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Articles

Controlled Synthesis of Siloxane Copolymers Having an Organosulfur Group by Polymerization of Cyclotrisiloxanes with Mixed Units

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ABSTRACT: The preparation of poly(dimethylsiloxane)s having part of the siloxane units substituted with a model organic thioether was investigated. The sulfur group was generated by the ene−thiol addition to the vinyl function bound to silicon. Two synthetic routes to this copolymer were compared (i) one-step kinetically controlled polymerization of organosulfur-substituted hexamethylcyclotrisiloxane and (ii) two-step synthesis including kinetically controlled polymerization of 1,3,3,5,5-pentamethyl-1-vinylcyclotrisiloxane followed by the thiol addition to the vinyl group in the polymer. A cryptand−lithium silanolate complex generated from [(trimethylsilyl)methyl]lithium was selected as the initiator in this polymerization, while *tert*-butyl mercaptan was used as the hydrosulfidation reagent. It was shown that synthesis routes lead to a high yield of copolymers having a fairly regular chain structure. The arrangement of siloxane units in the polymer chain was controlled by the propagation step. Polymerization of the vinyl-substituted monomer exhibited a significant degree of regioselectivity as one of the three possible modes of the monomer ring opening contributed over 70% to the propagation. Addition of *t*-BuSH to the vinyl group in the polymer proceeded without rearrangement of the polymer chain and could be performed without any side reaction of the vinyl group. Model copolymers of regular alternating structure were synthesized by the heterofunctional polycondensation of [2-(*tert*-butylthio)ethyl]methyldichlorosilane with a series of diols, $HO(Me_2SiO)_nH$, $n = 1-4$. They were used for comparison with the copolymers obtained by ring-opening polymerization.

Introduction

Synthesis of polymers and copolymers of siloxanes bearing a group of nucleophilic reactivity in organic radical pending to polymer chain has been recently extensively studied. These polymers combine unusual properties related to high flexibility of the polysiloxane chain with ability to enter into reactions with electrophiles. Thus, they could be applied for various purposes. They were used as efficient catalysts in homogeneous reaction systems,[1−3] phase transfer catalysts,[4] polymeric ligands for anchoring transition metal catalysts,[5−7] intermediates for chemical reactions,[8−11] polymer electrolytes,[12,13] ion extractants,[14,15] and materials for chromatography,[16] as well as for other applications.[9]

Siloxane copolymers with organic sulfide pending groups seem to be attractive in several aspects. These groups undergo interesting chemical transformations and have the ability of complexing heavy metal ions, such as cations of mercury, platinum, palladium, gold, silver, copper, nickel, cadmium, zinc, bismuth, tin, iron, and others.[17,18] Thioethers may be selective in this complex formation. For example, they interact much more strongly with the soft cations being at a lower oxidation state, e.g., Cu^+ than with harder cations such as Cu^{2+}.[19] Thus, polysiloxanes bearing a sulfide function could be interesting materials for selective sorbents, membranes, and materials in chromatography.

Certain organic sulfides or their derivatives have been used as biocides of diverse activity—antimicrobial,[20] insecticidal,[21] fungicidal,[22] herbicidal,[23] and others[21]—antioxidants,[24,25] corrosion inhibitors,[26] heat and light stabilizers,[27] and cross-linkers.[24,28] These functions could be performed as well by the thioether groups pending to polysiloxane chains.

Further perspectives for the sulfide-modified polysiloxanes are related to the oxidation reaction. The thioether group may be transformed by this reaction to highly polar and nucleophilic sulfoxide function.[29,30] Sulfoxides are used as nucleophilic catalysts[31,32] and activators.[33−35] The oxidation of sulfides may be performed stereoselectively to optically active sulfoxides with large specific rotation.[36−38] Generation of such sulfoxides pending to poly(dimethylsiloxane) would give the polymer interesting optical properties and the ability of stereoselective interacting with electrophiles. Thus, such polymers could find applications in chromatography or serve as catalysts for stereoselective transformations.

The attractive method of the introduction of the organic thioether group to silicon is based on hydrosulfidation of the silyl−vinyl function (thiol−ene addition). Advantage of this method is that the thiol−ene addition can occur on a free-radical route.[39,40] Thus, the reaction

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should not be accompanied by Si−C or Si−O bond cleavage. Vinyl-substituted silane monomers as well as siloxane polymers are available, and some addition reactions to the vinyl group at silicon have been employed for the modification of polysiloxanes.[41−43] The thiol−ene addition may open new possibilities of introduction of various interesting functions to polysiloxanes through a thioether bridge.

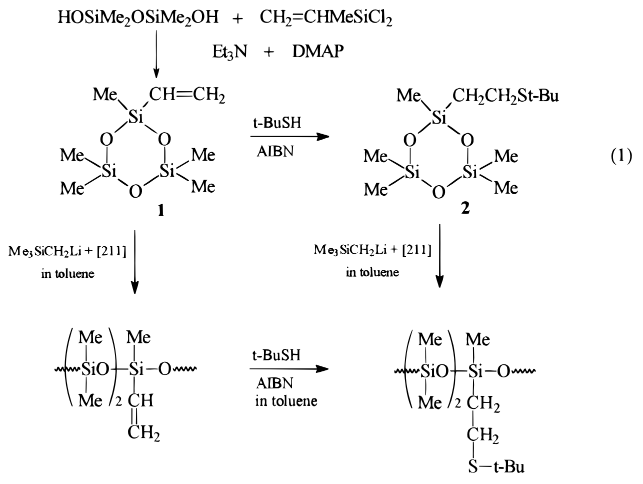
The present work is devoted to the controlled synthesis of dimethylsiloxane copolymers having part of the siloxane units substituted with a model organic thioether which will be further used as a precursor of a chiral sulfoxide group.[44] The chosen model is a *t*-BuSCH$_2$CH$_2$-function bound to the silicon atom. Our purpose is to examine some synthetic routes for generation of poly[dimethylsiloxane-*co*-[2-(*tert*-butylthio)ethyl]methylsiloxane]s. Particular attention is directed to synthesis of copolymers of well-defined structure including molecular size, quantity of the thioether groups, and their arrangement along the chain.

Results and Discussion

1. Synthetic Routes. Schemes of all syntheses performed here are presented in eqs 1 and 2. The kinetically controlled polymerization of cyclic trisiloxanes with mixed siloxane units is the principal process used here for the generation of the siloxane copolymers. This method has advantages over processes usually used for this purpose. Trivial copolymerization of siloxane comonomers when carried out with kinetic control leads to macromolecules of different composition of siloxane units.[45] Equilibration processes give the polymer chains having the unified composition; however, the arrangement of units is statistical.[45,46] The method used here gives the possibility of the generation of copolymers having siloxane units arranged in a more regular way.[11,47,48] In addition, it may lead to a lower heterogeneity of molecular size and a higher yield of the copolymer as compared with the equilibration.[11,47] In the first variant of the synthesis of the sulfur containing copolymers, the cyclic trisiloxane bearing the vinyl function 1 is polymerized; then the sulfide group is generated on the poly(dimethylsiloxane-*co*-methylvinylsiloxane)s by the ene−thiol addition (eq 1). In the second variant the sulfur is introduced to cyclotrisiloxane by the hydrosulfidation of the vinyl group in **1** producing monomer **2**, which is polymerized according to eq 1.

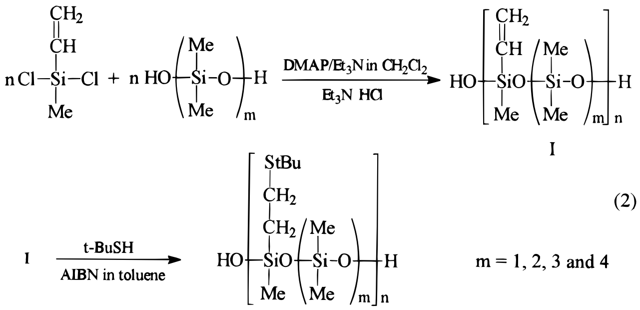
Heterofunctional polycondensation is another method explored here for synthesis of the thioether-containing polysiloxanes (eq 2). It permits the generation of copolymers with fully regular arrangement of the siloxane units.

Cyclotrisiloxanes are chosen as the monomers in the polymerization because the strain SiOSi linkage in the monomer is known to be more reactive than that in the polymer. Thus, the propagation is much faster than backbiting, producing cyclic oligomers, and chain scrambling, broadening the molecular weight distribution. Both these reactions also affect the arrangement of siloxane units in the copolymer. Since these undesired processes are reduced, the polymerization may lead to a high yield of polymer of uniform molecular size[49−51] and more regular structure.[11,47] Monomer **1** was produced using the method (eq 1) which was described earlier.[43,52,53] [2-(*tert*-Butylthio)ethyl]pentamethylcyclotrisiloxane **2**, a new compound, was obtained by addition of *tert*-butyl mercaptan to the vinyl group of **1**, exploiting well-known free-radical reaction promoted by azobis(isobutyronitrile) (AIBN)[39,40] (eq 1). The addition occurs with a high yield and selectively in an anti-Markovnikov fashion placing the sulfur atom in the β position to silicon. The contribution from the α substitution was <3%.



(1)

DMAP = 4-NN-dimethylaminopyridine



(2)

The necessary condition of the selective course of the polymerization is the use of a suitable initiation system producing propagation centers which react much faster with monomer than with polymer.[49] The well-known highly selective initiators convenient for this purpose are alkyllithium complexes with cryptands.[54−56] [(Trimethylsilyl)methyl]lithium + [211] cryptand has recently been used successfully[57,58] and was chosen as the initiator in this study. [(Trimethylsilyl)methyl]lithium when added by itself to the hydrocarbon solution of the siloxane monomer does not initiate the polymerization. However, transformation of the initiator to lithium silanolates occurs quantitatively. The silanolates in toluene are not reactive toward monomer, but cryptated lithium silanolate ion pairs are formed immediately on adding the [211] cryptand which induces a fast polymerization.[57,58]

2. Kinetically Controlled Ring-Opening Polymerization. Initiator and monomer solutions were prepared by a high-vacuum technique. The polymerization was carried out in a closed system under the atmosphere of prepurified argon (see the Experimental Section). The polymerization was followed by sampling and determining the monomer concentration by gas chromatography or NMR. The polymerization was quenched at a suitable time by addition of a small excess of Me$_3$SiCl. The isolated polymer was subjected to analysis to determine the yield, molecular weight, and heterogenity factor. Besides monomers **1** and **2**, the polymerization of the unsubstituted monomer D$_3$ and V$_3$—the monomer substituted by a vinyl group in all siloxane units (MeViSiO)$_3$—was also studied. The results are collected in Table 1.

The data in Table 1 proved that the initiating system was very efficient for the polymerization of monomers

Table 1. Anionic Polymerization of Cyclotrisiloxanes: Hexamethylcyclotrisiloxane, D_3, 1-[2-(*tert*-Butylthio)ethyl]-1,3,3,5,5-pentamethylcyclotrisiloxane, 2, 1,3,3,5,5-Pentamethyl-1-vinylcyclotrisiloxane, 1, and 1,3,5-Trimethyl-1,3,5-trivinylcyclotrisiloxane, V_3, Initiated by Me_3SiCH_2Li, in Toluene, with [211] under Argon

no.	monomer	$[M]_0$ (mol dm^{-3})	$[Li^+] \times 10^3$ (mol dm^{-3})	[211]/[Li$^+$]	T (°C)	monomer conversion^a (%)	polymer yield^b (%)	low MW fraction content (%)	$\bar{M}_n \times 10^{-3}$, SEC	$\bar{M}_w/\bar{M}_n$
1	D_3	2.30	14.0	1.5	20	100	89	11	25	1.4
2	D_3	1.60	1.01	1.7	2	38	30	8	40	1.1
3	D_3	1.65	1.02	1.7	2	90	82	8	100	1.4
4	**2**	1.22	13.4	2.1	20	100	48	52	20	1.6
5	**2**	1.37	2.05	2.5	20	100	85	15	110	1.4
6	**2**	1.41	1.95	2.0	2	95	86	9	40	1.2
7	**2**	1.40	1.00	2.0	2	65	60	5	80	1.1
8	**2**	1.41	1.02	2.1^d	2	80	71	9	70	1.3
9	**1**	1.46	2.00	2.2	20	98	89	9	130	1.3
10	**1**	1.60	1.00	2.7	2	97	89	8	190	1.3
11	**1**	1.61	1.00	2.1	2	90	81	9	30	1.2
12	**1**	1.65	1.02	2.2	2	98	85	13	160^e	1.5
13	**1**	1.66	10.0	0.2	2	86	82	4	40	1.5
14	V_3	1.43	1.00	2.1	2	96	89	7	40	1.3

[a] Checked by GC. [b] Polymer recovered after precipitation in MeOH. [c] In $CHCl_3$ on Waters columns with refractive index detector using a polystyrene calibration curve. [d] [221] was used instead of [211]. [e] $\bar{M}_n$ determined by osmometry in toluene at 37 °C.

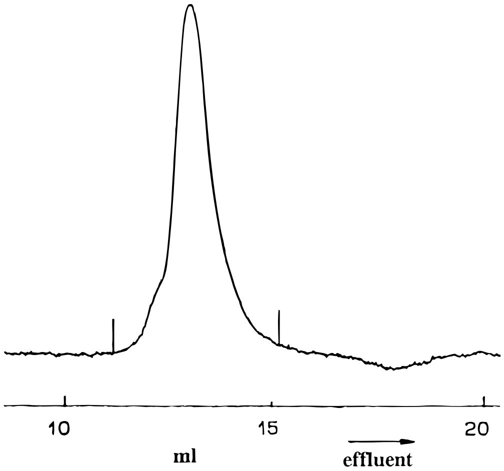


Figure 1. Size exclusion chromatogram of the copolymer obtained by the anionic polymerization of 1,2,2,3,3-pentamethyl-1-vinylcyclotrisiloxane, **1**, in toluene, at 2 °C, initiated by Me_3SiCH_2Li + [211], [211]/[Li$^+$] = 2.1, $\bar{M}_n$ = 30 000, $\bar{M}_w/\bar{M}_n$ = 1.2.

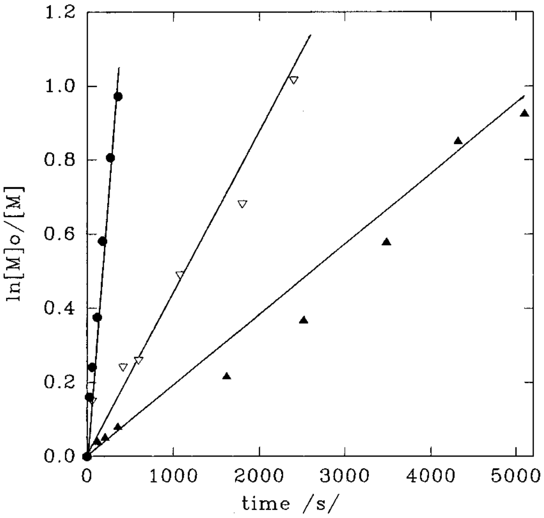


Figure 2. First-order dependence for the polymerization of cyclotrisiloxanes in toluene at 2 °C initiated by Me_3SiCH_2Li with cryptands, $[Li^+] = 1 \times 10^{-3}$ mol dm^{-3}, [cryptand]/[Li$^+$] = 2: (▽) hexamethylcyclotrisiloxane, D_3, with Li^+ + [211], (●) 1-[2-(*tert*-butylthio)ethyl]-1,3,3,5,5-pentamethylcyclotrisiloxane, **2**, with Li^+ + [211], and (▲) **2**, with Li^+ + [221] as counterions.

Table 2. Comparison of Rate Constants of Propagation on Cryptated Lithium Silanolates in the Polymerization of Cyclotrisiloxanes in Toluene at 2 °C^a

no.	monomer	cryptand	k_p (dm^3 mol^{-1} s^{-1})	$k_p/k_p(D_3)$
1	D_3	[211]	0.37	1
2	D_3	[211]	0.4^b	
3	**1**	[211]	0.55	1.5
4	**2**	[211]	2.6	7
5	**2**	[221]	0.22	0.6
6	V_3	[211]	7.2	19

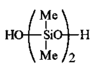
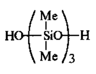
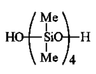
[a] $[SiO^-Li^+]_0 = 1 \times 10^{-3}$ mol dm^{-3}, [crypt]/[SiO^-Li^+] = 2, $[M]_0$ = 1.4 mol dm^{-3}. [b] From ref 55.

1 and **2**. The selectivity of the polymerization toward the formation of linear polymers was high as well. Polymer yields were much larger than in the equilibrium polymerization particularly for the monomer bearing the bulky 2-(*tert*-butylthio)ethyl group. Even when the polymerization was quenched at a high monomer conversion, the content of cyclic oligomers was relatively low, below 10%, showing that back-biting processes were considerably reduced. Thus, it is possible to achieve a yield of linear polymer of about 90% of the total amount of siloxane, while equilibration permits to obtain these polymers with 40−60% yields under the conditions used here.

The polymers had a relatively narrow molecular weight distribution. The $\bar{M}_w/\bar{M}_n$ ratio was within the range of 1.1−1.4 for polymerizations quenched below 99% of monomer conversion. This result is satisfactory taking into account that synthesis of polysiloxanes of narrow molecular weight distribution is particularly difficult when a monofunctional initiator is used.[60] This initiator gives rise to the polymer chain having an active propagation center only at one of its ends, while the presence of even traces of water may lead to a substantial amount of chains growing in two directions. Thus, separate populations of higher molecular weights may be formed. Polymers obtained here showed unimodal distributions of chain size; however, a shoulder on the high molecular weight wing of the SEC peak was sometimes observed due to this effect (see, for example, Figure 1).

The choice of a suitable cryptand having a ring size fitting the Li^+ ion size seems to be important. Although the Me_3SiCH_2Li + [211] complex was the initiator of choice an experiment with the polymerization of the organic sulfur group-substituted monomer **2** initiated by the Me_3SiCH_2Li + [221] complex was carried out as well (Table 1, entry 8) with the aim of decreasing the rate of propagation to make the control of this reaction

Table 3. Synthesis of Alternating Copolymers with Methylvinylsiloxane and Dimethylsiloxane Units by Polycondensation

experiment no	comonomer I	comonomer II	yield[a]	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$
15	$\mathrm{Me(CH_2{=}CH)SiCl_2}$	 $\mathrm{HO(SiMe_2O)_2H}$	32%	5000	2.3
16	$\mathrm{Me(CH_2{=}CH)SiCl_2}$	 $\mathrm{HO(SiMe_2O)_3H}$	35%	2600	2.3
17	$\mathrm{Me(CH_2{=}CH)SiCl_2}$	 $\mathrm{HO(SiMe_2O)_4H}$	30%	2600	2.4
18	$\mathrm{Me(CH_2{=}CH)SiCl_2}$	no	51%	2500	2.3
19	$\mathrm{Me(CH_2{=}CH)SiCl_2}$	$\mathrm{Me_2Si(OH)_2}$	22%	2900	2.4

[a] Yield of polymer recovered by precipitation in methanol.

easier. The polymerization proceeded at a much lower rate (see Figure 2), although the content of cyclic products was low and the heterogenity factor was still only 1.3. The sequencing of siloxane units in the copolymer chain was, however, less regular than that of the copolymer obtained with the [211] + $\mathrm{Li^+}$ complex. Another method for slowing down the reaction was to use a lower [211]/$\mathrm{Li^+}$ ratio (Table 1, entry 13). The molecular weight distribution was broader in this case, and complete neutralization and removal of lithium required a longer time. The polymerization proceeded according to the first-order internal kinetics up to a high monomer conversion (see Figure 2).

Rate constants of the polymerization of the four monomers studied are presented in Table 2. Since the initiation is fast and should be complete, the observed differences in rates reflect differences in reactivities in the propagation step. The initiator used here has recently been shown to produce quantitatively silanolate$-\mathrm{Li^+}$[211] ion pairs;[59] thus, the rate of monomer consumption may be represented by kinetic eq 3:

$$-\frac{d[M]}{dt} = k_p\{\equiv\mathrm{SiO^-Li^+} + [211]\}[M] \qquad (3)$$

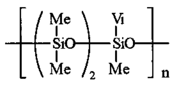
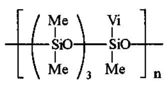
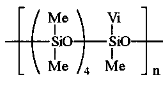
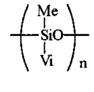
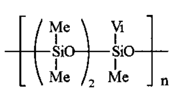
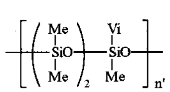
where the concentration of active propagation centers is equal to the initial concentration of [(trimethylsilyl)methyl]lithium when the ratio of [211]/$\mathrm{Li^+}$ is >1.

$$\{\equiv\mathrm{SiO^-Li^+} + [211]\} = [\mathrm{Me_3SiCH_2Li}]_0$$

The interesting observation is that the introduction of one vinyl group to D_3 changes only little the rate of polymerization, while the substitution of 1 vinyl group/silicon atom results in an increase of the propagation rate constant by a factor of 20. Thus, the effect of the substituent is not additive which implies that the reactivity–structure dependence is complex and more than one factor should be considered. The discussion of the influence of the structural effects on the rate of propagation will be continued in paragraph 5.

3. Synthesis of Model Poly(dimethylsiloxane-*co*-methylvinylsiloxane)s by Polycondensation. Some model dimethylsiloxane–methylvinylsiloxane copolymers of regular structure were synthesized by polycondensation of methylvinyldichlorosilane with oligo(dimethylsiloxane-α,ω-diol)s. The solution heterofunctional stoichiometric polycondensation was performed using triethylamine as the hydrogen chloride

Table 4. Modification of Poly(dimethylsiloxane-*co*-methylvinylsiloxane)s by Addition of *tert*-Butyl Mercaptan in Toluene at 60 °C

no	copolymer used		conditions		product			
	formula	origin[a]	$[\mathrm{t\text{-}BuSH}]_0/[\mathrm{Vinyl}]_0$	time of reaction h	conversion %	$\overline{M}_n$[b] observed	$\overline{M}_n$[c] calculated	$\overline{M}_w/\overline{M}_n$
1	 $[(\mathrm{SiMe_2O})_2\mathrm{SiMeViO}]_n$	het. polycond. 15	1.1	4	100	6000	6700	2.4
2	 $[(\mathrm{SiMe_2O})_3\mathrm{SiMeViO}]_n$	het. polycond. 16	1.5	4	100	2700	3200	2.4
3	 $[(\mathrm{SiMe_2O})_4\mathrm{SiMeViO}]_n$	het. polycond. 17	1.1	4	100	2700	3000	2.5
4	 $(\mathrm{SiMeViO})_n$	hydr. polycond. 18	1.1	8	91	4700	4500	2.3
5	 $[(\mathrm{SiMe_2O})_2\mathrm{SiMeViO}]_n$	r.o.p. 12	1.1	2	48	-	-	-
6	 $[(\mathrm{SiMe_2O})_2\mathrm{SiMeViO}]_{n'}$	r.o.p. 13	1.5	5	100	59000	58000	1.7

[a] Abbreviations: het. polycond., heterofunctional polycondensation; hydr. polycond., hydrolytic polycondensation; r.o.p., ring-opening polymerization. Numbers correspond to the numbers of experiments presented in Tables 1 and 3. [b] Measured by SEC. [c] From M_n of the starting copolymer and the conversion of Si-Vi groups.

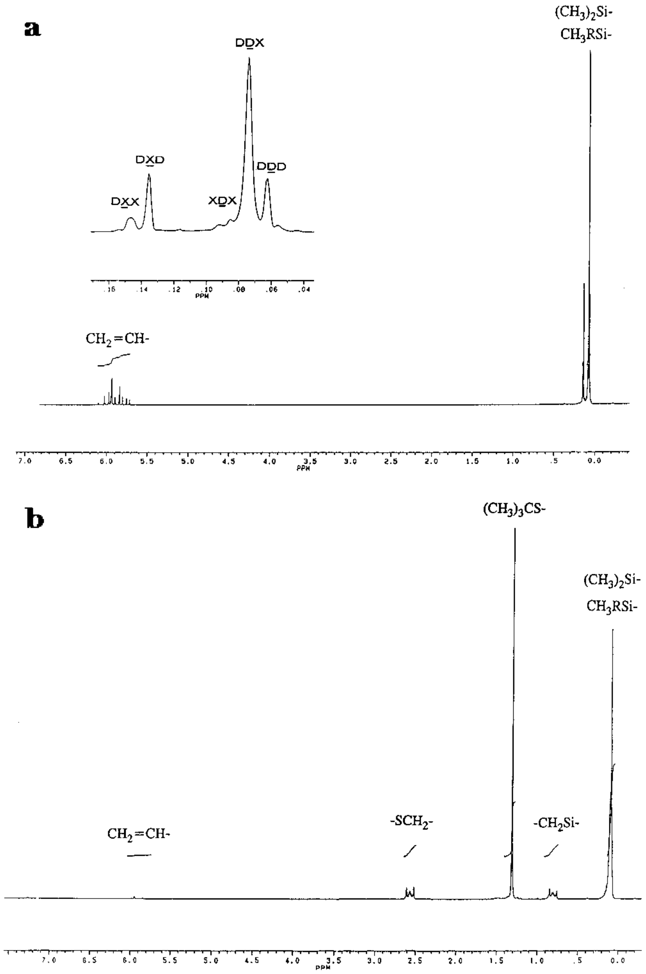


Figure 3. ^{1}H NMR spectra in C_6D_6 of (a) the MeViSiO–Me$_2$SiO copolymer synthesized by anionic polymerization of **1** (expt no. 12), $\bar{M}_n$ = 160 000, and (b) the same copolymer after modification by hydrosulfidation with *t*-BuSH; 92.6% of the vinyl groups were converted to the thioether groups.

acceptor and DMAP, 4-(*N*,*N*-dimethylamino)pyridine, as the nucleophilic catalyst[61] according to eq 2. Conditions were used to eliminate the homofunctional silanol condensation. Indeed, this undesired process played only a marginal role.

Hydrolytic polycondensation of MeViSiCl$_2$ was performed as well to obtain methylvinylsiloxane homopolymer. Characteristics of copolymers and the homopolymer are presented in Table 3.

4. Addition of the Organosulfur Group to Poly(dimethylsiloxane-*co*-methylvinylsiloxane)s. Poly(dimethylsiloxane-*co*-methylvinylsiloxane)s obtained by the polycondensation and the ring-opening polymerization were subjected to addition of *tert*-butyl mercaptan according to eq 1. The process proceeded on a free-radical route[39] and was initiated by AIBN. The reaction was stopped by cooling and the polymer isolated and subjected to ^{1}H NMR and SEC analyses. The progress of the reaction was deduced from comparison of the integration of vinyl signals at 5.7–6.05 ppm with those of $\equiv SiCH_2CH_2S$*t*-Bu at 0.85 and 2.55 ppm. Conditions of modification and characteristics of the modified polymers are presented in Table 4, and examples of ^{1}H NMR spectra are shown in Figure 3.

In many cases the reaction led to quantitative or almost quantitative transformation of the vinyl side groups. Free-radical reactions of the vinyl group, leading to branching and cross-linking, played a minor role under conditions used here, as good agreement was observed between molecular weight calculated and found (see Table 4). Instead, a significant increase in viscosity occurred when the polymer solution was heated with AIBN at 60 °C for a long time in the absence of the sulfur reagent. Thus, the presence of *t*-BuSH inhibits the branching process.

Generally, the reaction proceeds more slowly than the addition of *t*-BuSH to vinyl-substituted monomer **1**. The addition seems to occur more readily in polymers of lower molecular weight. The density of vinyl groups along the chain is also important. The homopolymer obtained by the hydrolytic polycondensation of MeViSiCl$_2$ having the vinyl group at every silicon atom is more reluctant to the addition (entry 4), while the reaction of the polymer having the vinyl group at every four silicon atoms proceeds smoothly to give complete vinyl conversion (entry 3). Thus, a considerable excess of mercaptan is recommended, particularly in the case of hydrosulfidation of copolymers having high molecular weight and a large proportion of vinyl groups, to accelerate the reaction and prevent the formation of branching and cross-linking.

The inspection of the ^{29}Si and ^{1}H NMR spectra before and after the modification led to the conclusion that the siloxane chain redistribution and depolymerization did not occur during the modification.

5. Polymer Chain Structure—Siloxane Unit Sequencing. The arrangement of siloxane units X = [*t*-BuS(CH$_2$)$_2$]MeSiO or ViMeSiO and D = Me$_2$SiO in chains of polymers obtained by the anionic polymerization of **1** and **2** as well as in the polymer modified by the addition of *t*-BuSH to the vinyl groups was studied by ^{29}Si NMR spectroscopy. The quantitative analysis of the chain microstructure was performed on the level of triads using a 300 MHz spectrometer. The assignment of signals for triads and pentads (Table 5) was made for the vinyl-substituted polymer using model polymers characterized in Table 3. The data from earlier studies of Ziemelis and Saam[46] were very helpful in this assignment. The inspection of the spectrum of the copolymer obtained by the quenched polymerization of **1** (Figure 4) permits to conclude that the arrangement of the siloxane units in the chain is controlled by the propagation step. In the MeViSiO resonance region, the X$\underline{X}$X triad is absent and signals of three pentads only appear, i.e., DD$\underline{X}$DD, DD$\underline{X}$DX, and DD$\underline{X}$XD. The remaining seven X-centered pentads, except XD$\underline{X}$DX, cannot be formed if the monomer **1** enters as integral into the polymer chain. Similarly the polymer does not contain three D-centered pentads: DD$\underline{D}$DD, XX$\underline{D}$XD, and XX$\underline{D}$XX, which could result from secondary reactions, such as back-biting, chain scrambling, or specific redistribution. Thus, the monomer enters the polymer chain as integral. Consequently, the sequencing of units in the chain is fully determined by the place in which the monomer ring is opened and attached to the chain end.

The analysis of triads is presented in Table 6. The percent contribution from triads in copolymers obtained in this study placed in columns A–C was determined from integrations of the peaks for the corresponding triads in the NMR spectrum. The addition of Cr(AcAc)$_3$ complex to the analyzed polymer samples and the use of inverse gated pulse technique ensured the quantitative integration. Theoretical triad contributions for three cases, (i) the arrangement assuming random monomer opening and addition with no other chain cleavage process (column D), (ii) regular structure

Table 5. ^{29}Si NMR Shifts (ppm) for Pentads and Triads of Poly(dimethylsiloxane-*co*-methylvinylsiloxane)s and Poly[[2-(*tert*-butylthio)ethyl]methylsiloxane-*co*-dimethylsiloxane]s Assigned on the Basis of Chemical Shifts for Model Copolymers in CDCl$_3$ at 25 °C

pentads[a]	X = MeViSiO	X = [t-BuS(CH$_2$)$_2$]MeSiO	pentads[a]	X = MeViSiO	X = [t-BuS(CH$_2$)$_2$]MeSiO
$\mathrm{DD\underline{D}DD}$	−21.66	−21.66	$\mathrm{XX\underline{X}XX}$	−34.63	−23.62
$\mathrm{XD\underline{D}DD}$	−21.58	−21.46	$\mathrm{DX\underline{X}XX}$		
$\mathrm{XD\underline{D}DX}$	−21.49	−21.36	$\mathrm{DX\underline{X}XD}$		
$\mathrm{DX\underline{D}DD}$	−21.18	−21.36	$\mathrm{XD\underline{X}XX}$	(−35.00)	
$\mathrm{XX\underline{D}DD}$	(−21.10)	(−21.30)	$\mathrm{DD\underline{X}XX}$		
$\mathrm{DX\underline{D}DX}$	−21.10	−21.19	$\mathrm{XD\underline{X}XD}$	(−35.13)	
$\mathrm{XX\underline{D}DX}$	(−21.01)	(−21.15)	$\mathrm{DD\underline{X}XD}$	(−35.19)	(−24.35)
$\mathrm{DX\underline{D}XD}$	−20.64	(−21.06)	$\mathrm{XD\underline{X}DX}$	−35.45	(−24.50)
$\mathrm{XX\underline{D}XD}$	(−20.59)	(−21.02)	$\mathrm{DD\underline{X}DX}$	−35.50	
$\mathrm{XX\underline{D}XX}$	(−20.54)	(−20.97)	$\mathrm{DD\underline{X}DD}$	−35.56	−24.68
triads			triads		
$\mathrm{D\underline{D}D}$	−21.49 to −21.66	−21.36 to −21.66	$\mathrm{X\underline{X}X}$	−34.63 to −34.80	−23.62 to −23.80
$\mathrm{X\underline{D}D}$	−21.01 to −21.18	−1.15 to −21.36	$\mathrm{D\underline{X}X}$	−35.00 to −35.19	−24.00 to −24.35
$\mathrm{X\underline{D}X}$	−20.54 to −20.64	−20.97 to −21.06	$\mathrm{D\underline{X}D}$	−35.45 to −35.56	−24.50 to −24.68

[a] D = Me$_2$SiO. Values in parentheses were deduced on the basis of literature data (ref 46) or from closer analysis of spectra of copolymers.

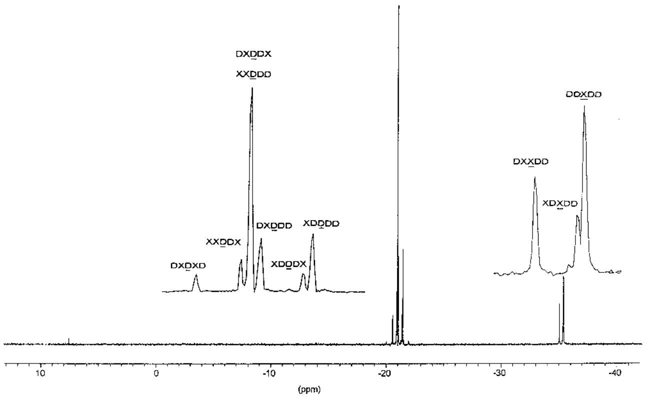
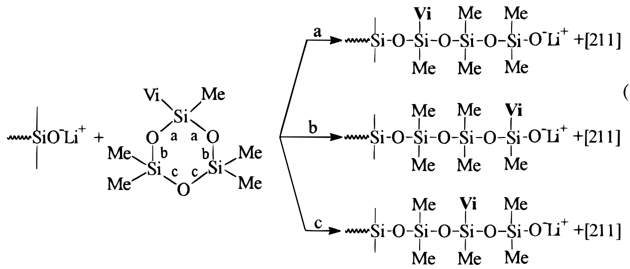


Figure 4. ^{29}Si NMR spectrum of the MeViSiO−Me$_2$SiO copolymer obtained by the anionic polymerization of 1-vinyl-1,3,3,5,5-pentamethylcyclotrisiloxane, **1**, in toluene, at 2 °C, initiated by Me$_3$SiCH$_2$Li + [211] ([Li$^+$] = 1 × 10^{-3} mol dm^{-3}, [211]/[Li$^+$] = 2.1), quenched at 90% of monomer conversion. The spectrum was taken in toluene-d_8 using the DEPT technique at 59.63 MHz.

assuming the same mode of the monomer addition, i.e., fully regioselective addition (column E), and (iii) the structure for the random equilibrium polymerization (column F), were calculated according to the method described in ref 62. Run number *R* was calculated from the mol % contribution of triads according to equation 4,[63] where $\mathrm{X\underline{D}D}$ denotes both undistinguishable triads $\mathrm{X\underline{D}D}$ and $\mathrm{D\underline{D}X}$, and similarly $\mathrm{D\underline{X}X}$ denotes $\mathrm{D\underline{X}X}$ and $\mathrm{X\underline{X}D}$:

$$R = [\mathrm{D\underline{X}D}] + {}^1/_2[\mathrm{D\underline{X}X}] + [\mathrm{X\underline{D}X}] + {}^1/_2[\mathrm{X\underline{D}D}] \quad (4)$$

The triad content pattern found for the polymer obtained by quenched polymerization of **1** (column A) shows closer similarity to this calculated for the copolymer from the random addition process than to that which would be formed when the addition was regioselective (column E). However, a more precise inspection of the data discloses that there is a significant preference of one way of addition. In particular, there is a higher content of $\mathrm{X\underline{D}D}$ triads and a lower content of $\mathrm{X\underline{D}X}$ triads as compared with that in the copolymer obtained by the random addition. The analysis of triads in connection with kinetic data in Table 2 permits to draw some conclusions about the way in which the monomer is opened. The open chain monomer unit may be added to the growing chain end on three different ways depending on the place in which the monomer is opened (eq 5).



(5)

Inspection of kinetic data in Table 2 leads to the conclusion that polar effects of substituents play a much more important role than their steric effects. It should be taken into account that the vinyl group exerts an electron-withdrawing inductive effect represented by the Taft parameter $\sigma^* = 0.4$.[64] This effect decreases the electron density on the silicon atom to which the vinyl group is attached making it more sensitive to nucleophilic attack, which promotes route a. On the other hand, this negative inductive effect stabilizes the negative charge on the silanolate anion thus promoting route b. The second variant (route b) is in a better agreement with the observed rate of polymerization of **1** relative to the rate of polymerization of D$_3$. In this case the effect of the stabilization of the charge on the silanolate is to make the ring opening easier (effect of a better leaving group) while decreasing the reactivity of the propagating center affecting the polymerization rate in the opposite direction. Thus, the net result is a similar rate of polymerization of **1** and D$_3$ (see Table 2). V$_3$ reacts much faster since the reaction is additionally promoted by the enhanced electrophilicity of the silicon center as the nucleophilic attack in this case must be directed to the MeViSiO unit which appears as the exclusive unit in this monomer. The effect of a better leaving group for monomer **1** is not very large. Although route b is privileged, the ring opening according to routes a and c occurs as well. Quantitative contributions from these three routes cannot be calculated on the bases of analysis of triads. A rough estimation is possible assuming that one of the three possible types of addition occurs predominantly and the remaining other two introduce perturbation to the regular polymer chain structure. Any of these irregular additions is preceded and followed by the regular one.[62]

Let us assume that preferential addition b constitutes fraction *p* of the total addition number. Assuming that this mode of the chain formation is perturbed by the irregular additions a and c constituting fractions *r* and

Table 6. Comparison of Contribution of Triads (mol %) Found for the Copolymers Obtained by Kinetically Controlled Polymerization of 1 (A) and 2 (B) and by the Ene−Thiol Addition to the Copolymer Obtained by the Polymerization of 1 (C) with Those Calculated for the Corresponding Copolymers on Assumption of Either Statistical Addition of Monomer to Polymer Chain (D) or Fully Regioselective Addition (E)[a]

	determined			calculated		
triad	A, X = MeViSiO from polymerization of **1**[b]	B, X = [*t*-BuS$(CH_2)_2$]MeSiO from polymerization of **2**[c]	C, X = [*t*-BuS$(CH_2)_2$]MeSiO from modification of copolymer in column A	D, statistical addition	E, regioselective addition	F, for equilibrium polymerization
$\mathrm{D\underline{X}D}$	24.5	20.8	24.9	25.9	33.3	14.8
$\mathrm{D\underline{X}X}$	8.8	12.4	8.4	7.4	0	14.8
$\mathrm{X\underline{X}X}$	0	0	0	0	0	3.7
$\mathrm{X\underline{D}X}$	4.1	7.7	4.2	7.4	0	7.4
$\mathrm{X\underline{D}D}$	50.4	42.8	51.4	44.4	66.7	29.6
$\mathrm{D\underline{D}D}$	12.1	16.2	11.0	14.8	0	29.6
R^d	58.2	56.1	59.0	59.2	66.7	44.5
$l_D{}^e$	2.26	2.37	2.26	2.26	2.0	3.0
$l_X{}^e$	1.13	1.19	1.13	1.13	1.0	1.5

[a] Data for fully equilibrated copolymer also is included (F). [b] Sample from polymerization no. 10. [c] Sample from polymerization no. 7. [d] Run number calculated from eq 4. [e] Average sequence lengths of D and X units, respectively.

s, respectively, we may write the following set of eqs 6. These equations are only approximate neglecting the possibility that the irregular addition may occur subsequently after each other:

$$[\mathrm{D\underline{X}D}] = \frac{100}{3}(p - r + s)$$

$$[\mathrm{X\underline{X}D}] = \frac{200}{3}r$$

$$[\mathrm{D\underline{D}X}] = \frac{200}{3}p$$

$$[\mathrm{D\underline{D}D}] = \frac{100}{3}(2r + s)$$

$$[\mathrm{X\underline{D}X}] = \frac{100}{3}s \qquad (6)$$

Calculated values were 0.76, 0.12, and 0.12 for *p*, *r*, and *s*, respectively, which means that over 70% of the addition occurs by route b.

Analysis of the arrangement of units in the polymer containing the thioether group was more difficult as signals of pentads are closer to each other and differentiation on the level of heptads complicates the spectra. Signals of pentads are broader, and some of them show splitting as shown in Figure 5. The assignment for pentads was made using model polymers characterized in Table 4. This assignment served for the separation of triads. Unfortunately signals for two pentads, i.e., $\mathrm{XD\underline{D}DX}$ and $\mathrm{DX\underline{D}DD}$, belonging to two different triads coincided (see Figure 6). The separation was made assuming that the contributions from both pentads are the same as in the vinylsiloxane copolymer. Contribution from triads is shown in Table 6—column B for the copolymer obtained by the polymerization of **2** and column C for the copolymer obtained by the addition of *t*-BuSH to the vinyl-substituted polymer. The comparison of the data in columns C and A indicated that the modification of the precursor polymer proceeded without a change in the arrangement of siloxane units as contributions from the corresponding triads in the polymer before and after the modification are the same within the experimental errors. This conclusion was fully confirmed by comparison of spectra of model copolymers before and after the modification (an example is shown in Figure 6). Analysis of the results in column E and those of spectra in Figure 5 made in an analogous way to the analysis for the vinyl copolymer permits to conclude that the microstructure is controlled by the propagation process and monomer enters as integral to the polymer chain. However, the regioselectivity of the ring opening is lower than in the polymerization of monomer **1**. The relatively high rate of the polymerization of **2** as compared with that of **1** could be explained at least in part by the inductive effect of the sulfur group assuming a different way of the monomer ring opening in the propagation step in the polymerization of **2** and **1**. The increase in the rate by the inductive effect of the sulfur substituent would be expected if the nucleophilic attack of silanolate active center was more often directed to the more electrophilic silicon of the sulfur-substituted siloxane unit.

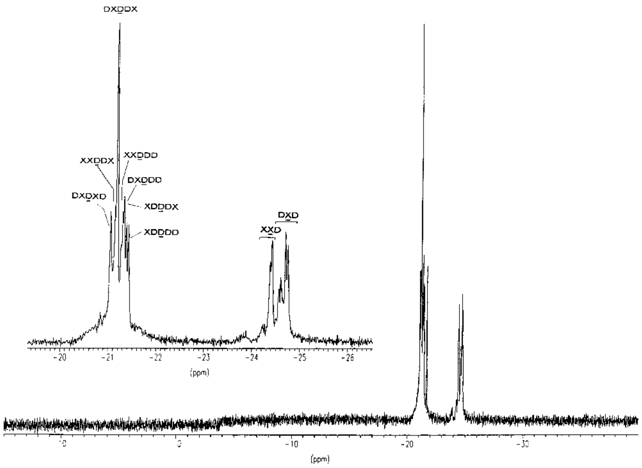


Figure 5. ^{29}Si NMR spectrum of the [*t*-BuS$(CH_2)_2$]MeSiO−Me_2SiO copolymer obtained by anionic polymerization of [*t*-BuS$(CH_2)_2$]MeSiO$(Me_2SiO)_2$, **2**, in toluene, at 2 °C, initiated by Me_3SiCH_2Li + [211], ($[Li^+] = 1 \times 10^{-3}$ mol dm^{-3}, [211]/$[Li^+] = 2.0$), quenched at 65% of the monomer conversion. The spectrum was taken in toluene-d_8 using the DEPT technique at 59.63 MHz.

In spite of low regioselectivity of the propagation in the studied polymerization of **2**, the polymer obtained by this way has the siloxane units arranged in a considerably more uniform way than in the statistical copolymer. This conclusion may be drawn from comparison of data in columns B and F of Table 6.

Experimental Section

Chemicals. Solvents used for synthesis: pentane, THF, toluene, and dioxane, were purified according to methods described in ref 65. Toluene used as the solvent in polymer-

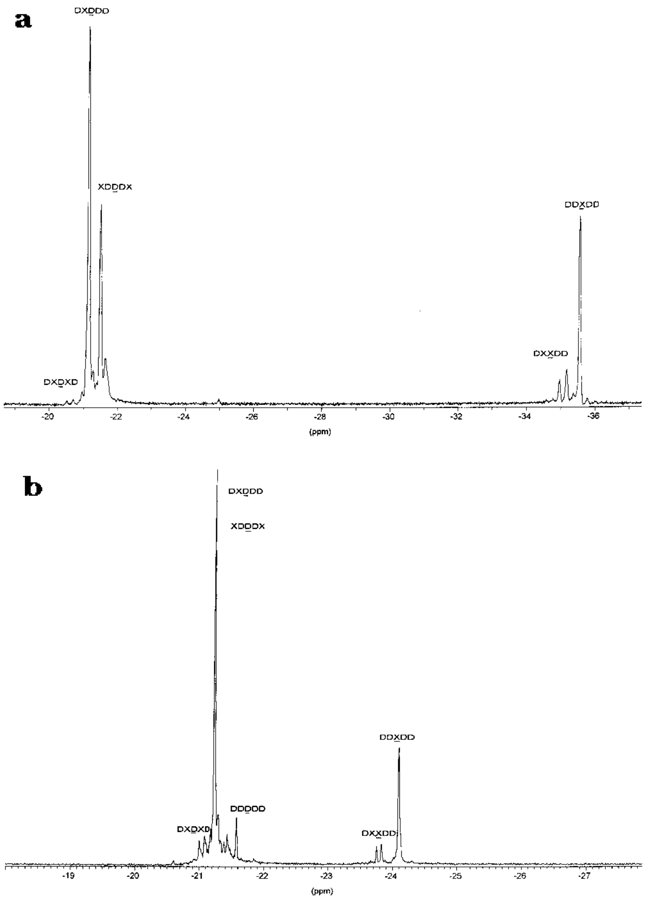


Figure 6. ^{29}Si NMR spectra of the MeViSiO−Me_2SiO copolymer obtained by the polycondensation of $HO(SiMe_2O)_3H$ with $MeViSiCl_2$ (a) before the addition of *t*-BuSH and (b) after the addition of *t*-BuSH. Spectra were taken in C_6D_6 solution using the IGATED technique at 59.63 MHz.

ization experiments was additionally refluxed over sodium during 48 h and then distilled and kept over freshly prepared sodium mirror. Hexadecane used as the standard in the GC analysis was first distilled from CaH_2.

Monomers: hexamethylcyclotrisiloxane, D_3 (**3**), 1,3,5-trivinyl-1,3,5-trimethylcyclotrisiloxane V_3 (**4**), vinylmethyldichlorosilane, and 1,1,3,3-tetramethyldisiloxane were reagent grade commercial products of ABCR GmbH & Co. They were purified by distillation. Their purity checked by gas chromatography was 99.5%, 99%, 98%, and 98.5% respectively.

Cyclic monomers were further purified by heating with CaH_2 for at least 15 h at 45−70 °C followed by vacuum distillation to the reactor in which the polymerization was performed.

Tertiary butyl mercaptan, Aldrich reagent grade, was distilled shortly before use. The initiator AIBN and the catalyst 5% Pd/C, both products of Aldrich, were used without purification. Cryptands [211] and [221] of Aldrich were purified by distillation under vacuum (for [211] bp 120 °C/10^{-4} mmHg) in a quartz apparatus.[55]

[(Trimethylsilyl)methyl]lithium initiator of the anionic polymerization sold as 0.1 N solution in pentane by Aldrich was purified on a high-vacuum line.[57] First pentane was removed from Me_3SiCH_2Li, which was then sublimated on the vacuum line to an ampule with a Rotaflo stopcock. Then prepurified toluene was distilled to the ampule to make the stock solution of the initiator. The concentration of the initiator in the stock solution was determined as an average of the concentrations determined by the titration of the Me_3SiCH_2Li solution with and without addition of an excess of $BrCH_2CH_2Br$ using 0.1 N analytical solution of HCl in water according to the procedure described for butyllithium in ref 66.

1,1,3,3-Tetramethyldisiloxane-1,3-diol was synthesized by a modified procedure described in ref 67. Thus, in a three-necked 250 mL flask fitted with a dropping funnel, a thermometer, and a condenser were placed dried dioxane, 50 mL, distilled water, 3.6 g (0.2 mol), and Pd/C, 0.12 g (0.056 mol). The flask was thoroughly purged with pure argon, and 1,1,3,3-tetramethyldisiloxane, 13.5 g (0.1 mol), was slowly introduced to the vigorously stirred reaction mixture through which argon was bubbled to remove the H_2 formed. The temperature was maintained at 40 °C during the disiloxane addition. Then, the reaction mixture was filtrated through silica gel. The filtrate was dried with $MgSO_4$, and dioxane was distilled off. 1,1,3,3-Tetramethyldisiloxane-1,3-diol was isolated, 15.8 g (0.095 mol), yield 95%. It was further purified by crystallization from Et_2O/hexane. Its melting point was 67−67.5 °C, and its purity checked by gas chromatography was 98%.

1,1,3,3,5,5-Hexamethyltrisiloxane-1,5-diol was synthesized by hydrolysis of the corresponding α,ω-dichlorooligosiloxane. Thus, 1,5-dichlorohexamethyltrisiloxane, 27.7 g (0.1 mol), was added dropwise during 1.5 h to a vigorously stirred mixture of 300 mL of diethyl ether, 300 mL of distilled water, 13.5 g (0.14 mol) of ammonium carbonate, and 0.2 g of (dimethylamino)pyridine at 0 °C in a three-necked flask. The mixture was stirred for a further 60 min; then it was saturated with sodium chloride, and the ethereal layer was separated and then dried over $CaCl_2$. The ether was then removed by evaporation, and the resulting oil was distilled under reduced pressure to give 21 g (0.087 mol) of 1,1,3,3,5,5-hexamethyltrisiloxane-1,5-diol, yield 87%, bp 48 °C/10^{-1} mmHg. Purity checked by gas chromatography was 99.2%.

1,1,3,3,5,5,7,7-Octamethyltetrasiloxane-1,7-diol and monomeric dimethylsilanediol were synthesized in an analogous way. The synthesis of 1,3,3,5,5-pentamethyl-1-vinylcyclotrisiloxane (**1**) was described earlier.[43]

1-[2-(*tert*-Butylthio)ethyl]-1,3,3,5,5-pentamethylcyclotrisiloxane (2). In a 20 mL three-necked flask equipped with a magnetic stirrer, a condenser, a syringe, and nitrogen inlets were placed 11.72 g (0.05 mol) of vinylpentamethylcyclotrisiloxane and 41 mg (0.25 mmol) of AIBN. The mixture was heated gently to 40 °C, and 4.96 g (0.055 mol) of freshly distilled *tert*-butyl mercaptan was introduced dropwise. Then, the mixture was stirred at 60 °C. After 3 h the mixture was distilled to give 14.60 g of pure **2**, yield 90%, bp 128 °C/10 mmHg. GC analysis revealed the presence of about 3% of the Markovnikov product (α adduct).

Polymerization. Polymerization of the cyclic trisiloxane monomers **1**, **2**, D_3, and V_3 was carried out in two steps under argon. Monomer was first allowed to react with Me_3SiCH_2Li in toluene during 2 h in order to obtain lithium silanolates. Then the promoter (cryptand [211] or [221]) was added to the stirred and thermostated mixture. No polymerization occurred even with a large excess of monomer until the promoter was added to the mixture. The polymerization was quenched by adding a small excess of Me_3SiCl. The polymer solution was washed with water and dried with magnesium sulfate; then the solvent was partly evaporated, and the concentrated polymer solution was introduced to a large volume of vigorously stirred methanol. The isolated polymer was heated at 60 °C/10^{-4} mmHg for 8 h. Polymers were characterized by SEC (Table 1).

Kinetic Studies of Polymerization. All the polymerization experiments were carried out in a thermostated apparatus under pure argon. Kinetics of the polymerization of cyclotrisiloxanes were followed by gas chromatography. The GC analysis was performed on a GIRDEL model 3000 apparatus equipped with a thermal conductivity detector and columns, length 2 m or 1.2 m × $^1/_8$ in. × 2 mm, packed with 10% silicone OV-101, on Chromosorb WHP, 80−100 mesh, with the following conditions: temperature 70−280 °C (10 °C/min), detection temperature 310 °C, injection temperature 250 °C, $I = 90$ mA. Hexadecane was used as the internal standard. Response factors were determined in separate experiments.

Synthesis of Model Copolymers by the Heterofunctional Polycondensation Method. A solution of 8.3 g (0.05 mol) of tetramethyldisiloxane-1,3-diol, 10.1 g (0.1 mol) of Et_3N, and 0.25 g (2 mmol) of DMAP in 30 mL of THF was added to a stirred solution of 7 g (0.05 mol) of vinylmethyldichlorosilane in 20 mL of THF. Stirring was continued for 5 h. Then, 0.55

g (5 mmol) of Me_3SiCl was introduced. After separation of the precipitate of $Et_3N{\cdot}HCl$, the solvent and the excess of Me_3SiCl were distilled off under reduced pressure. The polymer was dissolved in CH_2Cl_2, washed with water, dried, and precipitated with MeOH. The polymer was dissolved in CH_2Cl_2 and again precipitated with MeOH. Then it was heated at 60 °C/10^{-4} mmHg for 8 h.

In an analogous way the polymers were obtained by polycondensation of vinylmethyldichlorosilane with 1,1,3,3,5,5-hexamethyltrisiloxane-1,5-diol, 1,1,3,3,5,5,7,7-octamethyltetrasiloxane-1,7-diol or dimethylsilanediol. The polymers were characterized by SEC and ^{29}Si NMR (Table 3).

Modification of Polymers. The addition of *tert*-butyl mercaptan to the vinyl group attached to the polymer chain was carried out according to the procedure similar to that described earlier for the addition of the mercaptan to the monomer. The reaction was performed in dried toluene solution containing 1:1 (v/v) of the polymer; 10–50% excess of *t*-BuSH was used. For example, 2 g of the dimethylsiloxane–methylvinylsiloxane copolymer containing 8.3 mmol of vinyl groups (Me/Vi = 5:1; $\bar{M}_n$ = 42 000) obtained by anionic polymerization of **1** was dissolved in 2 mL of prepurified toluene. To this solution were introduced 7 mg (0.04 mmol) of AIBN and 0.83 g (9.2 mmol) of *tert*-butyl mercaptan. The mixture was heated at 60 °C. The course of the addition reaction was controlled by sampling and ^1H NMR analysis. The heating was stopped after 5 h. The reaction mixture was allowed to cool to room temperature and evaporated. Then 30 mL of methanol was introduced. The precipitated polymer was isolated and dissolved again in toluene, and the precipitation procedure was repeated. The polymer was heated at 60 °C under vacuum (10^{-3} mmHg) for 8 h; 2.7 g of the polymer was obtained, yield 95%. The modified polymer was characterized by SEC and ^{29}Si NMR (Table 4). $\bar{M}_n$ = 59 000.

Physicochemical Characterizations. Size exclusion chromatograms were taken with a LDC analytical refractor monitor IV and LBK 2150-HPLC pump (RIDK 102). (Columns: Waters 1000 + 500 + 100 + 100 for lower molecular weights or TSK-Gel G 4000 HXL + G 2000 HXL for molecular weights above 20 000.) THF or $CHCl_3$ was used as the solvent. The calibration curve was constructed applying polystyrene standards.

^{29}Si and ^1H NMR analyses were performed using a Bruker NSL 300 spectrophotometer working at 59.63 and 300 MHz, respectively. The spectra were recorded also with a AM 200 SY Bruker apparatus. Tetramethylsilane was used as the standard. The proton-decoupled ^{29}Si NMR spectra were taken using the DEPT or the IGATED PULSE technique. For the studies of chain microstructure, 30 wt % solutions of polymers in $CDCl_3$ or toluene-d_8 were prepared. Before analysis 0.8 wt % of the chromium tri(acetylacetonate) complex, $Cr(AcAc)_3$, was added as the reagent shortening the time of relaxation. The proton-decoupled ^{29}Si NMR spectra were performed using the IGATED PULSE technique with a 20 s pulse time and accumulation of 80–160 scans.

Conclusions

1. The possibility and advantages of the synthesis of thioether-substituted siloxane copolymers of defined structure by kinetically controlled anionic homopolymerization of cyclotrisiloxane having mixed siloxane units were demonstrated. The sulfur group is fully preserved in the polymerization. The thioether function is arranged along the chain in a much more uniform way than in the case of the equilibrium copolymerization. The ring-opening polymerization leads to a high yield of polymer of narrow molecular weight distribution. The synthesis of such substituted polysiloxanes may be also performed in an alternative way. The cyclic trisiloxane containing one vinyl group is first polymerized under kinetic control. Then, the copolymer is modified by the ene–thiol addition.

It was shown that the polymerization initiated with a selective initiator, such as Me_3SiCH_2Li + [211], proceeds with almost full exclusion of processes involving the siloxane bond cleavage in the polymer formed. The monomers are incorporated into the polymer chain as integral. Thus, the arrangement of siloxane units in the polymer chain is controlled by the propagation step. Although the arrangement of the vinyl groups in the copolymer is not regular, i.e., the copolymer does not have the alternating structure, one mode of addition is privileged, which is explained by the inductive effect of the vinyl group.

2. Organic thioether groups may be introduced to polysiloxanes and strained cyclosiloxanes by the free-radical ene–thiol addition to vinyl groups pending to a siloxane chain or ring. The reaction may be performed with high yield without siloxane cleavage. Other side reactions, such as cross-linking by a free-radical reaction of the vinyl group, may be avoided.

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