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Synthesis of Branched Polysiloxanes with Controlled Branching and Functionalization by Anionic Ring-Opening Polymerization

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ABSTRACT: Functionalized branched polysiloxanes with star-branched, comb-branched and dendritic-branched topologies were synthesized. The branched macromolecules were generated by coupling of reactive blocks using a grafting technique (*ACS Polym. Prepr.* **2001**, *42*, 227; *ACS Symp. Ser.* **2003**, *838*, Chapter 2). The living anionic ring-opening polymerization (ROP) of vinyl-substituted cyclotrisiloxanes $(\mathrm{ViMeSiO})_3$, V_3, and, $\mathrm{ViMe\overline{SiO(SiMe_2O)}_2}$, VD_2, and the copolymerization of these monomers with hexamethylcyclotrisiloxane, D_3, was explored to obtain reactive blocks. Termination of the living polymer, having a lithium silanolate end group, on a reactive core containing SiCl groups led to the grafting of living polysiloxane on the core. Transformation of vinyl groups in the polymer into the reactive SiCl groups by hydrosilylation with $\mathrm{Me_2HSiCl}$ made possible the grafting of a successive generation of branches. The reactive blocks of high and low density of the precursor vinyl group were obtained by the polymerization of monomers V_3 and VD_2, respectively. While the homopolymerization led to a uniform density of vinyl groups along the chain, the copolymerization of V_3 or VD_2 with D_3 produced a gradient distribution with the density decreasing in the direction of the chain growth. This arrangement led to a higher density of the vinyl group in the external part of the branched macromolecule. Study of kinetics of the copolymerization of V_3 with D_3 in THF initiated by BuLi gave the reactivity coefficients $k_{V_3} = 17.8$, $k_{D_3} = 0.036$ (25 °C), from which the density distribution of vinyl groups in reactive blocks may be determined. Four-arm star copolymers were obtained using $(\mathrm{MeCl_2SiCH_2})_2$ as the core, whereas the comblike polysiloxane was obtained from a linear copolymer of ViMeSiO and $\mathrm{Me_2SiO}$ treated with $\mathrm{Me_2HSiCl}$. Dendritic polysiloxanes of the first and second generation were obtained using the functionalized starlike polysiloxane as the core.

Introduction

Highly branched polymers (dendritic-branched, star-branched, comb-branched) attract considerable attention as they may find application in many fields, such as catalysis, chromatography, electronics, optoelectronics, magnetoelectronics, paints and coatings, and medicine.[1−10] Since the unusual flexibility of polysiloxane chain and the inorganic character of its skeleton may be beneficial, a considerable effort has been devoted to synthesis of polysiloxanes of dendritic[10−18] and star-branched[19−22] topologies. Branched polysiloxanes of mixed structures, including carbosilane, polysilane, or organic polymer fragments, have been synthesized as well.[10,11,21−25]

The methods used so far to synthesize branched polysiloxanes are not general enough to construct all basic types of branched topologies, i.e., dendritic-, star- and comb- (brush-) branched. Some methods are focused on the control of molecular weight and polydispersion,[10,11] although other features, such as density, length, arrangement of branching, and the density and distribution of functional groups, may be most important for some specific applications, such as catalysts, sensors, drug delivery carriers, and NLO materials.

Two general routes to the cascade branched polysiloxanes were used. A one-pot synthesis by polymerization of a polyfunctional monomer or macromonomer[16−18] is fast and relatively cheap; however, control over the structure of the polymer product is poor. The other approach, a stepwise successive addition of new generations of branches to a spherical macromolecule was successfully used to synthesize regular polysiloxane dendrimers.[12−15] Although the macromolecular structure in this approach is controlled, the method is burdensome and time-consuming. Many repetitive synthetic steps performed with theoretical yield are required to obtain a high molecular weight dendrimer.

We present here a universal approach to the synthesis of branched polysiloxanes of various topologies with controlled branching and functionalization. It should be less time- and work-consuming than the synthesis of regular dendrimers, although its precision is lower. Our approach uses a stepwise coupling of larger building blocks and is based on a grafting technique. The building blocks are synthesized by controlled anionic ring-opening polymerization (ROP) of cyclotrisiloxanes, and the grafting is achieved by termination of living polysiloxane on a functionalized core.

The anionic ROP of cyclotrisiloxanes is useful for obtaining linear polysiloxanes functionalized at the end groups and side groups with controlled molecular weight and polydispersity.[27,28] It has been used to synthesize highly branched polysiloxanes[16−21] and siloxane-organic copolymers.[23,29−32] In particular, poly(dimethylsiloxane) macromonomers obtained by the anionic ROP of cyclotrisiloxane were exploited in building a hyperbranched polysiloxane by a one-pot synthesis,[16] and they were used in generation of polysiloxane grafted organic copolymers.[29] The anionic ROP of cyclotrisiloxane was also used to synthesize starlike polysiloxane[19,10] and miktoarm siloxane-organic star copolymers.[23]

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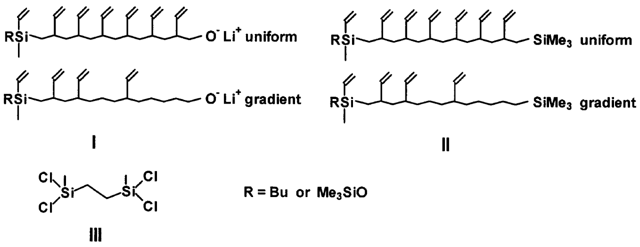
Scheme 1



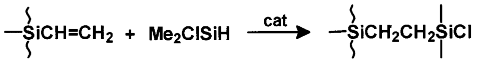
Results and Discussion

General Strategy. This study explores the anionic ROP of cyclotrisiloxanes as a universal method for synthesizing reactive building blocks to construct all-siloxane branched architectures. The anionic ROP of a cyclotrisiloxane produces a living polysiloxane having the silanolate active propagation center at one extremity. Termination of this living polymer with a SiCl group attached to a polysiloxane core leads to grafted polysiloxane on polysiloxane. Since the graft contains precursors of the SiCl groups, additional branches may be built. A similar grafting technique was used to synthesize some dendritic organic polymers,[33] with many branching points generated in one step. Thus, a highly branched polymer with high molecular weight can be obtained in only few steps. The control of density and arrangement of branching and functionalization could be achieved by using a graft with controlled density and arrangement of precursor groups.

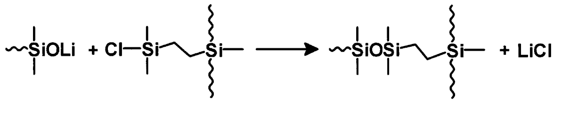
Branched polysiloxanes of various topologies were synthesized using the three types of building blocks shown in Scheme 1. They are as follows: (1) a living vinylmethylsiloxane polymer or its copolymer with dimethylsiloxane having a lithium silanolate group at one chain end (**I**); (2) a copolymer of vinylmethylsiloxane and dimethylsiloxane ending with nonreactive groups (**II**), (3) a low molecular weight polyfunctional core (**III**).

The polymeric building blocks contain vinyl functions pendant to the polysiloxane chain. Vinyl groups are precursors of coupling SiCl groups. They may also be precursors of numerous other functional groups as they undergo many addition reactions, such as hydrosilylation,[32] hydrophosphination,[34] ene-thiol addition,[35] and addition of transition-metal complexes.[36] The density of the vinyl groups along the chain may be controlled, being the highest if the vinyl group appears at each silicon atom. The lower density is achieved, when the methylvinylsiloxane are separated by Me_2SiO units. In such a case, the density of vinyl groups may be uniform or gradually decreasing in the direction of the polymer chain growth.

The formation of each generation of branched polysiloxane requires a sequence of two reactions: the transformation of the precursor groups into reactive functions (eq 1) and the coupling of the building blocks (eq 2). This approach can also be used for synthesis of star-branched polymer, if the living polymer is quenched by the core **III**.

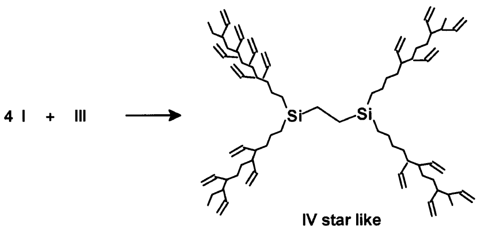


$$-\mathrm{SiCH{=}CH_2} + \mathrm{Me_2ClSiH} \xrightarrow{\text{cat}} -\mathrm{SiCH_2CH_2SiCl} \quad (1)$$



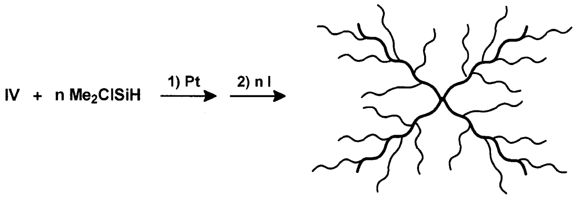
$$\sim\mathrm{SiOLi} + \mathrm{Cl{-}Si}\diagup\!\!\diagdown\mathrm{Si}- \longrightarrow \sim\mathrm{SiOSi}\diagup\!\!\diagdown\mathrm{Si}- + \mathrm{LiCl} \quad (2)$$

Constructions of various branched topologies according to this concept are shown in eqs 3−6.



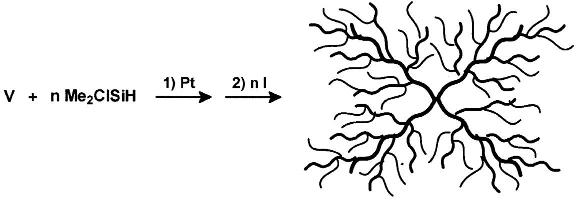
IV star like

(3)



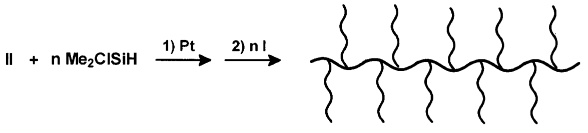
V dendritic graft / star

(4)



VI dendritic graft / graft / star

(5)

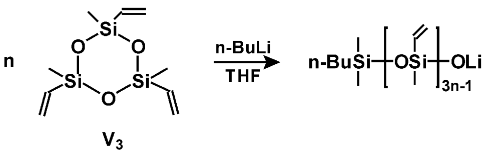


VII comb

(6)

Synthesis of Reactive Building Polysiloxane Blocks. Reactive blocks were synthesized using three monomers: 2,4,6-trivinyl-2,4,6-trimethylcyclotrisiloxane (V_3), 2-vinyl-2,4,4,6,6-pentamethylcyclotrisiloxane (VD_2) and hexamethylcyclotrisiloxane (D_3). Functionalized polysiloxanes **I** and **II** of different densities and distributions of vinyl groups along the chain may be generated by anionic ROP of V_3 and VD_2 and by copolymerization of these monomers with D_3.

High vinyl density polysiloxane is obtained by polymerization of V_3 according to reaction 7.

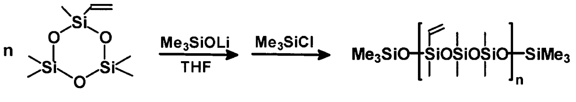


V_3

$$n\,V_3 \xrightarrow[\text{THF}]{\text{n-BuLi}} \text{n-BuSi}\left[\mathrm{OSi}\right]_{3n-1}\mathrm{OLi} \quad (7)$$

Although V_3 is a mixture of cis and trans isomers, the resulting polymer has a low polydispersion index.

Linear ViMeSiO—Me$_2$SiO Copolymer with a Uniform Arrangement of Vinyl Groups, used here as linear core, can be synthesized by the anionic ROP of VD_2 on lithium silanolate in THF (eq 8).



VD_2

$$n\,VD_2 \xrightarrow[\text{THF}]{\mathrm{Me_3SiOLi}} \xrightarrow{\mathrm{Me_3SiCl}} \mathrm{Me_3SiO}\left[\mathrm{SiOSiOSiO}\right]_n\mathrm{SiMe_3} \quad (8)$$

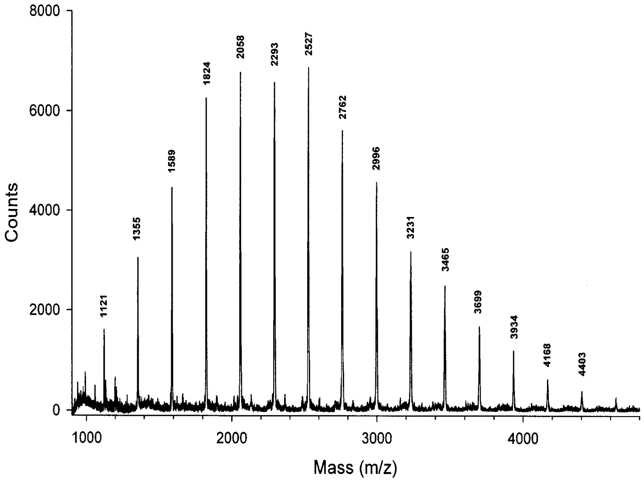
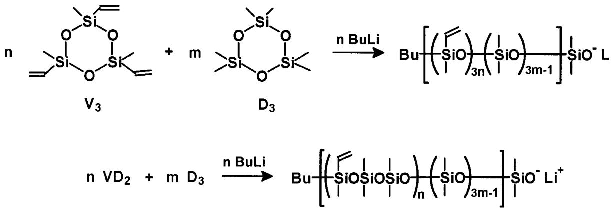


Figure 1. MALDI spectrogram of poly-ViMeSiO(Me$_2$SiO)$_2$, M_n = 4600, M_w/M_n = 1.12, obtained by polymerization of VD$_2$ initiated by Me$_3$SiOLi at −30 °C with NaI as the ionizing agent. Peak to peak mass increment corresponds to the mass of monomer unit (234.48). Labeled masses are by 3 g·mol^{-1} higher than the true masses of the Me$_3$Si[OSiMeVi(OSiMe$_2$)$_2$]$_n$-OSiMe$_3$ homologues, calculated from the equation: $M(n) = 234.48 \times n + 162.38 + 23$, which is within the range of error of the instrument operating in the linear mode.

We recently found that when this polymerization initiated by *n*-BuLi is carried out at −30 °C, chain randomization processes are mostly eliminated and even at nearly full conversion of monomer the M_w/M_n ratio (PDI) remains below 1.2.[27] About 90% of the monomer is opened by a nucleophilic attack at the silicon bearing the vinyl group, leading to almost regular arrangement of siloxane units. The anionic ROP of VD$_2$ at room temperature is less regioselective, with 68% of ring opening at ViMeSiO, although the polymer still has a narrow molecular weight distribution of 1.1−1.2, when the reaction is quenched below 90% of the monomer conversion.[27]

The high selectivity of polymerization carried out at −30° C was confirmed by MALDI TOF (Figure 1). Peaks representing macromolecules of the Me$_3$SiO[MeViSiO-(Me$_2$SiO)$_2$]$_n$SiMe$_3$ series appear almost solely, thus indicating that chain fragmentation does not occur during the polymerization.

Linear ViMeSiO—Me$_2$SiO Copolymer with a Gradient Distribution of Vinyl Groups. If a living copolymer of vinylmethylsiloxane with dimethylsiloxane is used as the reactive graft, the specific arrangement of the vinyl groups along its chain is important. The decreased density of the functional precursor group in the direction of the chain growth may be advantageous, since the potential branching points are located in the exterior part of the core. Such a structure secures a higher yield of grafting of the next generation, as the reactive groups are easily accessible to the graft. Moreover, the density of branching inside the volume occupied by the spherical molecules may be more uniform. Finally, the vinyl groups on the last generation are more easily transformed to other functional groups, which are also more accessible to an external reactant. A higher density of functionalization opposite the silanolate terminus may be attained by sequential copolymerization of a vinyl substituted monomer with D$_3$.[27] However, in the simultaneous living copolymerization of these monomers according to eq 9, the vinyl-substituted monomer, being much more reactive than D$_3$, preferentially enters the polymer chain. Thus, the density of vinyl groups along the chain decreases as the chain grows. As a result, a copolymer with gradient distribution of the vinyl groups is obtained.



(9)

The difference in the reactivity ratio of VD$_2$ with D$_3$ at 25 °C ($r_{VD_2} = 8.3$, $r_{D_3} = 0.22$) is large enough to secure an effective gradient in the density of vinyl groups.[27] These studies are extended here to the V$_3$ + D$_3$ system where a still larger difference in the reactivity ratios was expected. The conversion of both comonomers was followed (Figure 2). The best fit to the experimental points was determined by a computer simulation according to the simple copolymerization equation[37] based on the assumption that first-order Markov chain statistics is applicable. Despite this simplification the fit was excellent (Figure 2). The values of reactivity coefficients for both comonomers at 25° C were $r_{D_3} = k_{DD}/k_{DV} = 0.036$, $r_{V_3} = k_{VV}/k_{VD} = 17.8$. The large difference in reactivities of V$_3$ and D$_3$ should lead to a gradient distribution of the MeViSiO units close to that in the block copolymers obtained by sequential polymerization (Figure 3). This structure is confirmed by the ^{29}Si NMR spectrum showing strong signals for homopentads VV**V**VV, 34.92 ppm, and DD**D**DD, 21.91 ppm, and relatively small intensities of mixed pentads: VD**D**DD, 21.82 ppm; VV**D**DD, 21.33 ppm; VV**V**DD, 35.39 ppm; VV**V**VD, 34.99 ppm. The peak assignment was performed on the basis of earlier results reviewed by J. J. Kennan.[38] The ^{29}Si NMR spectrum of the copolymer is included as Supporting Information.

Synthesis of Branched Polysiloxanes. The viscosity change during the reaction of living lithium polydimethylsiloxanolate with various chlorosilanes in THF was followed by Wilczek and Kennedy.[19] They found that (Cl$_2$SiMeCH$_2$)$_2$, **III**, reacted much faster than SiCl$_4$, which was the reason for us to choose this compound as the core to obtain four-arm star polysiloxanes.

Thus, equivalent molar amounts of (poly-ViMeSiO)$^-$Li$^+$ or gradient (poly-ViMeSiO-*co*-Me$_2$SiO)$^-$Li$^+$ with **III** were reacted according to eq 3 using high vacuum and inert atmosphere techniques. The reactions went to completion, and the size-exclusion chromatograms showed unimodal peaks of the obtained star-branched polymers with fairly narrow molecular weight distributions. These chromatograms are provided in the Supporting Information. The ^{1}H NMR spectrum which was used for the calculation of molecular weight and number of vinyl groups is shown in Figure 4. Results of the NMR and SEC analyses are also listed in Table 1.

A combined high vacuum and inert gas atmosphere technique was also used to synthesize branched polysiloxane by the grafting method according to eqs 4−6. Three reactions were performed in one preparative experiment. The core activation by hydrosilylation of vinyl groups by Me$_2$HSiCl and the graft preparation by the anionic ROP of cyclotrisiloxanes were carried out in parallel in separate reactors coupled with each other. Then the products of both reactions were mixed together in one of these reactors to graft the living polymer on

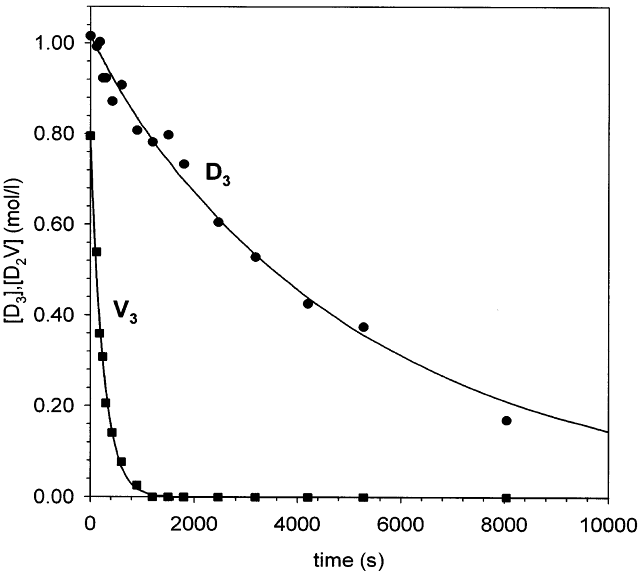


Figure 2. Conversion−time dependence of comonomers for the copolymerization of 2,4,6-trivinyl-2,4,6-trimethylcyclotrisiloxane, V_3, with hexamethylcyclotrisiloxane, D_3, in THF initiated with *n*-BuLi, $[\text{BuLi}]_0 = 2.1 \times 10^{-3}$ mol·dm^{-3} at 25 °C. Points were obtained from experiments, lines from the computer simulation using the Mayo−Lewis copolymerization equation.

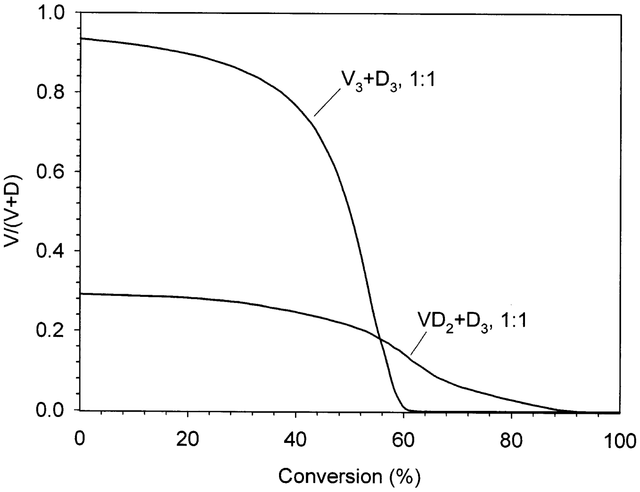


Figure 3. Density distribution of vinyl groups in Vi-to-Si ratio (V/(V + D)) along the polymer chain for the copolymerization of equimolar initial mixture of V_3 with D_3 and VD_2 with D_3. Conversion scale corresponds to the scale of the average living polymer chain length (in percent of the length at the full conversion). Dependencies were simulated using copolymerization equation of Mayo−Lewis[37] and values of reactivity coefficients of comonomers $r_{V_3} = 17.8$, $r_{D_3} = 0.036$ for the copolymerization of $V_3 + D_3$, as determined in this study, and $r_{VD_2} = 8.3$, $r_{D_3} = 0.22$ for the copolymerization of $VD_2 + D_3$ from ref 27.

the activated core. The modified Speier hydrosilylation method was used with chloroplatinic acid as catalyst.[39] A large excess of Me_2HSiCl was required in order to obtain a high yield of the hydrosilane addition and to prevent hydrolytic condensation of the SiCl groups on polymer by fortuitous traces of water. Water reacts more readily with Me_2HSiCl, which also undergoes fast condensation with the silanol formed. The volatile disiloxane condensation product can be easily removed. The hydrosilylation was finished by removing the excess of Me_2HSiCl from the reactor under high vacuum.

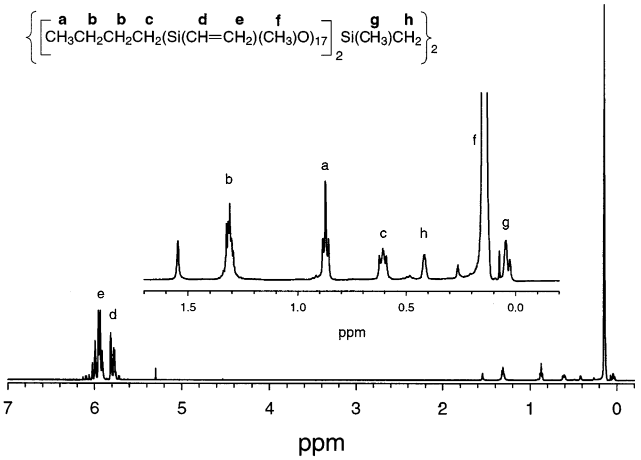


Figure 4. ^{1}H NMR spectrum of four-arm star-branched polysiloxane **IV-1**. Content of vinyl groups: 11×10^{-3} mol·g^{-3}.

The grafting process by the $\equiv$SiOLi + ClSi$\equiv$ condensation reaction, particularly at higher conversions, may proceed relatively slowly. This reaction requires penetration of the living polysiloxane chain into a branched macromolecular core, enabling the silanolate center to contact a chlorosilane function. Reaction of stoichiometric amounts of substrates would need a long time to reach full conversion. The lithium silanolate is able to cleave the siloxane bond in the branched polymer, which increases its polydispersity. A longer contact of the silanolate with the branched polysiloxane could also result in a multimodal molecular weight distribution, or even cross-linking, taking into account that the silanolate may be transferred to the branched polysiloxane and couple to another branched macromolecule. Cleavage of linear polymer with the formation of a polysiloxane with silanolate groups at both chain ends, which couples branched macromolecules, is also possible. A considerable excess of living polymer was used, particularly in the case of dense branching. The grafting was not driven to completion, but the reaction was terminated earlier using an excess of Me_3SiOLi, which penetrated and reacted faster than the living polymer, converting the remaining SiCl groups in the branched polysiloxane. The excess of ~SiOLi was neutralized by Me_3SiCl. Since the living polymer of relatively low molecular weight, $M_n < 1500$, was usually used as graft, the fraction of linear polysiloxane formed by terminating the living polymer with Me_3SiCl could be removed by repeated precipitation of the branched polysiloxane from dichloromethane solution.

Comb-branched and dendritic-branched polysiloxanes of unimodal and fairly narrow molecular weight distribution were obtained. They were characterized by ^{1}H and ^{29}Si NMR spectroscopy; examples of spectra are presented in Figures 5 (^{1}H NMR of polysiloxane **V-1**) and 6 (^{29}Si NMR of **VI-2**). The integration of signals of $C\mathbf{H}_2{=}C\mathbf{H}{-}Si$, $(C\mathbf{H}_3)_2Si$, $CH_3CH_2{=}CHSi$ and $C\mathbf{H}_3CH_2CH_2CH_2$ groups were used to determine the vinyl group content and the molecular weight.

Molecular weights from the analysis of SEC with refractive index (RI) detector based on polystyrene standards were much lower than expected (Table 1) because of different hydrodynamic behavior of the studied branched macromolecule and the linear polymer standard.[40,41] A dual detector Wyatt Technology technique, combining in tandem multiangle light-scattering (MALS) and RI detectors coupled with a size exclusion

Table 1. Synthesis of Branched Polysiloxanes Functionalized with Vinyl Groups[a]

		reactive blocks		characteristics				
symbol	topology	core	graft	M_n	M_w/M_n	n_B	n_V	d_V, $10^3 \cdot mol \cdot g^{-1}$
IV-1	star four arms	$Cl_2MeSiCH_2CH_2SiMeCl_2$	homopolym V_3 $M_n = 1500$; $n_V(g) = 17$	$6200^{c,d}$ 6100^{b}	1.37^{e}	4	68	11.0
IV-2	star four arms	$Cl_2MeSiCH_2CH_2SiMeCl_2$	gradient copolym $VD_2 + D_3$ $M_n = 7000$; $n_V(g) = 7$	$28\,000^{b}$	1.24^{e}	4	28	1.0
V-1	dendritic graft on star	**IV-1**^{g}	gradient copolym $V_3 + D_3$ $M_n = 1200$; $n_V(g) = 6$	$69\,000^{f}$ $66\,000^{c}$ $(28\,600^{e})$	1.64^{f} (1.59^{e})	54	300	4.35
V-2	dendritic graft on star	**IV-2** ^{g}	gradient copolym $VD_2 + D_3$ $M_n = 5000$; $n_V(g) = 6.7$	$270\,000^{f,h}$ $(170\,000^{b})$	$2.66\ ^{f}$	42^{h}	340	1.26
VI-1	dendritic graft/graft/ star	**V-1** ^{g}	gradient copolym $VD_2 + D_3$ $M_n = 1350$; $n_V(g) = 3.8$	$320\,000^{c}$ $(120\,000^{e})$	1.52^{e}	232	620	1.94
VI-2	dendritic graft/graft/star	**V-1** ^{g}	gradient copolym $V_3 + D_3$ $M_n = 1200$; $n_V(g) = 6.8$	$140\,000^{f}$	1.46^{f}	110	760	5.4
VII-1	comb uniform distribn of branching	homopolym $VD_2{}^{g}$ $M_n = 4600$; $n_V(c) = 19$ $M_w/M_n = 1.12$	gradient copolym $VD_2 + D_3$ $M_n = 2300$; $n_V(g) = 5$	$43\,000^{b}$ $(19\,600^{e})$	1.46^{e}	17	80	1.86
VII-2	comb gradient distribn of branching	gradient copolym V_3+$D_3{}^{g}$ $M_n = 8700^2$; $n_V(c) = 50$ $M_w/M_n = 1.29$	homopolym V_3 $M_n = 1200$; $n_V(g) = 13$	$33\,400^{c}$ $32\,000^{f}$ $(19\,900^{e})$	1.64^{f} (1.58^{e})	21	270	8.1

[a] Synthesis of polysiloxanes **IV-1**, **IV-2**, and **V-2** were performed using a molar equivalent substrate ratio; in other syntheses about 20−30% of excess of living polymer was used. Time of reaction was 1−2.5 h. All synthesis were performed in room temperature, ca. 22° C, in 10−40 wt % solution in THF. n_V, $n_V(g)$, and $n_V(c)$ are numbers of vinyl groups in macromolecule, graft, and core, respectively. n_B and $n_B(c)$ are numbers of branches in macromolecule and core, respectively. d_V is vinyl group content in moles per gram of polysiloxane, [b] Data were obtained from synthesis (stoichiometry, yields). [c] Data were obtained from ^1H NMR. [d] Data were obtained from ^{29}Si NMR. [e] Data were obtained from SEC. [f] Data were obtained from MALS. [g] Hydrosilylated by $ClMe_2SiH$. [h] Partial coupling between macromolecules (SEC peak was unsymmetrical).

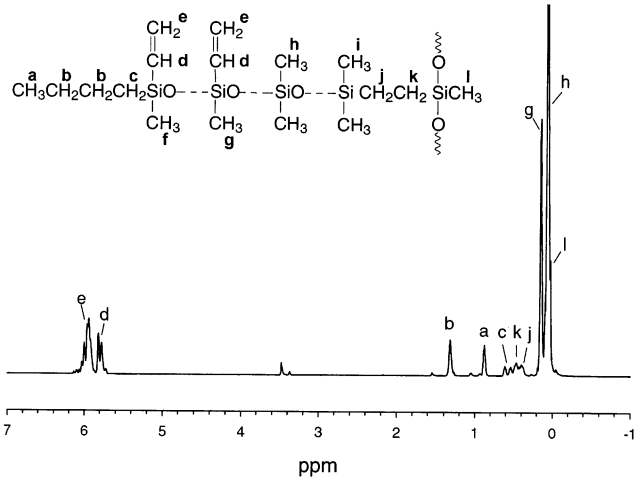


Figure 5. ^1H NMR spectrum of dendritic branched polysiloxane **V-1**. Content of vinyl groups: 4.35×10^{-3} mol·g^{-1}.

chromatograph, was used to evaluate the absolute values of average molecular weights.[42] An example of chromatogram of dendritic polysiloxane **V-1** (Table 1) is shown in Figure 7 and that of comb polymer **VII-2** is provided in the Supporting Information. The values of M_n obtained by this method for some branched polysiloxanes are presented in Table 1. They were calculated by the instrument which determined average values of the refractive index increment (d*n*/d*c*) and used them in the M_n calculations. Thus, the M_n value is valid, assuming that the composition of the copolymer macromolecules is uniform, independent of molecular weight. This assumption was confirmed comparing the SEC traces taken using the RI and UV detectors. Traces for both detectors superimposed to each other. Chromatogram of dendritic polysiloxane **VI-2** (Table 1) taken with both detectors is provided as Supporting Information.

The number of branches in macromolecule, n_B (Table 1, column 7), was calculated from eq 10

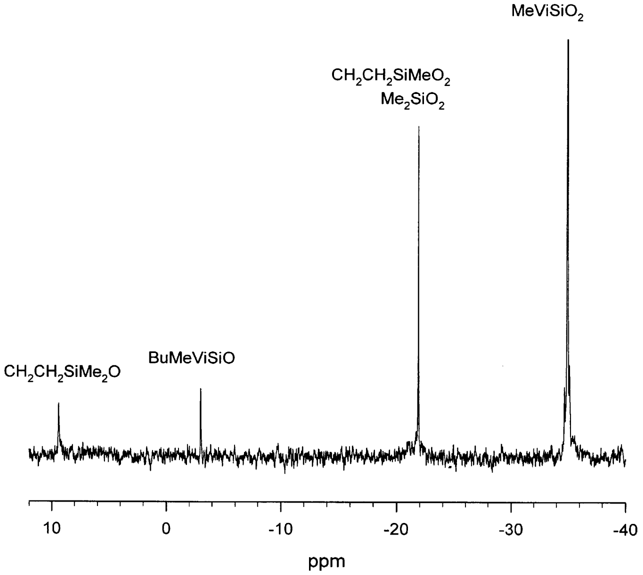


Figure 6. ^{29}Si NMR spectrum of comb-branched polysiloxane **VII-2**. Content of vinyl groups: 8.08×10^{-3} mol·g^{-1}.

$$n_B = n_B(\text{core}) + \frac{M_n - M_n(\text{core})}{M_n(\text{g}) + M_n(\text{link})} \qquad (10)$$

where M_n is the number-average molecular weight of the resulting polymer (Table 1, column 5, the first value for each polymer), $M_n(g)$ and $M_n(\text{core})$ are number-average molecular weights of grafted linear polysiloxane and core respectively, $M_n(\text{link}) = 59$ (link is Me_2SiH), and $n_B(\text{core})$ is the number of branches in the core.

Since each of grafted branch has a butyl group at its extremity the ratio of integration of the ^1H NMR ($C\mathbf{H}_3$-$CH_2CH_2CH_2$) signal at 0.9 ppm (Figures 5 and 6), I_{BuSi}, and that of the $C\mathbf{H}_2{=}C\mathbf{H}$ signals at 5.7−6.1 ppm, I_{ViSi}, permits one to calculate the number of vinyl groups in macromolecules, n_V (eq 11), and its content in 1 g of polysiloxane, d_V. They are listed in Table 1, columns 8

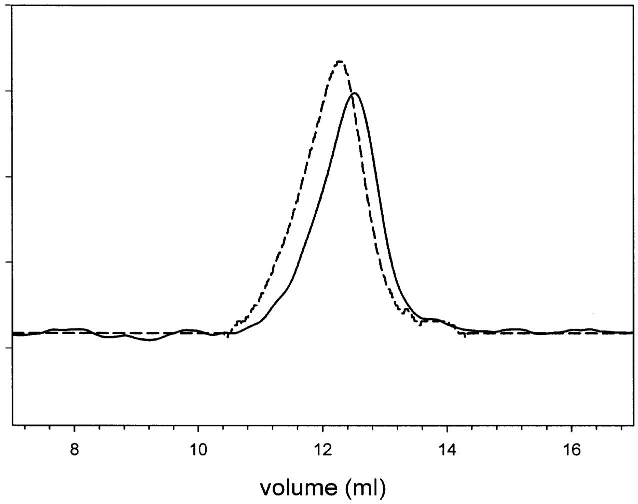


Figure 7. Size exclusion chromatograms of dendritic polysiloxane **V-1** taken with dual detector MALS–RI from Wyatt Technology. Continuous line is the MALS trace, and dashed line is the RI trace. $M_n = 69\,000$; $M_w/M_n = 1.64$. Vinyl group content: 4.35×10^{-3} mol·g^{-1}.

and 9.

$$n_V = n_B \cdot \frac{I_{ViSi}}{I_{BuSi}} \tag{11}$$

Conclusions

A general route to defined branched polysiloxanes with functionalized side groups was presented. The method permits generation of comb-, star-, and dendritic-branched polysiloxanes with a fairly narrow molecular weight distribution. It makes possible the control of density and arrangement of branching and functional groups. The method used the anionic ring-opening polymerization and copolymerization of vinyl substituted cyclotrisiloxanes to produce living polysiloxane that is grafted onto an activated core with ≡SiCl functions. The core is activated by hydrosilylation of vinyl groups with Me_2HSiCl_2. A high excess of the hydrosilylating reagent prevents undesired coupling of branched macromolecules by fortuitous traces of water.

Star-branched polymers on a polyfunctional low molecular weight core may be synthesized using stoichiometric amounts of living polysiloxane. However, an excess of the living polymer is recommended when the core is densely functionalized. The excess may be removed from the branched polysiloxane product after neutralization by Me_3SiCl by repeated precipitation if the grafting chains are short ($M_n < 1500$).

Experimental Section

Chemicals. THF, a product of Polskie Odczynniki Chemiczne (POCh) (analytical grade), was purified by refluxing and distillation from sodium and kept over Na/K alloy in an ampule fitted with a Rotaflo stopcock. Toluene (POCh) (analytical grade) was dried by distillation from sodium and stored in an ampule equipped with a Rotaflo stopcock. *n*-Heptane, *n*-decane, and dichloromethane (POCh), were purified by standard methods described in ref 43. *n*-Heptane and *n*-decane were distilled from CaH_2. Dichloromethane was shaken with SO_3/H_2SO_4 (oleum), washed successively with water and then a water solution of Na_2CO_3 and water, dried over $MgSO_4$, and distilled from CaH_2 into an ampule fitted with a Rotaflo stopcock. Dimethylchlorosilane, $(CH_3)_2SiHCl$ (ABCR), was purified by distillation, while methyldichlorosilane, CH_3SiHCl_2, and methylvinyldichlorosilane (ABCR) were used as received.

Monomers. Hexamethylcyclotrisiloxane, D_3 (Dow Corning), was kept melted over CaH_2 in an ampule equipped with a Teflon stopcock for 3 days and distilled under vacuum directly to the reactor. 2-Vinyl-2,4,4,6,6-pentamethylcyclotrisiloxane, VD_2, was synthesized as described in ref 35 and purified in analogous way to D_3. 2,4,6-Trivinyl-2,4,6-trimethylcyclotrisiloxane, V_3, was synthesized as described earlier[44] by the Takiguchi method.[45] In most cases, the purity of monomers (GC) was higher than 99%.

Initiator. *n*-Buthyllithium, 2.5 M in *n*-heptane (Aldrich), was analyzed by a method described in ref 46. Lithium trimethylsilanolate was prepared and analyzed according to ref 46. H_2PtCl_6/cyclohexanone was prepared from dry H_2PtCl_6 (POCh) and dry cyclohexanone in an ampule equipped with a Teflon stopcock under dry argon. Karstedt catalyst (PSO85) was the commercial product (ABCR).

Synthesis of Building Blocks. 2,2,5,5-Tetrachloro-2,5-disilahexane, $CH_3Cl_2SiCH_2CH_2SiCH_3Cl_2$, was synthesized by hydrosilylation of methylvinyldichlorosilane with methyldichlorosilane in the presence of the Karstedt catalyst in bulk using the procedure similar to that described in ref 47. The crystal product was purified by sublimation. The required amount of the product was sublimed under high vacuum to thin wall glass vials which were sealed.

Polymerization of 2-Vinyl-2,4,4,6,6-pentamethylcyclotrisiloxane, VD_2. The reaction was carried out in a glass reactor attached to a high vacuum line through a Rotaflo stopcock and glass joint. VD_2 (6.51 g, 2.78×10^{-2} mol) and THF (7.3 mL) were distilled into the reactor under high vacuum. The reactor was filled with argon and was cooled to −40 °C keeping a positive pressure of argon. Then Me_3SiOLi (0.99×10^{-2} g, 1.03×10^{-3} mol) in *n*-heptane (0.76 mL) was introduced to the mixture with a precision Hamilton syringe. The reactor was then placed in a NESLAB criostate and kept at $-30 \pm 2°$ C for 28 h. Then the reaction was quenched with Me_3SiCl (0.12 g, 1.1×10^{-3} mol). The excess Me_3SiCl and solvent were removed under vacuum. Polymer was dissolved in dichloromethane and precipitated in methanol. This procedure was repeated twice, and the polymer was dried by heating at 40 °C (10^{-2} mmHg) for 5 h. Polymer **1** (4.12 g, 63% yield) was obtained. The SEC analysis showed $M_n = 4600$ and $M_w/M_n = 1.12$.

Synthesis of Gradient Copolymer of Vinylmethylsiloxane with Dimethylsiloxane. V_3 (8.01 g, 3.1×10^{-2} mol), D_3 (8.99 g, 4.0×10^{-2} mol) and THF (18 mL) were distilled on a high vacuum line to a glass reactor. The reactor was filled with dry nitrogen, and *n*-decane (0.61 g, 4.29×10^{-3} mol) (standard for GC) and *n*BuLi (0.134 g, 2.1×10^{-3} mol) in *n*-hexane solution (0.84 mL) were introduced. The mixture was stirred by a magnetic stirrer at room temperature for 2 h. Then the polymerization was quenched by introducing Me_3SiCl (0.25 g, 2.3×10^{-3} mol). The gas chromatography analysis indicated full conversion of V_3 and 90% conversion of D_3. Solvent and excess Me_3SiCl were evaporated under vacuum. The polymer was precipitated twice from dichloromethane solution with methanol. Copolymer **2** was heated for several hours and subjected to ^1H and ^{29}Si NMR and SEC analysis: $M_n = 8700$, $M_w/M_n = 1.29$, $M_n(MeViSiO) = 4300$, $M_n(Me_2SiO) = 4400$.

Kinetics of the Copolymerization of 2,4,6-Trivinyl-2,4,6-trimethylcyclotrisiloxane, V_3, with D_3. Known amounts of V_3, D_3, and THF were distilled to a glass reactor installed on a high vacuum line to obtain a 50 wt % solution of the monomers in THF. The reactor was fitted with magnetic stirrer and thermostated at 25 °C. The reactor was filled with nitrogen and under a positive pressure of nitrogen known amounts of decane (standard for GC analysis) and the 2.5 M solution of *n*-BuLi in *n*-hexane were introduced. The mixture was stirred at 25 °C, and at time intervals samples were withdrawn by a Hamilton syringe through the stopcock under a positive pressure of nitrogen. The samples were analyzed by gas chromatography.

Syntheses of Branched Polysiloxanes. Star polysiloxanes were obtained in a single reactor attached to a high vacuum line. Instead, the syntheses by grafting on a polysiloxane were carried out in a glass apparatus composed of two reactors connected with each other through a glass pipe with a Rotaflo stopcock. In one of these reactors, A, the hydrosilylation of core and grafting reactions were performed while the other reactor, B, served for the preparation of living polysiloxane. Both reactors were equipped with a magnetic stirrer and connected through an additional stopcock to a sample receiver. They were also connected through Rotaflo stopcocks and glass joints to a high vacuum line.

Synthesis of Star-Branched Functionalized Polysiloxane, IV-1. The synthesis was performed in a glass reactor equipped with magnetic stirrer connected through a Rotaflo stopcock and a glass joint with a high vacuum line. A sidearm fused to the reactor contained a thin wall glass vial with 2,2,5,5-tetrachloro-2,5-disilahexane (0.391 g, 1.53×10^{-3} mol) in THF (5 mL) and a glass hammer. V_3 (8.8 g, 3.41×10^{-2} mol) and THF (10 mL) were distilled into the reactor under high vacuum. Then the reactor was filled with argon and, with a positive pressure of argon being maintained, *n*-BuLi (0.392 g, 6.13×10^{-3} mol) in *n*-hexane solution (2.44 mL) was introduced using a precision Hamilton syringe to initiate the polymerization. After 10 min of stirring (time needed to achieve 90% of monomer conversion), the vial was broken with a glass hammer and the solution of the coupling agent was introduced to the reactor to quench the reaction. The mixture was stirred for about 1 h to bring the coupling reaction to completion. The THF was evaporated under vacuum, and the star-branched polymer was dissolved in dichloromethane, washed with water, dried, and precipitated with methanol. The precipitation procedure was repeated three times. The polymer was heated at 40 °C at 10^{-3} mmHg for several hours. Star-branched polymer **IV-1** (5.2 g, preparative yield 58%) was isolated. The ^{1}H NMR spectrum in $CDCl_3$ is shown in Figure 4. ^{29}Si NMR (δ ppm) in $CDCl_3$: MeVi**Si**O_2, −34.93 m; Me**Si**$(CH_2)O_2$, −21.01 m; BuViMe**Si**O, −2.96 m. The SEC showed a monomodal peak (Supporting Information); data are listed in Table 1.

The star-branched polymer **IV-2** was obtained in a similar way.

Synthesis of Dendritic-Branched Functionalized Polysiloxane, V-1. Star-branched polysiloxane **IV-1**, (0.55 g, vinyl groups content: 6.05×10^{-3} mol) was placed in reactor A. The reactor was evacuated, and toluene (5 mL) was distilled onto the polymer. Then the reactor was filled with argon and a colloidal suspension of H_2PtCl_6 (2.87×10^{-3} g, 7×10^{-6} mol in cyclohexanone (0.29 mL) was introduced by means of a precision Hamilton syringe under a positive pressure. The mixture was stirred for 30 min and Me_2HSiCl (1.8 g, 1.9×10^{-2} mol) was added under a positive N_2 pressure. The mixture was stirred at room temperature for 48 h. Volatile components were distilled off under high vacuum and THF (15 mL) was distilled into the reactor. In the meantime, D_3 (6.31 g, 2.84×10^{-2} mol), V_3 (5.12 g, 1.98×10^{-2} mol) and THF (14 mL) were successively distilled on a high vacuum line into reactor B. Then, the reactor was filled with argon and, while a positive pressure of argon was kept, *n*-BuLi (0.624 g, 9.75×10^{-3} mol) in *n*-hexane solution (3.9 mL) was introduced using a precision Hamilton syringe. The copolymerization was carried out for 2.5 h, which corresponds to 100% and 90% conversion of V_3 and D_3, respectively.

Then the living copolymer was mixed with the hydrosilylated core in reactor A to graft the copolymer on the core. The mixture was stirred for 2.5 h. Then Me_3SiOLi (1.30 g, 1.35×10^{-2} mol) in THF (10 mL) was introduced and the mixture was stirred for another 30 min. The excess of Me_3SiOLi and living polymer were neutralized by introduction of Me_3SiCl (1.2 g, 1.1 mol). The precipitated LiCl was filtered off and volatile components were evaporated under vacuum. The mixture was washed several times with diluted solution of Na_2CO_3 and with water. Volatile components were removed under a high vacuum. Polysiloxane was dissolved in dichloromethane and precipitated with methanol. This procedure was repeated twice. The polymer was heated at 50 °C/10^{-3} mmHg for several hours. Dendritic-branched polysiloxane **V-1** was obtained (5.5 g, preparative yield 68%; a certain amount of the dendritic copolymer is lost in the purification procedure). The copolymer was analyzed by ^{1}H NMR (Figure 5), ^{29}Si NMR, and SEC with RI detector and with dual detector (Figure 7, data listed in Table 1). ^{29}Si NMR (δ in ppm) in $CDCl_3$: MeVi**Si**O_2, −35.40 to −34.68 m (−34.93 dominant); Me_2**Si**O_2, −22.7 to −21.3 m (−21.80 dominant); BuViMe**Si**O, −2.97 s; CH_2Me_2**Si**O, 8.16 m; $BuMe_2$**Si**O, 9.23 s.

Other dendritic-branched and comb-branched polysiloxanes presented in Table 1 were synthesized in an analogous way.

Simulation Procedure. Kinetics of copolymerization of $V_3 + D_3$ was simulated by numerical solving of the approximate differential kinetic equations using the same procedure as described in ref 27. In the first approximation, the aggregation of silanolate ion pairs was neglected and a first-order reaction was assumed both in the monomers and in silanolate. The kinetic equations used for simulations are presented in the Supporting Information.

Analysis. ^{1}H and ^{29}Si NMR spectra were taken with a Bruker 500 MHz or Bruker AC200 MHz spectrometer using $CDCl_3$ as solvent. Conditions of analysis were the same as in ref 27.

SEC analysis was performed on a Wyatt Technology Corp. instrument equipped with LKB 2150 HPLC pumps and Wyatt Optilab 903 RI and MALS DAWN DSP laser photometer detectors. The laser operated at wavelength of 632.8 nm. Samples were injected onto the battery of two TSK columns: 7.8 × 300 G4000HXL with 6 μm bead size, 10^4 Å porosity, and 7.8 × 300 G2000HXL with 5 μm bead size, 250 Å porosity. The eluent was dichloromethane, flow rate 0.8 mL/min. Dual detector MALS/RI SEC analysis including d*n*/d*c* determination was performed using ASTRA v. 4.72 software (Wyatt), assuming 100% mass recovery. The calibration constant value for the RI detector was determined separately according to the procedure recommended by the producer. Simple analyses were also done using LDC Analytical refractoMonitor IV instrument working with a constaMetric 3200 RI detector fitted with two columns: SDV 8 × 300, 5 μm bead size, 10^4 Å porosity, and SDV 8 × 300, 5 μm bead size, 100 Å porosity. Eluent: toluene, 0.7 mL/min.

MALDI/TOF analysis was performed on a Voyager-Elite instrument equipped with N_2 laser operating at $\lambda = 337$ nm (pulse rate of 10 Hz) with positive polarity in the linear mode. The accelerating voltage was 20 kV. The applied pressure was 3.59×10^{-7} Torr. 1,8-Dihydroxy-9[10*H*]-anthracenone (dithranol) was used as the matrix and NaI as the ionization promoter. The molar ratio of analyte to matrix and to salt was 1:1000:10. The solutions of the analyte in THF and of the salt and matrix in acetone were mixed together at given proportions, introduced to the sample holder, and dried.

Gas chromatography analyses were performed on a Hewlett-Packard 6890 apparatus with thermal conductivity detector and 30 m capillary column HP-1 HP 190592−023, using He as carrier gas; the column temperature was changed from 60 to 240 °C, at 10 °C min^{-1}. Detector temperature: 250 °C. Injector temperature: 250 °C.

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Supporting Information Available: Figures showing the ^{29}Si NMR spectrum of gradient copolymer ViMeSiO−Me_2SiO and SEC traces of star-, comb-, and dendritic-branched polysiloxanes discussed in text and text showing a set of kinetic equations used for computer simulation. This material is available free of charge via the Internet at http://pubs.acs.org.

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