo-oxidative stabilities, it is not often used to monitor polymerization reactions. However, for siloxane polymerizations it is quite helpful because it can distinguish between small volatile cyclics and larger, more thermally stable, open-chain linear polymers that are both present in the same samples. The results obtained with dynamic TGA in nitrogen taken at various indicated stages of polymerizations in Systems A-C, are shown in Figure 4.22.

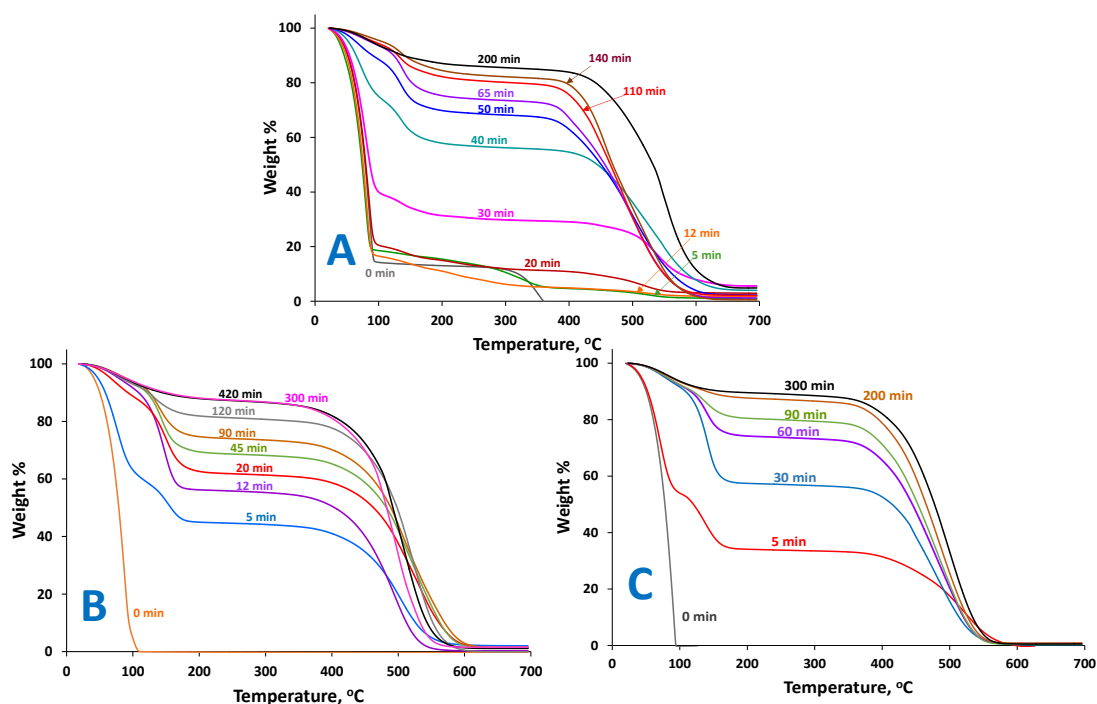


Figure 4.22. TGA traces of samples of the polymerization reaction mixtures of Systems A, B and C at indicated reaction times.

The TGA traces of reaction mixture samples from all three polymerization Systems (A - C), showed two distinctly different types of behavior in two temperature ranges. At temperatures below 170 °C, sharp drops in mass were observed, corresponding to evaporation of low boiling point components (monomers and reaction-formed higher cyclics), while flat, constant mass plateaus appeared at higher temperatures. These plateaus, which extended to about 400 °C, are typical for dynamic TGA patterns of high molecular weight PDMS with no left-over initiator from the polymerization reaction.<sup>13, 14, 202</sup> This distinction enabled a simple and easy determination of the relative amounts of cyclic and linear components (polymer yield) present in the samples of the reaction mixtures taken at indicated reaction times as shown in Figure 4.23.

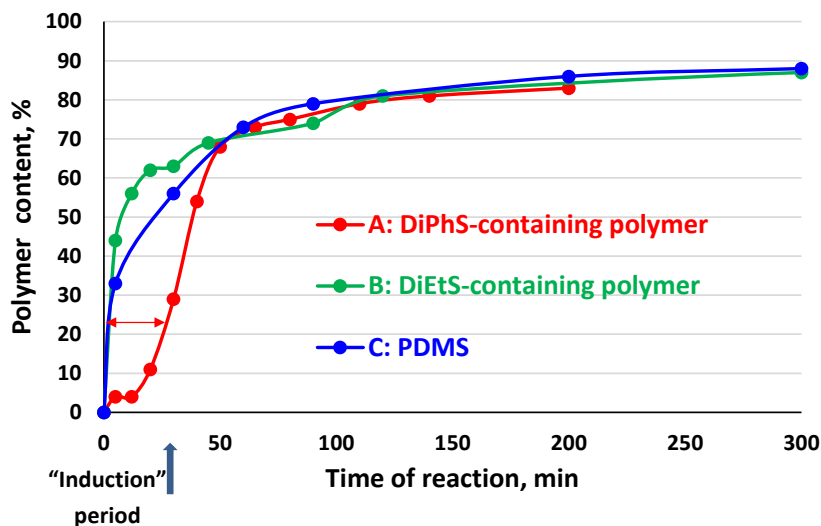


Figure 4.23. Formation of linear polymer products in the three polymerization systems examined in this work as a function of the reaction time (as determined by TGA).

It can be seen from this figure that while Systems B and C behaved similarly to one another, System A behaved differently (consistent with SEC in toluene; compare with Figures 4.20 and 4.22). While in the former two systems, a substantial yield of the linear polymer products (ca. 40 wt. %) was obtained after only 5 min of the reaction times, it took about 20 min for only 10 wt. % polymer yield to be achieved in System A, and more than 30 min for it to reach the 40 wt. % value. Furthermore, comparison of the data, shown

in Figure 4.23, revealed that while Systems B and C behaved in a practically identical manner, a distinct "induction period" for polymer formation was found in System A. This "induction period" lasted for about 30-40 min of the reaction time, and only after it was completed, did the reaction in System A "take off" in a manner identical to those in Systems B and C (compare slopes of three curves in Figure 4.23). Nevertheless, System A "caught up" with Systems B and C after about 60 min of the reaction time, and from that point on, all three systems behaved in a nearly identical manner.

#### **4.4.4 Physical Appearance of the Reaction Mixture of System A**

The "induction period" in DiPhS-containing polymerization System A, which delayed early buildup of both polymer yield and molecular weight (compare Figures 4.21 and 4.23), coincided with an important change that occurred in the physical state of its reaction mixture. Namely, the first thing one notices when performing copolymerization of  $D_4$  and  $D_4^{Ph2}$  cyclic siloxanes shown in Reaction Scheme 4.1, is the heterogeneous nature of the polymerization system at the very beginning of the process (see Figure 4.24, 0 min). The  $D_4^{Ph2}$  monomer is poorly soluble in the reaction mixture containing mostly  $D_4$  (with smaller amounts of TMAS and DiViEB) at reaction temperature of 105 °C used in this work (maximum reported solubility of  $D_4^{Ph2}$  in  $D_4$  is 4.53 g/100 g at 160 °C, <sup>203</sup>), and even small amounts of  $D_4^{Ph2}$  that were employed (3.6 mol %) still remained floating as insoluble solid in the liquid reaction mixture, as shown in Figure 4.24 by the photo taken at 0 min of the reaction time. This heterogeneity lasted for about 30 min of the reaction time, during which the solid slowly and gradually disappeared ("dissolved"), and the reaction mixture eventually became homogeneous, clear and transparent (see the 30 min photo in Figure 4.24). At that point, viscosity of the reaction mixture significantly increased, and continuing vigorous stirring resulted in entrapment of gas bubbles in the viscous liquid and the reaction mixture changed to turbid and cloudy (see last two photos on the right in Figure 4.24).

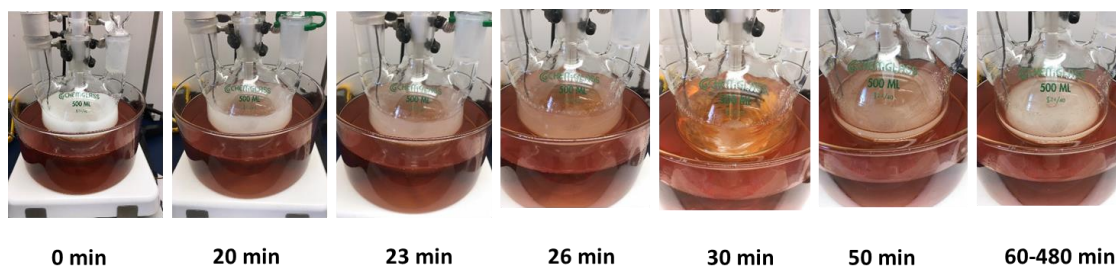


Figure 4.24: Changes in the physical appearance of the reaction mixture of System A as a function of reaction time.

In contrast to this, the  $D_3^{Et2}$  cyclic monomer is completely soluble in its  $D_4$  counterpart (at least at the relative amounts of two monomers used in this work), and in all preparations of System B the reaction mixtures remained homogeneous and transparent, one-phase liquids throughout the entire course of the polymerization processes.

#### 4.4.5 Monitoring of the Polymerization in System A by SEC using THF as Eluent

In an attempt to further understand the behavior of System A, the course of its polymerization was once again evaluated by SEC, only this time using THF instead of toluene as the eluent. This was done in order to separate the signals from two reacting cyclic monomers ( $D_4$  and  $D_4^{Ph2}$ ) sufficiently to enable their individual monitoring as the reaction progressed. Namely, since refractive index of  $D_4$  is very similar to that of THF (i.e., 1.396 vs 1.407 at 20 °C), but very different from that of toluene (1.496), in SEC traces of samples of polymerization System A taken in toluene, the very intense  $D_4$  signals overwhelmed those of  $D_4^{Ph2}$ , (this reaction mixture contained 96 mol % of  $D_4$  and only 3.6 mol % of  $D_4^{Ph2}$ ), while in THF they were subdued enough to allow convenient detection of both. This can be easily seen from Figure 4.25, which should be contrasted with chromatograms shown in Figure 4.20. At the same time, signals from the growing polymer and from the reaction-formed higher oligomer cyclics could also be either clearly discerned, or deconvoluted from the corresponding multiplets to enable simple and practical following of not only the yields of these reaction products, but also the increase in the growing polymer molecular weight (see Figure 4.25).



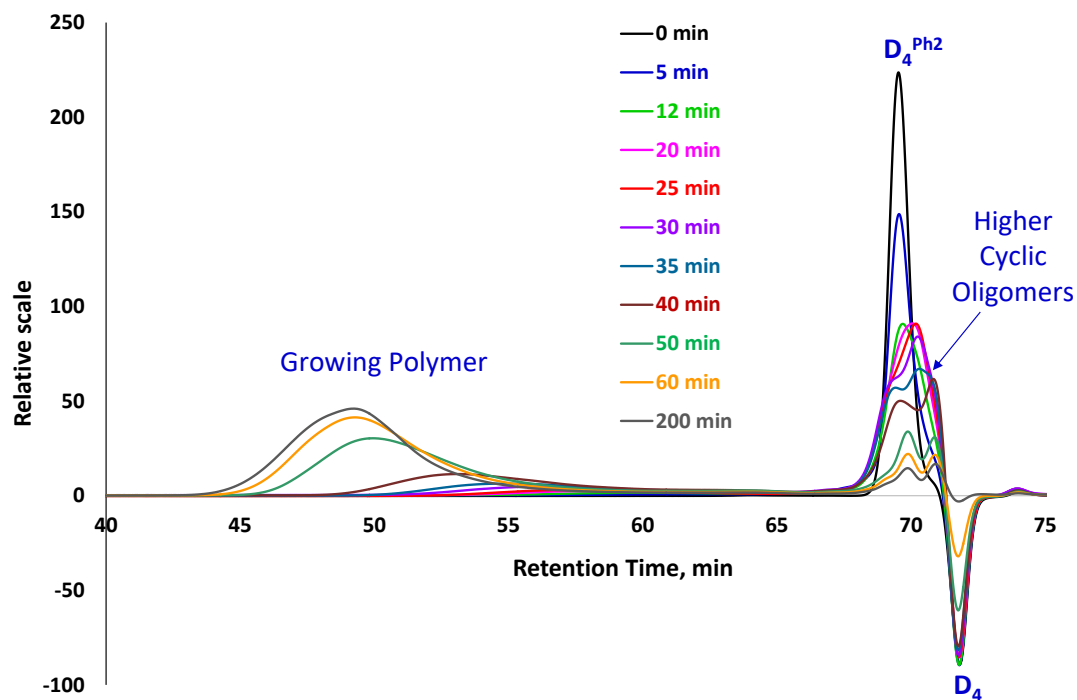


Figure 4.25. SEC chromatograms of samples of the polymerization reaction mixture of System A at indicated reaction times. Eluent: THF. The "0 min" sample was taken before addition of TMAS initiator.

Based on these data, Figures 4.26-4.28 show relative rates of the disappearance of two monomers from the reaction mixture from integration of areas of  $D_4^{\text{Ph}2}$  and  $D_4$  SEC signals obtained by deconvolution of the cyclic oligomers region of Figure 4.25 (as they were incorporated into the growing polymer chains), and the corresponding rate of polymer formation (yield) (Figure 4.29). It can be seen from Figure 4.26 that during the first 30-40 min of the reaction time (i.e., during the "induction period"), it was almost exclusively  $D_4^{\text{Ph}2}$  that polymerized, so that approximately 80 % of this monomer was used up and incorporated into the polymer product, compared to only ca. 20 % of  $D_4$  (blue arrows in Figures 4.26 and 4.27). This was in good agreement with the well-known, significantly higher reactivity of  $D_4^{\text{Ph}2}$  (than  $D_4$ ) toward dimethylsilanolates,<sup>203-205</sup> which results from the more pronounced electrophilicity of  $D_4^{\text{Ph}2}$  silicons compared to their counterparts in  $D_4$ .

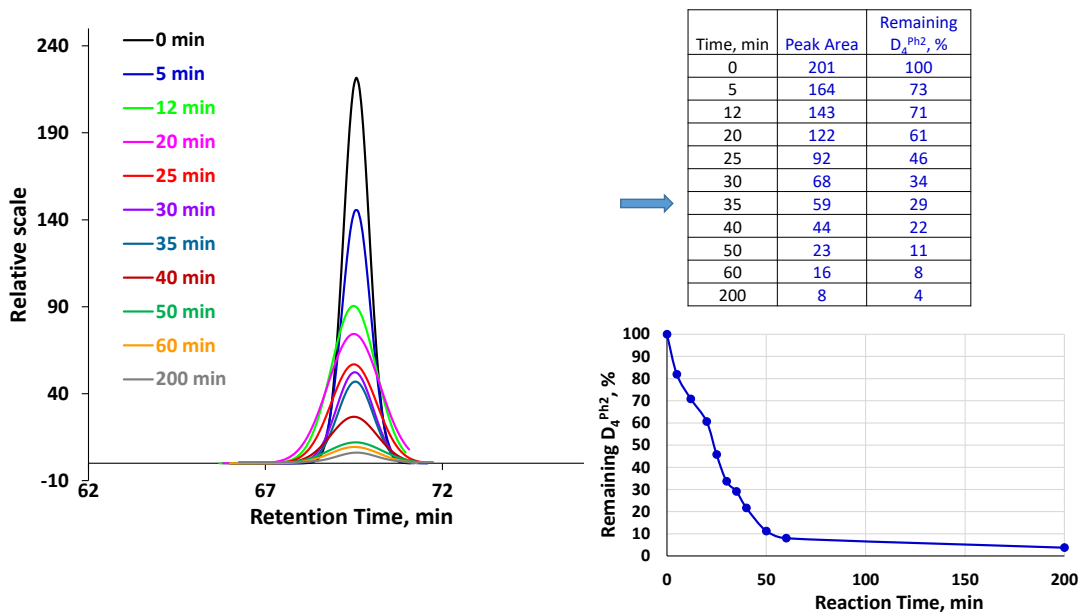


Figure 4.26. Disappearance of D<sub>4</sub><sup>Ph<sub>2</sub></sup> during the polymerization in System A., Eluent: THF.

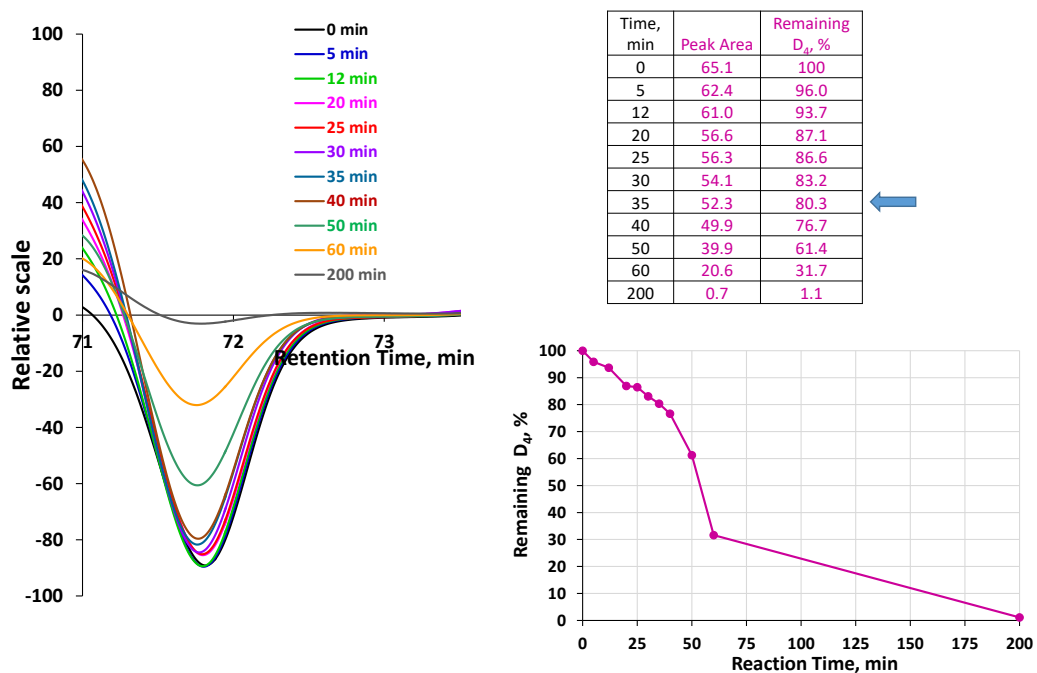


Figure 4.27. Disappearance of D<sub>4</sub> during the polymerization in System A. Eluent: THF.

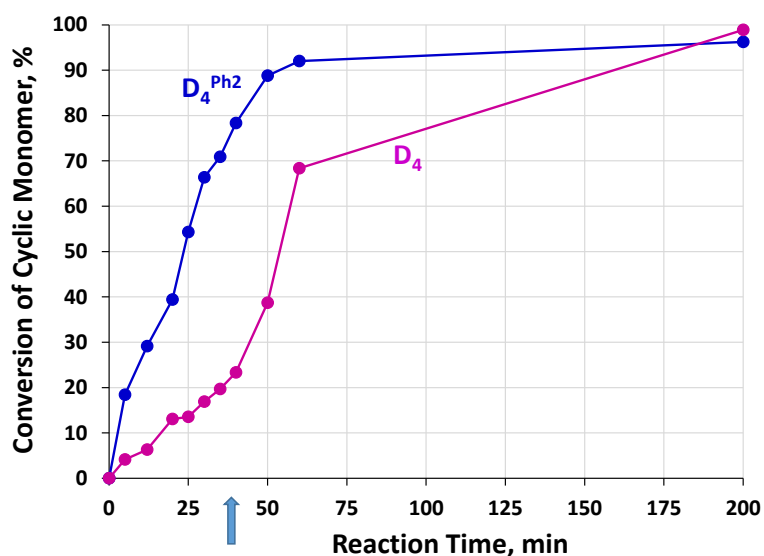


Figure 4.28. Comparison of the conversion rates of  $D_4^{\text{Ph}_2}$  and  $D_4$  during polymerization in System A, from data of Figures 4.26 and 4.27. Eluent: THF.

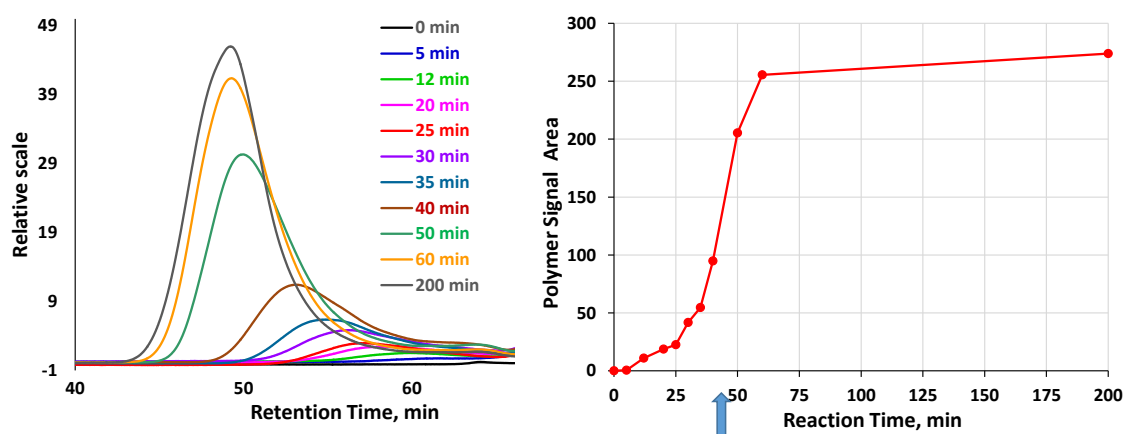


Figure 4.29. Yield of the growing polymer in polymerization in System A, as a function of reaction time; from SEC signals at 44-65 min of the retention time of Figure 4.25.

Eluent: THF.

It follows from these data that during the "induction period" in System A, the TMAS silanolate initiator preferred to react with  $D_4^{\text{Ph}_2}$  monomer, and only after this stage was over, did  $D_4$  "take over" (since it became the predominantly remaining reagent in the

reaction mixture), and the polymerization accelerated to become similar to homopolymerization of pure D<sub>4</sub> in System C (compare Figures 4.21 and 4.23).

#### 4.4.6 Monitoring of the Polymerization Reactions by <sup>29</sup>Si NMR

To complement the above described SEC and TGA data, <sup>29</sup>Si NMR was further applied to the monitoring of the three investigated reaction systems. Figure 4.30 shows the DiMeS (a) and DiPhS (b) spectral regions for samples of the reaction mixture of System A taken at indicated reaction times. It can be seen from Figure 4.30a, that during the "induction period" (until about 30 min of the reaction time), no substantial change in the intensity of DiMeS signals from D<sub>4</sub> monomer (at -19.3 ppm) could be seen, with barely detectable signals from DiMeS units being incorporated into the growing polymer chains (observable at -22 ppm only with 20X magnification, as shown in the inset to Figure 4.30a). However, once the "induction period" was over, the DiMeS signals from D<sub>4</sub> monomer rather quickly decreased in intensity and almost disappeared (see spectrum after 50 min of the reaction time), while the signal from the DiMeS units being incorporated into the polymer chains quickly increased to its maximum intensity.

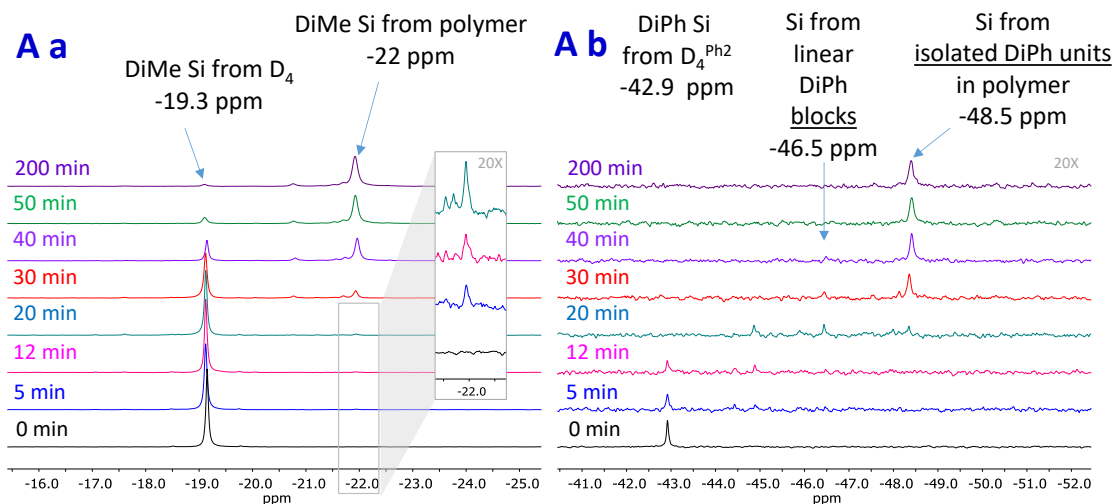


Figure 4.30. DiMeS (a) and DiPhS (b) regions of <sup>29</sup>Si NMR spectra of the samples of the polymerization reaction mixture of System A, taken at indicated reaction times.

In the DiPhS spectral region, on the other hand, rapid disappearance of  $D_4^{\text{Ph}_2}$  signals could be seen at  $-42.9$  ppm (completely eliminated from the spectra at about 20 min of the reaction time), accompanied by the simultaneous appearance of a signal at  $-46.5$  ppm, characteristic for open chain, blocky, DiPhS structures.<sup>118</sup> The latter dominated this spectral range until about 40 min of the reaction time, although from about 20 min on, a new signal at  $-48.5$  ppm (characteristic for single DiPhS units separated by extended DiMeS segments) notably appeared, and increased in intensity through the end of the process.

A similar analysis of Systems B and C (Figure 4.31), showed that these two systems behaved identically to one another, yet dramatically differently from System A (consistent with both SEC and TGA data described above). In both of these systems, DiMeS signals from  $D_4$  (at  $-19$  ppm) disappeared quickly (in less than 20 min of the reaction time), and signals from DiMeS units incorporated into the growing polymer species appeared already in the first reaction mixture samples, taken after only 5 min of the reaction time. This was also consistent with SEC and TGA data described above, confirming again that copolymerization of  $D_4$  and  $D_3^{\text{Et}_2}$  in System B occurred practically identically to the homopolymerization of  $D_4$  in System C, and indicating that reactivity of  $D_3^{\text{Et}_2}$  toward tetramethylammonium silanolates was identical or at least very similar to that of  $D_4$ .

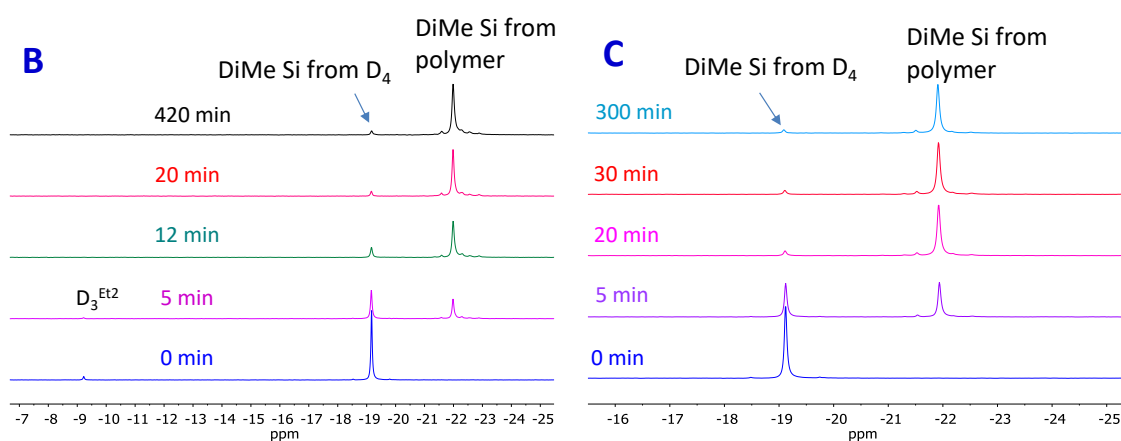
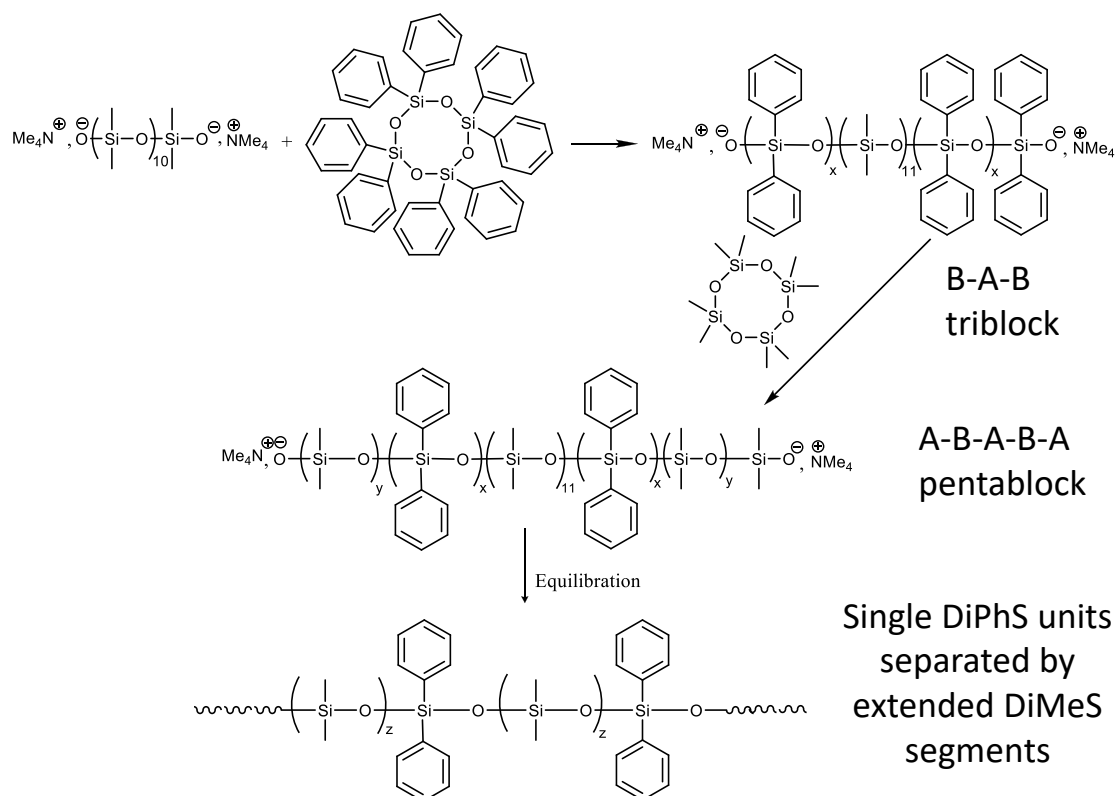


Figure 4.31.  $^{29}\text{Si}$  NMR spectra of samples of the polymerization reaction mixtures of systems B ( $D_4 + D_3^{\text{Et}_2}$ ) and C ( $D_4$ ), respectively, taken at indicated reaction times.

#### 4.4.7 Mechanism of Dimethylsilanolate-Initiated Copolymerization of D<sub>4</sub> and D<sub>4</sub><sup>Ph2</sup>

Based on the results described in Sections 4.4.2-4.4.6, the following reaction mechanism for the copolymerization of D<sub>4</sub> and D<sub>4</sub><sup>Ph2</sup> initiated by a dimethylsilanolate such as the oligodimethylsiloxy- tetramethylammonium disilanolate, TMAS, used in this work can be proposed:



Reaction Scheme 4.6. Three-step mechanism of dimethylsilanolate-initiated copolymerization of D<sub>4</sub> and D<sub>4</sub><sup>Ph2</sup>.

During the first stage of this complex process, the "induction period", the initiating dimethylsilanolate anions preferentially react with D<sub>4</sub><sup>Ph2</sup> monomer, incorporating four DiPhS units into the growing polymer chains each time the reaction occurs. This is limited, however, to a fraction of D<sub>4</sub><sup>Ph2</sup> monomer that is at any given instant dissolved in the liquid reaction mixture, with its relative amount being determined by the limited solubility of D<sub>4</sub><sup>Ph2</sup> in D<sub>4</sub> at the selected reaction temperature. As the dissolved D<sub>4</sub><sup>Ph2</sup> undergoes ROP, equivalent amount of this monomer is supplanted from its yet

undissolved solid phase, which floats in the liquid reaction mixture, steadily decreasing as the process unfolds. For System A described in this work (i.e., 3.6 mol % of  $D_4^{\text{Ph}_2}$ ), this took about 30-40 min to complete at reaction temperature of 105 °C.

As a consequence of significantly higher reactivity of  $D_4^{\text{Ph}_2}$  toward silanolate anions compared to that of  $D_4$ , mostly  $D_4^{\text{Ph}_2}$  polymerizes during the "induction period", to initially create B-A-B triblock [diphenylsiloxy]-[dimethylsiloxy]-[diphenylsiloxy] species with the DP of block A corresponding to the DP of TMAS dimethyldisilanolate initiator used (ca. 11 in this work; see experimental Section 3.4), and convert the TMAS active chain-ends from dimethylsilanolates to diphenylsilanolates. Although less nucleophilic, the latter are still more reactive toward  $D_4^{\text{Ph}_2}$  than toward  $D_4$ , continuing the triblock formation until the content of  $D_4^{\text{Ph}_2}$  in the reaction mixture was greatly diminished. However, due to a very low concentration of dissolved  $D_4^{\text{Ph}_2}$  in the monomer feed of System A during the "induction" period, there was also a finite probability for some  $D_4$  to incorporate into the B blocks of B-A-B triblock species being formed (see Figures 4.27 and inset to 4.30a), so that the composition of B blocks should be understood as rich in DiPhS units but not completely free of DiMeS ones.

Once most of  $D_4^{\text{Ph}_2}$  is consumed by ROP (at least 80 % of it, as judged by SEC in THF data of Figure 4.28),  $D_4$  starts to polymerize in the manner identical to its homopolymerization in System C, or copolymerization with  $D_3^{\text{Et}_2}$  in System B (as  $D_3^{\text{Et}_2}$  appears to react very similarly to  $D_4$  under these reaction conditions). As a consequence, the triblocks convert at this stage into A-B-A-B-A pentablock species, where A end-blocks are now created by ROP of  $D_4$  after the "induction period" is over (while the center A block originates from TMAS initiator).

In parallel with the above described ROP, however, siloxane equilibration reaction also takes place in all three reaction systems, but it is significantly slower than ROP, and its effects become visible only in the later stages of the process in System A. It enables every silanolate species present in the reaction system to react with every siloxane bond, resulting, after hundreds of minutes of the reaction time, in an observable redistribution of DiPhS blocks (formed during the "induction period"), into individual DiPhS repeat units separated by extended DiMeS segments. The lengths of these segments, i.e., the relative molar concentration of individual DiPhS units in the resulting polymer chains,

depend on the composition of the starting reaction mixture, and in the case of System A described in this work they correspond to a 3.6 mol % content of DiPhS. It should be noted, however, that this relatively small concentration of DiPhS repeat units in the resulting polymers is not only sufficient enough to completely prevent crystallization of the obtained products (otherwise characteristic for pure PDMS) (see Figure 4.1), but it also results in a significant and characteristic chain-branching (see Figures 4.2 and 4.3 and Reaction Scheme 4.2).<sup>189</sup> The reason for this branching<sup>189</sup> and herein described "induction period" in System A, appears to be one and the same: the significantly higher electrophilicity of  $D_4^{Ph2}$  silicons relative to those of their  $D_4$  counterpart, which causes higher reactivity of both  $D_4^{Ph2}$  cyclics and in-chain DiPhS units toward dimethylsilanolates.<sup>190</sup>

#### 4.5 MePhS-Containing Terpolymers

As above described analysis of branching in DiPhS-containing terpolysiloxanes (see Sections 4.2) demonstrated and experiments with model, Ph-T-branched PDMS confirmed, desilylation of Reaction Scheme 4.2 *did not* proceed beyond the Ph-T-branch stage, i.e., by splitting the second Ph group from the DiPhS units. This indicates that attachment of the third dimethylsiloxy- segment to the Ph-T-branched silicons decreased their electrophilicity enough to become comparable to that of their DiMeS counterparts, thus eliminating the driving force for further desilylation to occur. Based on these results, it was postulated that methylphenylsiloxy-containing terpolymers with MePhS units (an idealized Ph-T-branch analogues), purposely imbedded into these polymers' structures to begin with, may not be susceptible to nucleophilic attacks by dimethylsilanolates at all, and may remain resistant to branching observed in the DiPhS-containing polymers, retaining a perfectly linear chain configuration. An interesting question also arose whether or not introduction of MePhS repeat units would also prevent the PDMS-like crystallization in these polymers, particularly at the Ph-content level similar to that of their DiPhS-containing counterparts.

In order to test this hypothesis and crystallization behavior of such polymers, polymerization of Reaction Scheme 4.1, in which  $D_4^{Ph2}$  monomer was replaced with its  $D_4^{MePh}$  counterpart, was examined and the obtained MePhS-containing copolymers were



evaluated by SEC, DSC and  $^{29}\text{Si}$  NMR. Furthermore, the course of polymerization was monitored for selected MePhS-containing system and the results were compared with those described DiPhS analogue in Section 4.4.

To accomplish this, two dimethylvinylsilyl-terminated telechelic terpolysiloxanes, 18 and 19, of the general formula  $[\text{DiMe}_x\text{MePh}_y\text{MeVi}_z]$ , where  $x$ ,  $y$ , and  $z$  represent relative molar contents of DiMeS, MePhS and MeViS repeat units, were prepared as shown in Reaction Scheme 4.1. Their DPs were targeted at 600 (controlled by the amount of DiViEB end-blocker added), as shown in Table 3.3, and the relative amounts of MePhS units were targeted at 3.6 and 7.2 mol %, respectively. The determined properties of the obtained polymers 18 and 19 are shown in Table 4.3.

SEC-MALS-VIS analysis of these polymers showed expected values for their molecular weights, with chromatograms having clean monomodal distributions and PDIs of 1.6, typical for linear equilibrated polysiloxanes (see Figure 4.32). Additionally, molecular weight vs. retention time plots were monotonically decreasing without any indication of abnormal elution from SEC columns, which would typically occur if there was any branching.<sup>194, 206</sup>

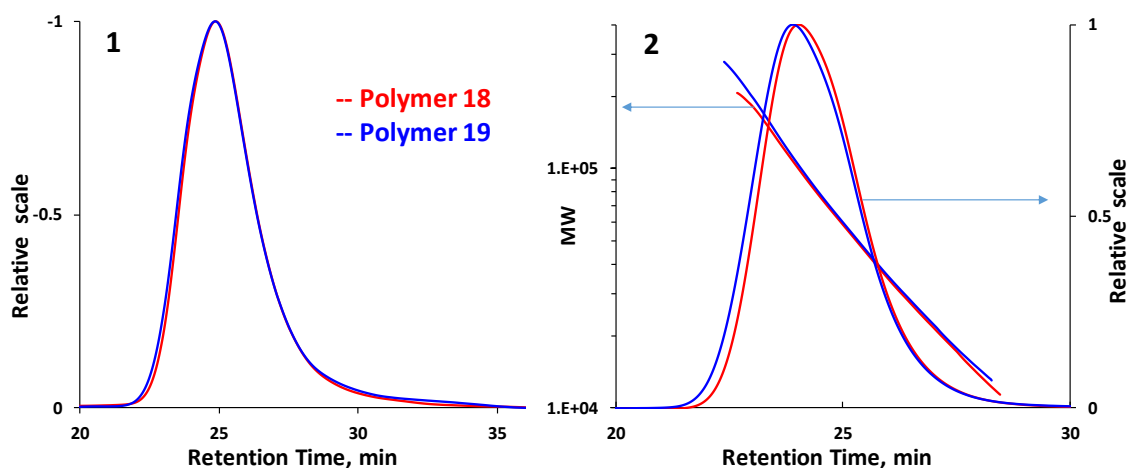


Figure 4.32. SEC data: differential refractometer, **1**, and MALS detector, **2**, responses for MePhS-containing polymers 18 and 19. Eluent: toluene.

The Mark-Houwink-Sakurada (MHS) plots, obtained from combined multiangle light-scattering and viscometry detection responses (Figure 4.33), gave in both cases identical values for exponent  $a$  of the respective MHS equations of 0.69, also typical for flexible linear polymers in a thermodynamically good solvent.<sup>200, 206</sup>

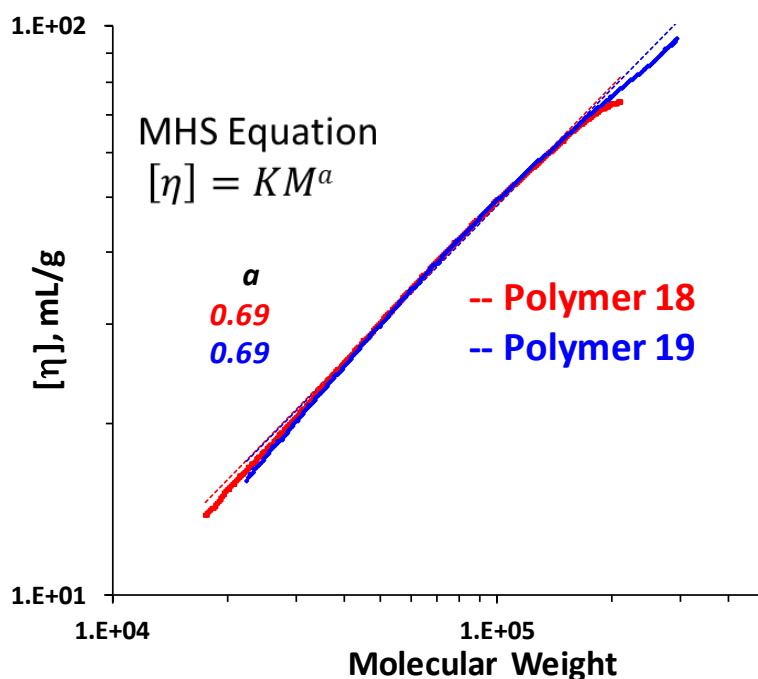


Figure 4.33. Mark-Houwink-Sakurada plots for MePhS-containing polymers 18 and 19.  
 Eluent: toluene.

The composition of MePhS-containing copolymers 18 and 19 was calculated from relative intensities of  $^1\text{H}$  NMR signals (Figure 4.34) assigned to protons from methyl (0.1 – 0.4 ppm),  $I(\text{H}_{\text{Me}})$ , and phenyl (7.3 - 7.7 ppm),  $I(\text{H}_{\text{Ph}})$ , substituents,<sup>182</sup> to be 3.9 and 7.8 mol %, respectively. Calculation protocol involved determination of molar contributions  $n(\text{DiMeS})$  and  $n(\text{MePhS})$  of the respective repeat units from Equations 4.2 and 4.3:

$$I(\text{H}_{\text{Me}}) = 6 n(\text{DiMeS}) + 3 n(\text{MePhS}) \quad (4.2)$$

$$I(\text{H}_{\text{Ph}}) = 5 n(\text{MePhS}) \quad (4.3)$$

from which molar percentages of DiMeS units (x) and MePhS units (y) were determined as:

$$x = 100 n(\text{DiMeS}) / (n(\text{DiMeS}) + n(\text{MePhS})) \quad (4.3)$$

and

$$y = 100 - x \quad (4.4)$$

The fact that these values were slightly higher than the content of these units in the respective reaction mixtures (see Table 3.3) is consistent with the higher reactivity of  $\text{D}_4^{\text{MePh}}$  cyclics (relative to  $\text{D}_4$ ) in the silanolate-initiated ROP copolymerization of these monomers.<sup>187</sup>

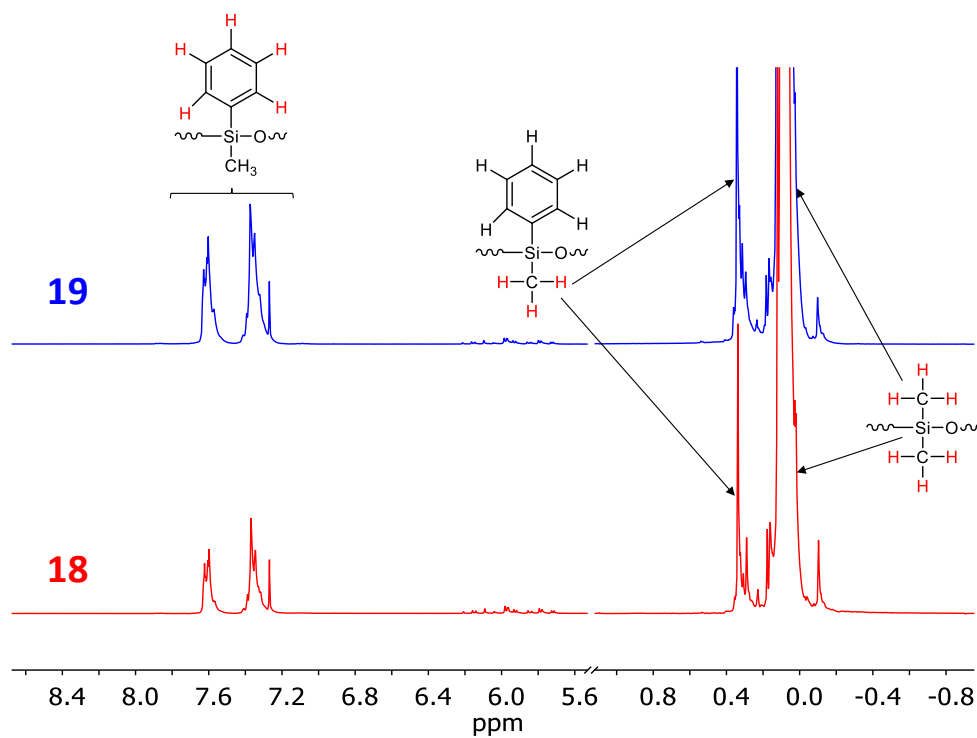


Figure 4.34.  $^1\text{H}$  NMR spectra of MePhS-containing polymers 18 and 19.

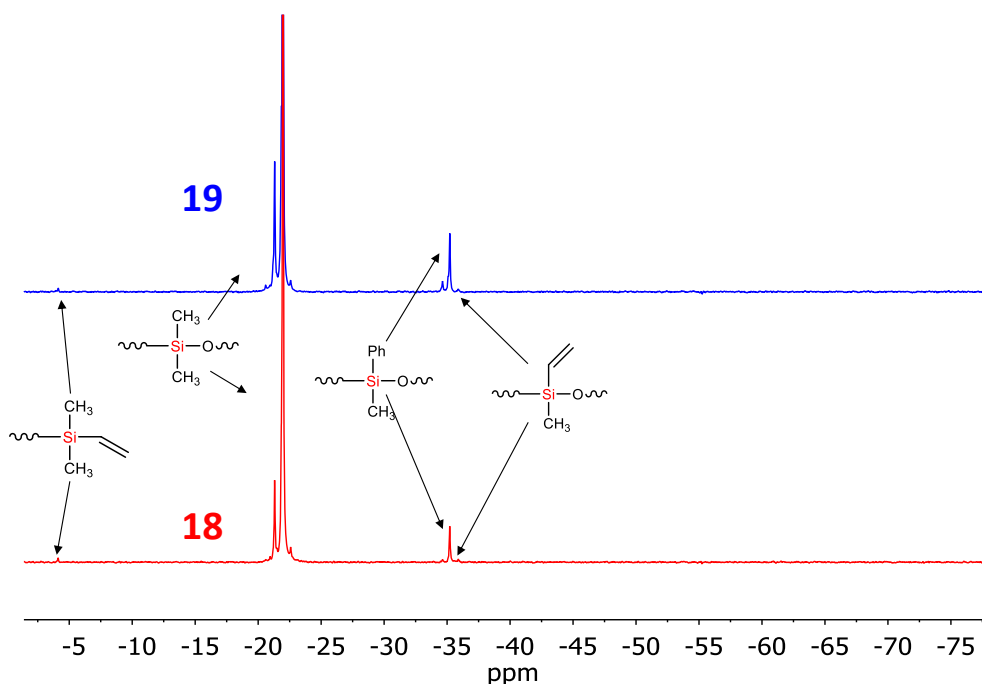
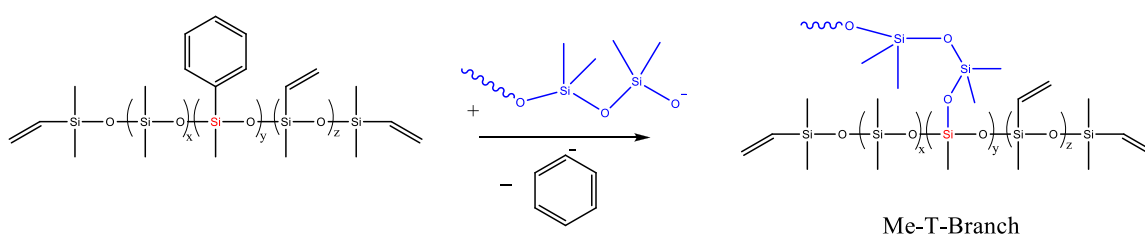


Figure 4.35.  $^{29}\text{Si}$  NMR spectra of MePhS-containing polymers 18 (3.9 mol % MePhS) and 19 (7.8 mol % MePhS).

Analysis of both polymers by a high resolution  $^{29}\text{Si}$  NMR (see Figure 4.35) was performed using the following assignments for the respective structural units: DiMeS:  $-22$  ppm, terminal DiMeViS end-groups:  $-4.1$  ppm, MePhS:  $-35.2$  ppm, and MeViS:  $-35.9$  ppm.<sup>182, 197, 198, 207</sup> If desilylation of these polymers' Si-C<sub>Ar</sub> side-bonds was occurring during their syntheses (as in the case of the cleavage of the first Ph group from DiPhS units shown in Scheme 4.2), the cleavage of the phenyl groups from MePhS-containing polymers would be expected to occur as shown in Scheme 4.7, and the formation of Me-T-branches would be expected to be revealed by a signal appearing at around  $-66$  ppm.<sup>182, 197, 198</sup>



Reaction Scheme 4.7. Possible mechanism of branching in MePhS-containing terpolysiloxanes.

However, as it can be seen from Figure 4.35, there was no indication of any such signal in the spectra of the two evaluated MePhS-containing polysiloxanes, which clearly suggested an apparent resistance of these polymers to desilylation by a nucleophilic attack of dimethylsilanolate, and reconfirmed the linear structure of the resulting products, in agreement with the above described SEC data. This insensitivity of Si-C<sub>Ar</sub> bonds in MePhS units to reaction with dimethylsilanolate can be explained as a consequence of an indistinguishable difference in relative electrophilicities of these silicons and their DiMeS counterparts. As a result, there is no driving force for desilylation reaction observed with the first Ph group of their DiPhS derivatives (shown in Section 4.2) to occur.<sup>189</sup>

DSC analysis of MePhS-containing terpolysiloxanes 18 and 19 showed no evidence of melting transitions (see Figure 4.36) which, for unsubstituted PDMS, is typically seen between -50 and -40 °C.<sup>13, 156, 161, 177, 208</sup> While it has been known that the replacement of 7.5-15 mol % of DiMeS repeat units with MePhS ones leads to complete elimination of PDMS-like crystallization,<sup>175</sup> it was interesting to find out in this work that even as low content as 3.9 mol % of MePhS units (see Table 4.3), was sufficient to achieve the same result.

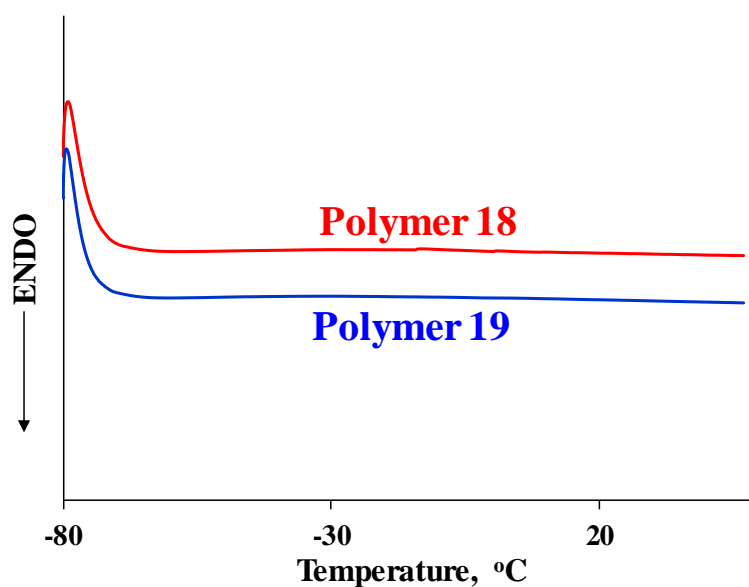


Figure 4.36. DSC thermograms of MePhS-containing polysiloxane terpolymers 18 (3.9 mol % MePhS) and 19 (7.8 mol % MePhS).

#### 4.5.1 Microstructural Analysis of MePhS-Containing Terpolymers

In order to gain deeper understanding of structure-properties relationship of MePhS-containing terpolymers, particularly the fact that such low concentration of MePhS repeat units in these siloxane terpolymers was effective enough to completely prevent their crystallization, high resolution  $^{29}\text{Si}$  NMR was employed to analyze their repeat units sequence distribution using a simple-linkage-probability method (described in detail in Section 2.7 of this work).<sup>184, 183, 185</sup> Neglecting the very small number of MeViS repeat units, for Polymers 18 and 19, the experimental run numbers for their DiMeS sequences were calculated from:

$$R_{exp} = k_{DiMeS} X_{DiMeS} \quad (4.1)$$

where  $X_{DiMeS}$  denotes the molar percent of DiMeS units in the respective polymer, and  $k_{DiMeS}$  is a variable containing information on the ratio of triad signal intensities:

$$k_{DiMeS} = 2 - 2 \sqrt{\frac{F_0}{\sum_{i=0}^2 F_i}} \quad (4.2)$$

where  $F_0$  is the integral of the signal for dominant (DiMeS)<sub>3</sub> triad, and  $F_i$  is the integral of the  $i$ -th signal of a triad with  $i$  being the number of the nearest neighbor monomer units of the second (i.e., MePhS) species.

The average run number for a statistically random polymer, such as those expected to be produced by equilibration of cyclic siloxanes of this work, is given by:

$$R_{random} = \frac{X_{DiMeS} X_{MePhS}}{50} \quad (4.3)$$

so that if  $R_{exp} > R_{random}$ , the copolymer microstructure consists predominantly of alternating monomer units/sequences, if  $R_{exp} = R_{random}$  the microstructure is random (statistical), and if  $R_{exp} < R_{random}$  the microstructure of the copolymer consists of sequences containing blocks of the corresponding co-monomer units.

Figure 4.37 shows  $^{29}\text{Si}$  NMR spectral regions of DiMeS and MePhS signals of polymer 18, while the calculated run numbers for both polymers are listed in Table 4.7.

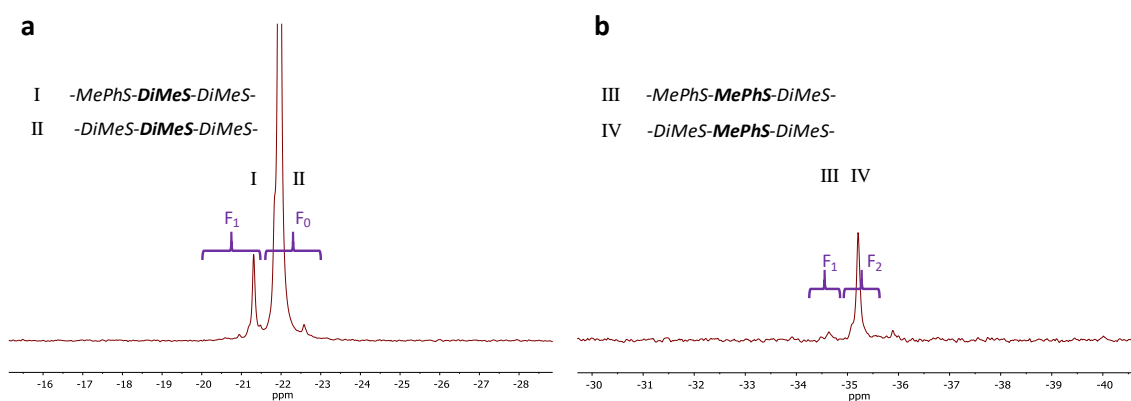


Figure 4.37. DiMeS (a) and MePhS (b)  $^{29}\text{Si}$  NMR spectral regions of Polymer 18, prepared targeting 3.6 mol % MePhS units.

Closer inspection of the DiMeS spectral region shows fine structure that can be assigned to the various configurations involving the presence of MePhS units in the nearest-neighbor position using triad nomenclature. The major signal observed at  $-22$  ppm, which is assigned to triad sequence of three DiMeS units (triad II in Figure 4.37a), is accompanied by the signal of smaller intensity at  $-21.3$  ppm indicating the presence of DiMeS units neighboring with one MePhS units (triad I in Figure 4.37a). Similarly, beside the dominant signal at  $-35.2$  ppm in MePhS spectral region, corresponding to the triad sequence IV in which central MePhS unit borders with DiMeS units on both sides, there is also a signal at  $-34.6$  ppm, which indicates the presence of very small amounts of blocks of two MePhS units (triad III in Figure 4.37b).

Table 4.7. Microstructural analysis of Polymers 18 and 19 from high resolution  $^{29}\text{Si}$  NMR data.

Polymer ID	MePhS content, mol %	$F_0$	$F_1$	$k_{\text{DiMeS}}$	$R_{\text{exp}}$	$R_{\text{random}}$
18	3.57	86.65	9.78	0.104	10.0	6.9
19	7.26	76.20	16.54	0.187	17.3	13.5

It can be seen from these data that experimentally determined run numbers for both examined polymers significantly exceeded calculated values for random distribution of

their repeat units, strongly suggesting alternation of single MePhS units and extended PDMS sequences. This was particularly visible for Polymer 18, which contained only 3.9 mol % of MePhS units, but whose MePhS  $^{29}\text{Si}$  NMR region showed almost exclusively isolated MePhS repeat units (signal from triad sequences IV in Figure 4.37b). Interestingly, even at such low concentration, this type of placement of individual MePhS units was effective enough to prevent rather long DiMeS segments (estimated at 28 repeat units long for feed MePhS content of 3.6 mol %) from packing into PDMS-like crystalline domains, the unit cells of which are generally accepted to accommodate 8 DiMeS repeat units.<sup>160, 162</sup>

#### 4.5.2 Monitoring of the Course of the Ring Opening Polymerization in MePhS-Containing Terpolymer System

Similarly to the polymerization Systems A-C of Section 4.4, anionic ROP of MePhS-containing terpolysiloxanes was monitored for the System D of Table 3.7, designed to target the same level of phenyl substitution as System A. A 7.2 mol % MePhS-containing reaction mixture D:  $\text{D}_4 + \text{D}_4^{\text{MePh}}$  also contained small amount of  $\text{D}_4^{\text{MeVi}}$  monomer (0.3 mol %), which is (as above) omitted from the following nomenclature.

Table 4.8. SEC-MALS-Vis characterization of the polymer fraction of the reaction mixture D ( $\text{D}_4 + \text{D}_4^{\text{MePh}}$ ) of Table 3.7 using samples taken at indicated reaction times.

Polymerization System	Reaction time, min	$\text{dn/dc}^a$ , mL/g	$M_w$ , g/mol	$M_n$ , g/mol	$M_p^b$ , g/mol	PDI <sup>c</sup>	$[\eta]^d$ , mL/g	$R_h^e$ , nm	$R_z^f$ , nm
D $\text{D}_4 + \text{D}_4^{\text{MePh}}$	3	-0.076	19,300	13,200	20,000	1.46	43.2	4.9	10.0
	12	-0.069	62,300	42,600	59,700	1.46	32.0	6.6	9.8
	20	-0.070	63,800	42,600	61,500	1.50	31.0	6.6	9.7
	30	-0.068	66,500	44,600	63,400	1.49	30.4	6.6	9.6
	45	-0.069	66,800	44,960	62,600	1.49	31.3	6.7	10.0
	60	-0.070	67,300	44,700	62,500	1.50	31.9	6.7	10.1
	90	-0.070	67,900	44,800	62,800	1.51	32.4	6.8	10.5
	120	-0.070	68,800	45,200	63,550	1.52	32.1	6.8	10.4
	180	-0.070	68,700	45,200	63,300	1.52	32.4	6.8	10.5
240	-0.070	68,100	44,200	62,900	1.54	31.9	6.8	10.2	

<sup>a</sup>  $\text{dn/dc}$  was determined online, using 100 % mass recovery.

<sup>b</sup>  $M_p$ : peak molecular weight

<sup>c</sup> PDI: polydispersity index;  $\text{PDI} = M_w/M_n$ .

<sup>d</sup>  $[\eta]$ : intrinsic viscosity as determined by Visco Star II online detector.

<sup>e</sup>  $R_h$ : hydrodynamic radius.

<sup>f</sup>  $R_z$ : root-mean square radius (RMS radius)



As shown in Figure 4.38, the dynamics of the increase in the polymer molecular weight and the formation of higher oligomers in the reaction mixture D, of Table 4.8, followed a pattern similar to that observed in the PDMS and DiEtS-containing systems of Figures 4.20 and 4.21. The formation of the polymer and the reaction-formed cyclic oligomers was detected as early as 3 minutes from the beginning of ROP, and the molecular weight of polymer quickly reached its targeted (plateau) value (see Figure 4.39a). Polydispersity of the polymer fraction was constant throughout the entire course of the ROP: PDI=1.5, which was practically identical to the PDI profiles observed in the DiEtS-containing and PDMS Systems B and C of Figure 4.21, respectively (compare: Table 4.6).

Comparison of molecular weight vs. reaction time plots for MePhS-containing System D and DiPhS-containing System A of Figure 4.39a and b clearly demonstrated the impact that solubility of two different Ph-containing cyclosiloxane monomers,  $D_4^{\text{MePh}}$  and  $D_4^{\text{Ph}_2}$ , had on the courses of these polymerization reactions. While very limited solubility of solid  $D_4^{\text{Ph}_2}$  monomer in the  $D_4$  reaction medium retarded the polymerization in System A during the first 30 minutes of the reaction time (“induction period” of Figure 4.23) in the  $D_4^{\text{MePh}}$ -based System D the polymer started forming immediately after the addition of initiator. The rate of the molecular weight increase in this initial segment of the polymerization in MePhS-containing system was very similar to the one observed in System A after expiration of the induction period, and in Systems B and C from the beginning.

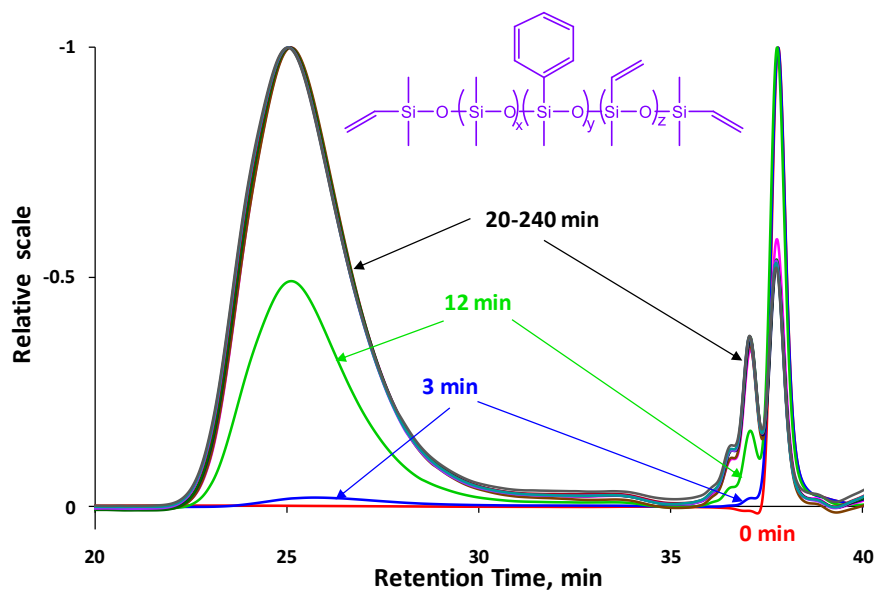


Figure 4.38. SEC chromatograms of samples of polymerization reaction mixtures of System D, at indicated reaction times. Eluent: toluene.

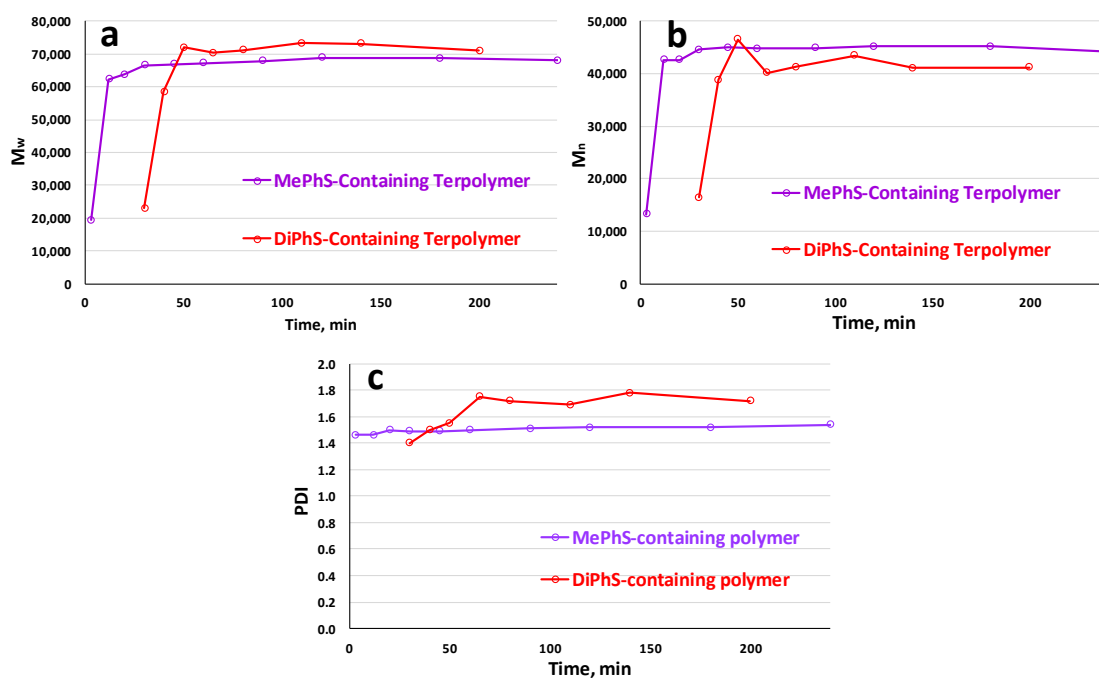


Figure 4.39. Weight-average (a), number-average (b), molecular weights and polydispersity (c) of polymers formed in phenyl containing polymerization Systems A and D, as a function of the reaction time.

During the ROP of the MePhS-containing System D polymer fraction reached substantial yield (ca. 60 %) within only 12 minutes of the reaction time, as evident from the high temperature plateaus in TGA traces at different reaction times (see Figure 4.40). At higher conversions, polymer yield vs. reaction time plot of System D followed similar trend as the DiPhS-containing polymer of System A (Figure 4.41).

The entire amount of  $D_4^{\text{MePh}}$  reacted within the first 3 minutes of ROP, as indicated by the complete disappearance of the  $^{29}\text{Si}$  NMR signal at  $-30.8$  ppm<sup>182, 183</sup> assigned to silicons of  $D_4^{\text{MePh}}$  (Figure 4.42 B) while conversion of  $D_4$  during this brief initial period was suppressed (similar to the DiPhS-containing polymerization case). This was confirmed by only slight decrease in the intensity of  $^{29}\text{Si}$  NMR signal at  $-19.2$  ppm and, accordingly, hardly visible signal from silicon of DiMeS units of polymer at  $-22$  ppm (Figure 4.42 A). These results suggest that, at the beginning of the reaction, TMAS initiated ROP of MePhS-containing cyclic siloxane preferentially occurred, in a manner similar to that described for the DiPhS-containing system in Section 4.4.7. This is further supported by the fact that the yield of polymer formed upon complete consumption of  $D_4^{\text{MePh}}$ , i.e., after 3 minutes of the reaction time, was 16 wt. % (Figure 4.40), only slightly higher than the weight fraction of  $D_4^{\text{MePh}}$  cyclic in the starting reaction mixture of System D (13 wt. %) (see Table 3.7).

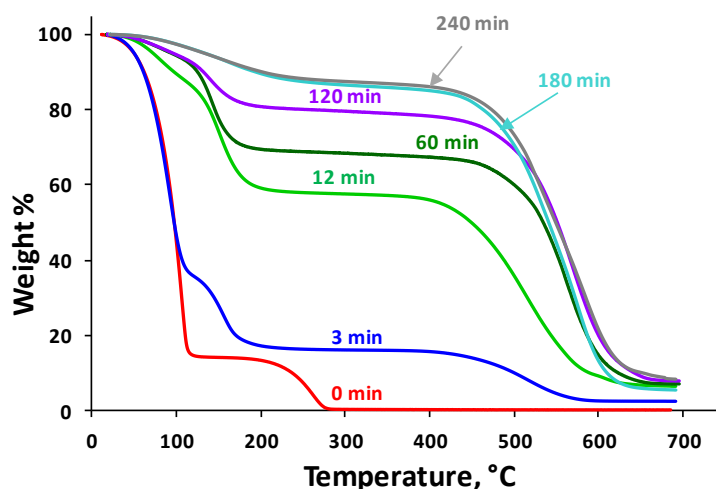


Figure 4.40. TGA traces of samples of the polymerization reaction mixture of MePhS-containing System D, at indicated reaction times. TGA in nitrogen at a heating rate of  $10$  °C/min.

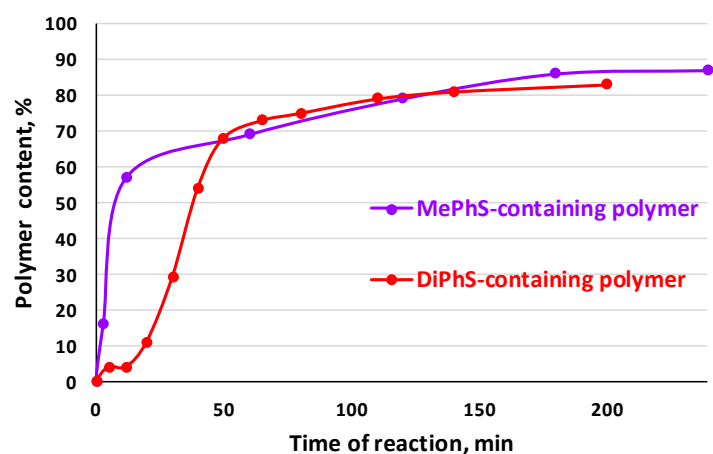


Figure 4.41. Comparison of the formation of linear polymer products in the MePhS-containing System D and DiPhS-containing System A as a function of the reaction time (as determined by TGA).

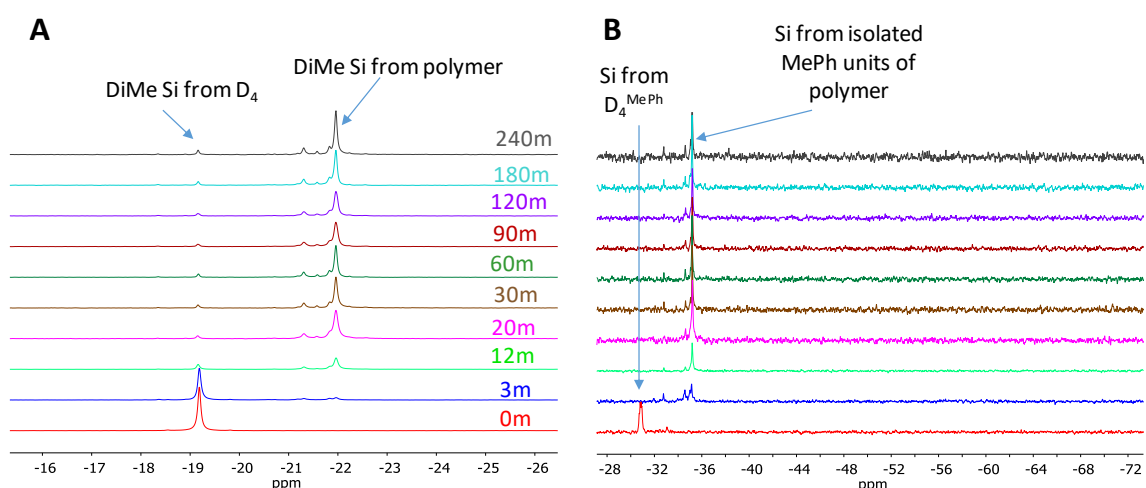


Figure 4.42. DiMeS (A) and MePhS (B)  $^{29}\text{Si}$  NMR spectral regions of the samples of the MePhS-containing polymerization reaction mixture of System D, taken at indicated reaction times.

The rate of the disappearance of two cyclic monomers,  $\text{D}_4$  and  $\text{D}_4^{\text{MePh}}$ , and the rate of polymer formation were additionally evaluated by quantitative SEC, using THF as eluent. Overlay of SEC chromatograms of samples of the MePhS-containing polymerization reaction mixture, taken at different indicated reaction times, is shown in Figure 4.43. As

in the case of DiPhS-containing polymerization System A, the separation of major signals from the growing polymer and the reacting cyclic monomers was good enough to enable reliable estimate of the yield of linear fraction and conversion of monomers from changes in respective peak areas with reaction time.

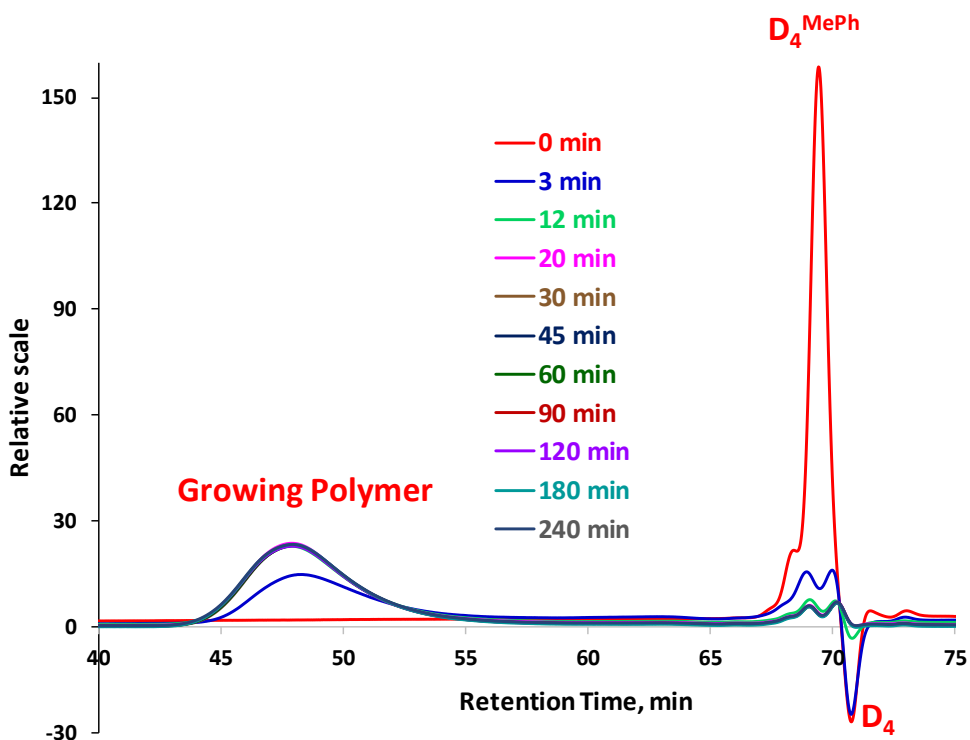


Figure 4.43. SEC chromatograms of samples of the polymerization reaction mixture of System D, at indicated reaction times. Eluent: THF. The "0 min" sample was taken before addition of TMS initiator.

The conversion of D<sub>4</sub> monomer, as estimated from the changes in intensity of the peak at retention time of 70.8 min and from integration of areas of D<sub>4</sub> SEC signals of Figure 4.43 at indicated reaction times (Figure 4.43), was initially (during the first 3 min) very low, while more reactive MePhS cyclic was preferentially reacting. However, dramatic turn in events occurred after that brief initial period, and quantitative consumption of D<sub>4</sub> was obvious after 20 min from the beginning of reaction.

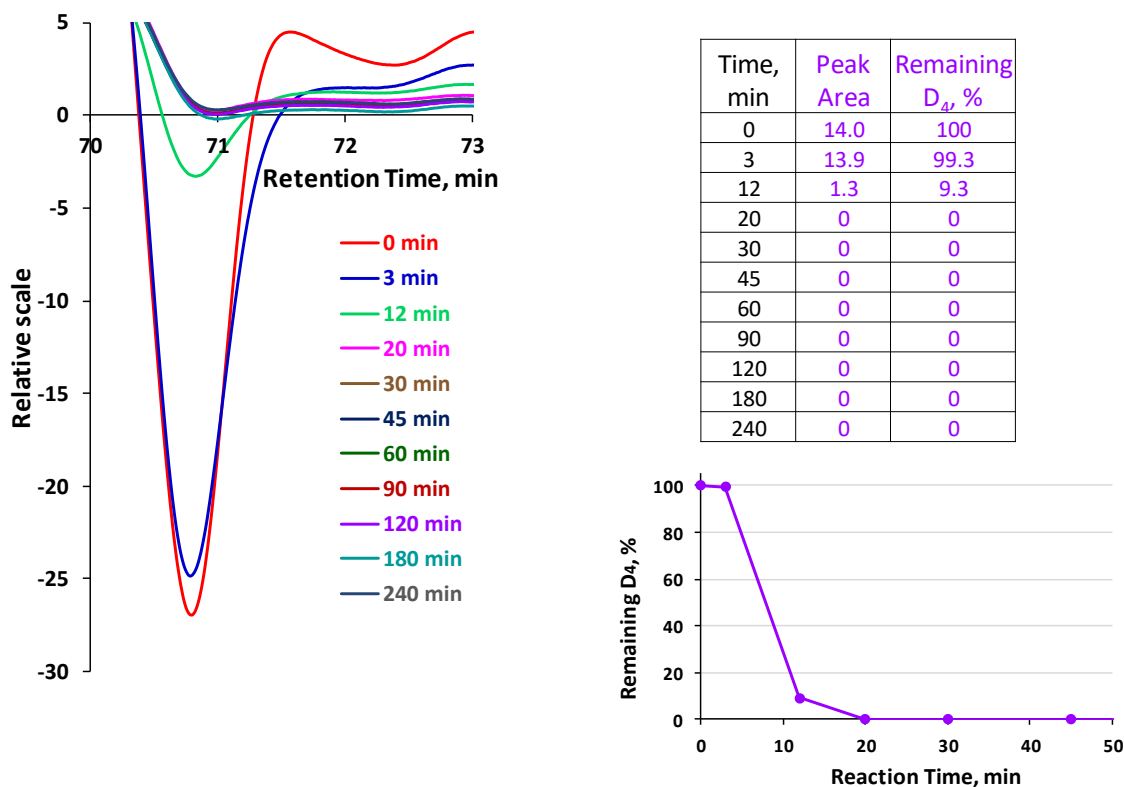


Figure 4.44. Disappearance of D<sub>4</sub> during the polymerization in System D. Eluent: THF.

In addition to this, the high intensity SEC signal from MePhS cyclic monomer at retention time of 69.3 minutes (Figures 4.43 and Figure 4.45 with integrated areas of D<sub>4</sub><sup>MePh</sup> SEC deconvoluted signals of Figure 4.43 at indicated reaction times), completely disappeared after the first 3 minutes, consistent with the findings of <sup>29</sup>Si NMR analysis (Figure 4.42 B). Simultaneously, besides the strong peak from the forming polymer at retention time of 48 minutes (Figure 4.47), smaller peaks appeared in the low molecular weight region of the chromatograms, indicating formation of mixed and higher cyclic oligomers resulting from equilibration (Figures 4.43 and 4.45).

Comparison of the rates of conversion of cyclic monomers in the two phenyl-containing Systems, A and D, estimated from quantitative SEC monitoring experiments (Figure 4.46), clearly demonstrated how solubility of the phenyl-containing cyclic monomers in D<sub>4</sub> controls the overall rate of polymerization in these systems. Even though D<sub>4</sub><sup>Ph<sub>2</sub></sup> is more susceptible to silanolate-initiated ring opening than its D<sub>4</sub><sup>MePh</sup> counterpart, its very limited solubility in the reaction medium (D<sub>4</sub>) significantly postpones the start of the

efficient polymer growth until the induction period is over. Mechanistically, the ROP in MePhS-containing System D is identical to the one occurring in DiPhS-containing system (A), with the exception of the induction period, which allows for faster completion of polymer formation and its randomization.

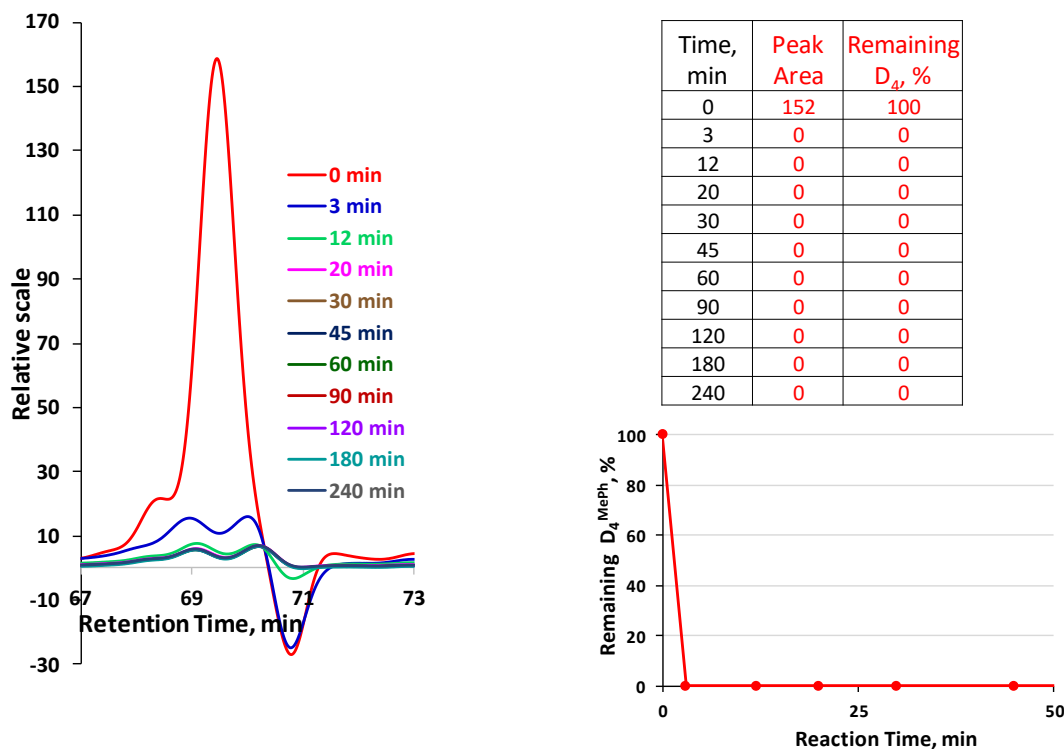


Figure 4.45. Disappearance of  $D_4^{\text{MePh}}$  during the polymerization in System D. Eluent: THF.

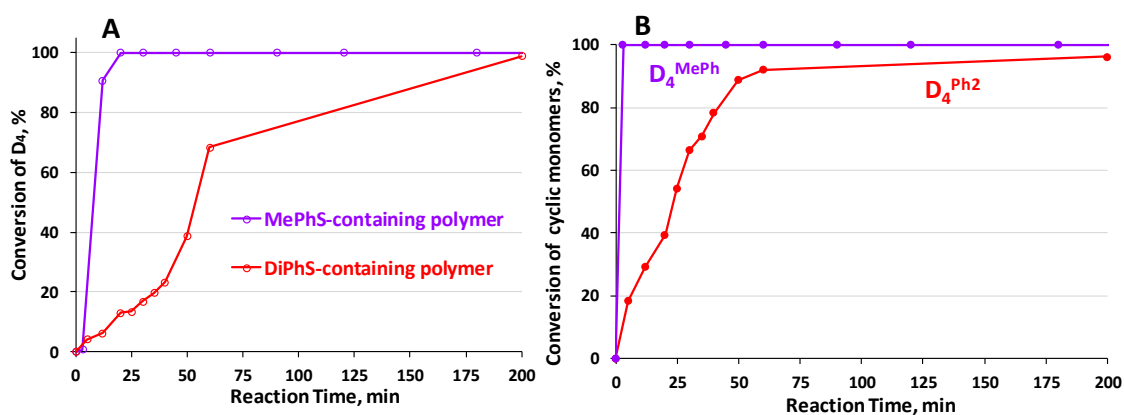


Figure 4.46. Comparison of the conversion rates of  $D_4$  (A) and the phenyl-containing cyclic monomers (B) during polymerizations in MePhS- and DiPhS-containing Systems D and A.

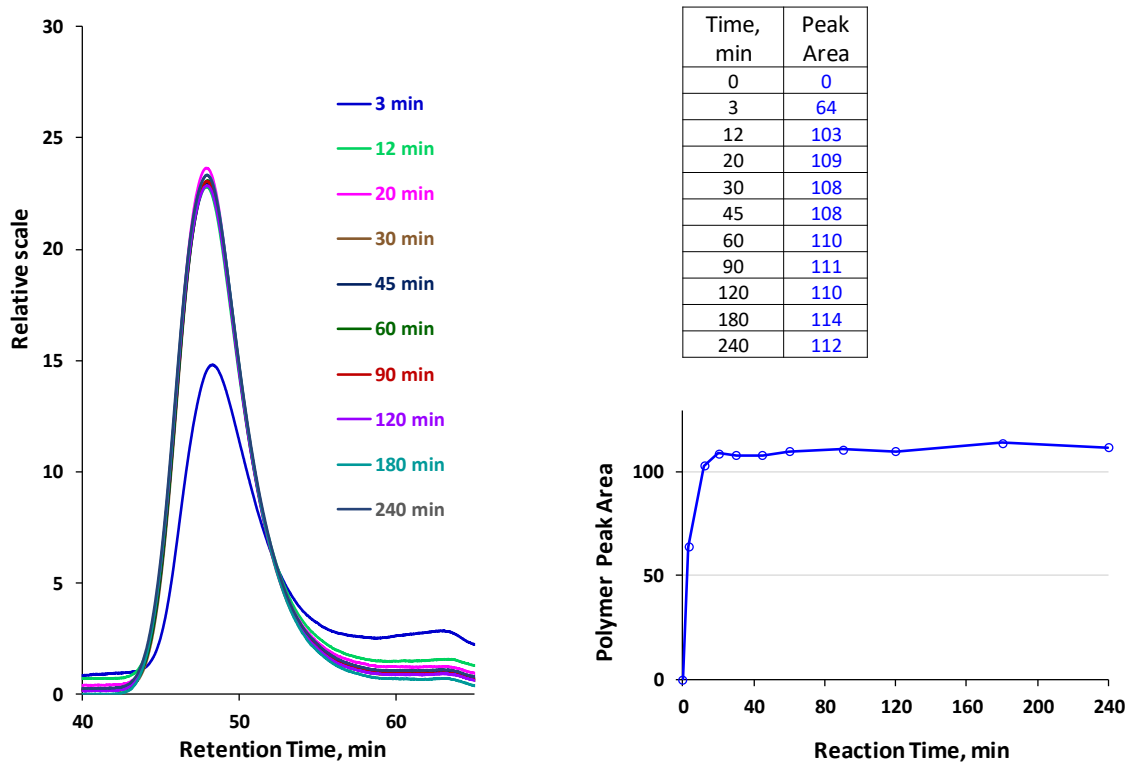


Figure 4.47. Yield of the growing polymer in System D, as a function of reaction time; from SEC signals at 44–65 min of the retention time of Figure 4.43 Eluent: THF.



## 5. CONCLUSIONS

Three families of vinyl-functional dimethylsiloxane, DiMeS, -based terpolymers, containing small amounts (5 mol % or below) of methylvinylsiloxo-, MeViS, diphenylsiloxo-, DiPhS, or diethylsiloxo-, DiEtS, or methylphenylsiloxo-, MePhS, repeat units, were reproducibly synthesized via silanolate-initiated anionic ring opening polymerization, ROP, using an  $\alpha,\omega$ -bis(tetramethylammonium) oligodimethylsiloxo-disilanolate, TMAS, as a "transient" initiator, and an  $\alpha,\omega$ -telechelic dimethylvinylsiloxo end-blocker, DiViEB, as the polymer chain terminator and molecular weight regulator.

Within the families, containing DiPhS and DiEtS repeat units, polymers with degrees of polymerization ranging from 80 to 600 were prepared. In addition, a sub-series of DiPhS-containing terpolysiloxanes, targeting  $DP$  of 160 was also prepared in order to study and quantify the effect of silanolate initiator concentration on the polymer architecture and properties. Furthermore, two MePhS-containing polymers were finally prepared to test the chain-branching hypothesis in the DiPhS-containing polymers and evaluate their crystallization behavior.

Substitution of only 3.6 mol % of DiMeS units in these terpolysiloxanes by DiPhS ones led to complete suppression of polymer crystallization (as evaluated by DSC), for all targeted  $DP$ s, indicating that even a relatively large separation of DiPhS "crystallization disruptors" (estimated at several nanometers between the neighboring units) along these polymer chains was effective enough to prevent regular PDMS segmental packing into crystalline domains.

$^{29}\text{Si}$  NMR and SEC results showed presence of trifunctional Ph-T-branch junctures in the DiPhS-containing polymers, while the same feature was clearly absent in their DiEtS-containing analogues. This branching in DiPhS-containing polymers was identified using purposely prepared model polymers by signals at  $-80$  ppm in  $^{29}\text{Si}$  NMR and specific SEC and MHS behaviors. Investigation of the effect of silanolate initiator concentration on the structure and properties of DiPhS-containing terpolysiloxanes within the series with targeted  $DP$  of 160 revealed that the onset of branching occurred when concentration of silanolate in the polymerization system exceeded 1.25 mmol/mol ( $\text{SiR}_2\text{O}$ ). At the highest

utilized level of initiator concentration ( $[\text{DiViEB}]/[\text{TMAS}]=1$ ), almost one half of DiPhS units of terpolymer were desilylated (as estimated by  $^{29}\text{Si}$  NMR), leading to a highly branched polymer structure with enhanced compactness (low value of 0.444 for the exponent  $a$  of MHS equation).

Substitution of one Ph group from a DiPhS unit by the third polydimethylsiloxy- branch stabilized the remaining Ph group on the same silicon atom, as no indication of the formation of quaternary Q-branches could be detected.

It is proposed that this branching in DiPhS-containing terpolymers was caused by increased electrophilicity of the two-Ph-groups-bearing silicons in DiPhS repeat units and consequent increase in sensitivity of their Si-C<sub>Ar</sub> side bonds to desilylation by the nucleophilic attack of silanolate anions used for initiation of these ring opening polymerizations reactions.

Ethyl side-groups in DiEtS repeat units of DiEtS-containing terpolymers were apparently large and bulky enough to disrupt PDMS crystallization just as effectively as DiPhS units did. Their minimum required molecular concentration to do so was found to be only slightly higher, i.e., about 5 mol % (relative to 3.6 mol % for DiPhS units), while on the weight basis it was actually lower (6.7 wt. %) than the corresponding DiPhS concentration in diphenyl-substituted analogues (9.0 wt. %).

Both DiEtS cyclic trimer and tetramer ( $\text{D}_3^{\text{Et}_2}$ ,  $\text{D}_4^{\text{Et}_2}$ ) were equally effective for random incorporation in polymer products by this silanolate initiated ROP route. In contrast to this, an attempt to utilize DiEtS "hydrolyzate" for this purpose led to products that apparently contained extended PDES blocks rather than randomly placed DiEtS units. It is proposed that this was due to insufficiently long reaction times allowed for equilibration in the "hydrolyzate"-utilizing systems.

Most importantly, incorporation of DiEtS repeat units into PDMS chains (even at as low as 5 mol % content level) by this silanolate-initiated ROP, provided well-defined linear chain products which showed no crystallization *and* no chain branching. Together with their MePhS-containing derivatives (see below) this combination of properties makes these polymers the polymers of choice for application as precursors for crosslinked elastomers for extremely low temperature applications.

Investigation of the dynamics of dimethylsilanolate-initiated bulk homopolymerization of  $D_4$  (System C) and three copolymerizing mixtures of  $D_4$  with  $D_4^{\text{Ph}2}$ ,  $D_3^{\text{Et}2}$  and  $D_4^{\text{MePh}}$  (Systems A, B and D, respectively), was conducted by monitoring the courses of their occurrence by SEC, TGA and  $^{29}\text{Si}$  NMR. It was found that while Systems B, C and D behaved in a virtually identical manner, characterized by a very fast initial polymer growth, System A was significantly different and much more complex.

The polymerization of  $D_4$  and  $D_4^{\text{Ph}2}$  in System A was found to be dominated by two factors: a significantly higher reactivity of  $D_4^{\text{Ph}2}$  toward dimethylsilanolate than  $D_4$ , and a rather low solubility of solid  $D_4^{\text{Ph}2}$  in a  $D_4$ -dominated reaction mixture. As a consequence, the  $D_4 + D_4^{\text{Ph}2}$  copolymerization begins in a two-phase system via an "induction period" during which mostly  $D_4^{\text{Ph}2}$  polymerizes by ROP. Only after this first stage is completed, the polymerization of  $D_4$  commences, resulting in a major build-up of both polymer yield and molecular weight.

Parallel to ROP, siloxane equilibration reaction also occurs in all investigated reaction systems (although significantly more slowly), involving all silanolate anions and siloxane bonds present. In the end, the two reactions result in an equilibration of molecular sizes and compositions of the reaction products. Based on the data obtained from this monitoring study, a new three-stage reaction mechanism is proposed to describe the course of the occurrence of this complex process in the System  $D_4 + D_4^{\text{Ph}2}$ .

As pointed out above, while the presence of only 3.6 mol % of DiPhS units in the DiPhS-containing terpolysiloxanes was enough to completely prevent their crystallization (which is otherwise characteristic for PDMS), it also gave rise to undesirable chain-branching. It is proposed that the reason for both processes, the appearance of this chain-branching and the appearance of "induction period", is one and the same: a significantly more pronounced electrophilicity of DiPhS silicons relative to their DiMeS counterparts, which causes significantly higher reactivity of  $D_4^{\text{Ph}2}$  than  $D_4$  toward dimethylsilanolate initiators.

The aspect of miscibility of comonomers was further explored through the monitoring study in the System D ( $D_4 + D_4^{\text{MePh}}$ ) designed to have the same level of Ph-substitution as System A ( $D_4 + D_4^{\text{Ph}2}$ ). Although having less electrophilic silicons than its DiPhS analogue, the  $D_4^{\text{MePh}}$  monomer is still significantly more reactive toward silanolate

initiators than D<sub>4</sub>. Unhindered by miscibility issues, however, quantitative ROP of MePhS cyclic monomer in homogenous System D occurs very quickly upon the addition of initiator, followed by ROP of D<sub>4</sub> and siloxane redistribution.

The presence of electron-donating methyl group in MePhS units, i.e., decreased electrophilicity of its silicon compared to that of DiPhS units, stabilizes Si-C<sub>Ar</sub> side bond of MePhS-containing terpolysiloxane against nucleophilic attack by silanolate (which would lead to polymer branching), just as in the case of Ph-T-branches of branched DiPhS-containing polymers described earlier.

It is also interesting to note that as low as 1.95 mol % of Ph-substituents (i.e., 3.9 mol % MePhS content) was enough to completely prevent the PDMS-like crystallization in the MePhS-containing terpolymers, provided that randomization of repeat units was achieved by equilibration.

Consequently, as pointed out above for their DiEtS counterparts, MePhS-containing polymers should be also considered as polymers of choice for applications requiring completely linear, thermally stable polysiloxanes, free of low temperature crystallization.

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## BIOGRAFIJA AUTORA

Alisa Zlatanić je rođena 08.04.1967. godine u Pljevljima. Osnovnu školu i gimnaziju je završila u Priboju. Na Tehnološko-metalurški fakultet Univerziteta u Beogradu upisala se školske 1985/86. godine. Diplomirala je 15.02.1993. na smeru Organska Hemijska Tehnologija i Polimerno Inženjerstvo odbranom diplomskog rada na temu: "Sinteza i karakterizacija nezasićenih poliestara sa završnim akrilatnim grupama". Poslediplomske studije na Tehnološko-metalurškom fakultetu Univerziteta u Beogradu upisala je školske 1993/94. godine na smeru Hemija i Inženjerstvo Polimera, a završila 20.10.1997. godine odbranivši magistarsku tezu pod nazivom: „Sinteza i reološko ponašanje nezasićenih poliestara sa završnim akrilatnim grupama”. Školske 2016/17 mr Alisa Zlatanić upisala je III godinu doktorskih studija na Tehnološko-metalurškom fakultetu - studijski program Hemija, mentor dr Marije Nikolić.

Alisa Zlatanić, magistar tehničkih nauka, bila je zaposlena na Tehnološko-metalurškom fakultetu Univerziteta u Beogradu od 06.12.1993. do 31.10.1999. godine, kao asistent-pripravnik na Katedri za opštu i neorgansku hemiju, a zatim kao asistent na istoj Katedri (u zvanje asistenta izabrana je 12.10.1998. godine). Od 1.11.1999. godine do danas je zaposlena kao viši istraživač saradnik u Centru za istraživanje polimera na Državnom univerzitetu u Pitsburgu, Kansas, SAD (Pittsburg State University).

Oblast naučno-istraživačkog rada mr Alise Zlatanić obuhvata sintezu, karakterizaciju i primenu polimera, kao što su polisiloksani, poliestri, polietri, poliuretani, poliakrilamidi. Značajan deo naučno-istraživačkog rada mr Alise Zlatanić bio je posvećen izučavanju polimera na bazi prirodnih i modelnih triglicerida i njihovoj primeni i komercijalizaciji u oblasti celularnih poliuretanskih materijala, adheziva i kompozita. Od početka 2015. godine, mr Alisa Zlatanić je, pod rukovodstvom prof. dr. Petra Dvornića, aktivno angažovana u okviru projekta Državnog univerziteta u Pitsburgu sa kompanijom Honeywell, na istraživanju i razvoju polisiloksana i siloksanskih elastomera, koje je vezano za izradu njene doktorske disertacije.

Kao rezultat celokupnog naučno-istraživačkog rada mr Alise Zlatanić do sada je objavljeno jedno poglavlje u monografiji međunarodnog značaja, 15 radova u međunarodnim časopisima, preko 30 saopštenja na skupovima nacionalnog i međunarodnog značaja, dva patenta i jedna patent aplikacija.

Alisa Zlatanić je dobitnik nagrade „Presidential Green Chemistry Challenge Award” za 2007. godinu u kategoriji Dizajna čistijih hemikalija koju je američka Agencija za zaštitu životne sredine dodelila timu istraživača Centra za istraživanje polimera, Državnog univerziteta u Pitsburgu i kompaniji Cargill Inc. za plodotvornu saradnju u razvoju i komercijalizaciji BiOH™ poliola na bazi prirodnih ulja.

Od 2002. godine član je Američkog hemijskog društva.

## Изјава о ауторству

Име и презиме аутора Alisa Zlatanić

Број индекса 4038/2016

### Изјављујем

да је докторска дисертација под насловом

The Effect of Structure of Cyclic Monomers on the Course of Anionic  
Polymerization and the Properties of Vinyl-Terminated Polysiloxanes

Uticaj strukture cikličnih monomera na tok anjonske polimerizacije i svojstva  
vinil-terminiranih polisiloksana

- резултат сопственог истраживачког рада;
- да дисертација у целини ни у деловима није била предложена за стицање друге дипломе према студијским програмима других високошколских установа;
- да су резултати коректно наведени и
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Потпис аутора

У Питсбургу, 19.02.2019.



## Изјава о истоветности штампане и електронске верзије докторског рада

Име и презиме аутора Alisa Zlatanić

Број индекса 4038/2016

Студијски програм Hemija

Наслов рада The Effect of Structure of Cyclic Monomers on the Course of Anionic  
Polymerization and the Properties of Vinyl-Terminated Polysiloxanes

Uticaj strukture cikličnih monomera na tok anjonske polimerizacije i  
svojstva vinil-terminiranih polisiloksana

Ментор Prof. dr Marija Nikolić

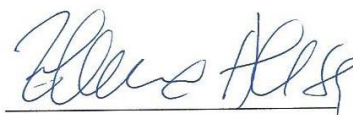
Изјављујем да је штампана верзија мог докторског рада истоветна електронској верзији коју сам предао/ла ради похрањена у **Дигиталном репозиторијуму Универзитета у Београду**.

Дозвољавам да се објаве моји лични подаци везани за добијање академског назива доктора наука, као што су име и презиме, година и место рођења и датум одбране рада.

Ови лични подаци могу се објавити на мрежним страницама дигиталне библиотеке, у електронском каталогу и у публикацијама Универзитета у Београду.

Потпис аутора

У Питсбургу, 19.02.2019.



## Изјава о коришћењу

Овлашћујем Универзитетску библиотеку „Светозар Марковић“ да у Дигитални репозиторијум Универзитета у Београду унесе моју докторску дисертацију под насловом:

The Effect of Structure of Cyclic Monomers on the Course of Anionic Polymerization and the Properties of Vinyl-Terminated Polysiloxanes

Uticaj strukture cikličnih monomera na tok anjonske polimerizacije i svojstva vinil-terminiranih polisiloksana

која је моје ауторско дело.

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У Питсбургу, 19.02.2019.

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