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Synthesis of Highly Branched Alkoxysiloxane−Dimethylsiloxane Copolymers by Nonhydrolytic Dehydrocarbon Polycondensation Catalyzed by Tris(pentafluorophenyl)borane

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ABSTRACT: A new approach to the synthesis of highly branched alkoxy functionalized polysiloxanes has been developed. Dehydrocarbon polycondensation of tetraalkoxysilanes with 1,1,3,3-tetramethyldisiloxane ($^{H}MM^{H}$) catalyzed by tris(pentafluorophenyl)borane [$B(C_6F_5)_3$] leads to highly branched organopolysiloxanes substituted with alkoxy groups at silicon atoms. These copolymers could be used as silanol-free hydrophobic silicone resins. Polycondensations of $^{H}MM^{H}$ with tetramethoxysilane (TMOS) and with tetraethoxysilane (TEOS), catalyzed by $B(C_6F_5)_3$, were studied. Use of TMOS or TEOS lead to stable, soluble, branched copolymers containing a great number of reactive alkoxy groups. Dehydrocarbon polycondensation is accompanied by a metathetic exchange of functional groups as well as cleavage of siloxane bonds adjacent to the Si−H group. Both of these reactions, as well as dehydrocarbon polycondensation, occur via the tertiary silyloxonium borate intermediate.

Introduction

Great interest in the synthesis of branched, hydroxyl free polysiloxanes, bearing a large number of reactive alkoxy groups bound to the polysiloxane chain, stems from the demand for hydrophobic reactive silicone resins. The unique combination of properties such as high thermal stability, excellent dielectric properties, and resistance to oxygen, water and UV irradiation yields broad applications as electrical insulators, thermally stable coatings, composite materials with extreme thermal stability, components of silicone paints resistant to adverse atmospheric conditions and release and nonsticky materials.[1,2] Silicone resins are often used in hybrid materials with organic and inorganic components such as blends with organic polymers such as polyesters to form high performance coatings[3] or interpenetrating network materials.[4]

Commercial silicone resins are manufactured by hydrolytic polycondensation of organochlorosilanes or organoalkoxysilanes. They contain uncontrollable amounts of silanol groups yielding hydrophilic properties, making their compounding with hydrophobic materials difficult.[5] Presence of the silanol groups may also affect long-term stability of the silicone resins as they show a great propensity toward condensation.

In order to avoid formation of silanol rich resins, hyperbranched ethoxy-functional polysiloxanes were synthesized by polycondensation of AB_3 monomers such as triethoxysilanol or acetoxytriethoxysilane.[6] However, the synthesis of those AB_3 monomers is troublesome due to their inherent reactivity. Recently, ethoxy-functional hyperbranched polysiloxanes were prepared via polycondensation of tetraethoxysilane with acetic anhydride catalyzed by an organotitanium catalyst.[7] This process requires high temperatures and long reaction times. Stable, alkoxy-functional polysiloxanes were also obtained by hydrolytic polycondensation of alkoxysilanes in the presence of a substoichiometric amount of water.[8] The hydrolytic polycondensation method does not enable complete elimination of hydroxyl groups.

In this paper we describe a new synthetic methodology that allows for the synthesis of highly branched alkoxy substituted polysiloxanes under mild conditions. The new process presented in this paper is a nonhydrolytic dehydrocarbon polycondensation of alkoxysilanes with hydrosilanes catalyzed by tris(pentafluorophenyl)borane [$B(C_6F_5)_3$]. The prepared alkoxy-functional polysiloxanes are free of silanol groups and have excellent long-term stability.

The Lewis acid $B(C_6F_5)_3$ has been broadly used as a catalyst in organic synthesis[9] and in polymer chemistry.[10] It has recently been found that $B(C_6F_5)_3$ is an extremely efficient catalyst of such important reactions in organosilicon polymers as the dehydrocondensation of dihydrosilanes with disilanols[11] and the dehydrocarbon condensation of dihydrosilanes with dialkoxysilanes.[12] Subsequently, a group exchange reaction of hydrosilanes with alkoxysilanes was discovered.[13] The discovery that a $B(C_6F_5)_3$−hydrosilane complex catalyzes the cleavage of the siloxane bond adjacent to hydrosilane was exploited in the metathesis of tetramethyldisiloxane, yielding dimethylsilane and a series of $H(SiMe_2O)_nSiMe_2H$ oligomers.[14] Some of the $B(C_6F_5)_3$−hydrosilane systems are also able to cleave the SiOSi bond in the strained cyclotrisiloxane ring.[15] The synthetic method described in this paper is based on the dehydrocarbon condensation as the process leading to growth of macromolecule. The other aforementioned reactions, i.e., silyl hydride−alkoxysilane methathesis, and HSiOSi cleavage, which accompany the copolymerization, may have some impact on the final resin structure.

Quite recently, when this paper was in preparation, Thompson and Brook reported the synthesis of branched permethylsiloxane oligomers of special architecture via the dehydrocarbon condensation process.[16]

Experimental Part

Chemicals. Tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS), Aldrich reagent grade, were distilled from sodium. $HMe_2SiOSiMe_2H$ ($^{H}MM^{H}$), ABCR reagent grade product, was kept over calcium hydride and distilled. Purity of all substrates was checked by gas chromatography and was above 98%. Solvent, toluene (POCH - Polskie Odczynniki Chemiczne), was shaken with H_2SO_4, washed with water, dried over $MgSO_4$, distilled over P_2O_5

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and distilled again from sodium. Catalyst, tris(pentafluorophenyl)borane (Aldrich), was reagent grade with a declared purity of 95%. It was either sublimed at 50 °C on a vacuum line or used without further purification.

A stock solution of 5×10^{-2} mol·dm^{-3} of the tris(pentafluorophenyl)borane catalyst in toluene was prepared under nitrogen.

Analytical Methods. *NMR Spectroscopy.* ^{1}H NMR spectra were recorded on Bruker DRX 500 operating at 500 MHz. ^{29}Si NMR spectra were recorded on the same instrument working at 99.36 MHz in the inverse gated pulse sequence mode with relaxation delay 3 s, scan number 10 K, time domain 65 K and 90 deg pulse 15.00. The Cr(acac)$_3$ complex was added. The solvent was CDCl$_3$. Chemical shifts of oligomers obtained earlier[17] were helpful in the assignment of peaks.

Gas Chromatography (GC). Gas chromatography analyses were performed using a Hewlett-Packard HP 6890 chromatograph equipped with a thermal conductivity detector (TDC) and standard Hewlett-Packard HP1 capillary column length 30 m diameter 0.53 mm packed with cross-linked polydimethylsiloxane (PDMS) (0.88 μm film thickness). Further specifications include the following: helium carrier gas; flow rate 5 mL/min; detector temperature 250 °C; injector temperature 250 °C; column temperature program, 3 min at 40 °C isoth., 40−240 °C, rate 10 °C/min 10−15 min at 240 °C isoth. *n*-Dodecane was used as the internal standard.

Gas Chromatography−Mass Spectroscopy (GC−MS). Mass spectra were recorded with a GC−MS Finnigan MAT 95 instrument using chemical ionization. The reactive gas (H^+ carrier) was isobutane at the pressure of 10^{-4} Torr. The mass spectrometer worked in tandem with the gas chromatograph that was fitted with a standard capillary column DB-1 30 m length packed with cross-linked PDMS. The temperature was programmed to fit to the corresponding chromatogram recorded on the HP-6890 instrument.

Since the ionization occurs under mild conditions, the fragmentation of analyzed species was limited. Siloxane oligomers not having SiH functions gave strong $M + 1$ peaks and/or its simple fragmentation product, which dominated over other fragmentation products. Silicon compounds having the Si−Me groups give $(M + 1) - 16$ signals, which is usually of a lower intensity than that of $M + 1$. Compounds having methoxy or ethoxy groups at silicon center gave signals $(M + 1) - 32$ or $(M + 1) - 46$ respectively. Examples of the mass spectrogram are included as Supporting Information (Figures 1ABC and 2ABC in the Supporting Information).

Size Exclusion Chromatography (SEC). Weight average molecular weights (M_w) and polydispersity (M_w/M_n) were measured using an LDC analytical Refracto-Monitor instrument with two Phenogel (PSS SDV) columns 8 × 300 mm length, filled with 5 μm polystyrene-*co*-divinylobenzene beads having 10^2 Å and 10^5 Å pores covering the molecular weight range 10^2−10^5 g/mol and a refractive index detector. Toluene was used as the eluent with flow rate 0.7 mL/min and temperature 25 °C. Linear polystyrene (PS) was used as standards.

Synthesis. Most of syntheses were performed in a 25 mL Schlenk flask equipped with a magnetic stirrer and a three-way stopcock through which argon was flowing. Substrates, catalysts, GC standard and solvent were introduced through this stopcock by means of a precision Hamilton syringe with a long needle. Larger scale syntheses (50−100 mL of reaction volume) were performed in a 150 mL glass reactor fitted with a magnetic stirrer, dropping funnel, neck with septum, reflux condenser and neutral gas inlet and outlet. During some of the synthesis the reaction samples were withdrawn at various time intervals and neutralized by the addition of 3-ethylpyridine or hexamethyldisilazane and subjected to GC or SEC analysis. *n*-Dodecane was used as the GC standard. Most of experiments were performed at room temperature (23 °C), but some of them were carried out at lower temperatures (−10 or −25 °C).

Reaction of TMOS with 1,1,3,3-Tetramethyldisiloxane ($^{H}MM^{H}$). *The Reaction According to Variant I (Table 1, Entry 1).* The reactor was purged with nitrogen and charged with TMOS (3.04 g, 2.00×10^{-2} mol/kg), toluene (12.5 g, 14.6 mL) and $B(C_6F_5)_3$ (7.7×10^{-3} g, 1.50×10^{-5} mol, corresponding to a concentration of 8.2×10^{-4} mol/kg in the postreaction mixture). Traces of water were removed by the addition of 10^{-2} g of $^{H}MM^{H}$. Then $^{H}MM^{H}$ (2.68 g, 2.00×10^{-2} mol) was introduced from a B/Braun syringe driven by an AP Ascar pump at the rate of 1.5 mL/h while the reaction mixture was vigorously stirred. After the addition was completed, the reaction mixture was stirred for additional hour. The reaction was stopped by the addition of an excess of 3-ethylpyridine to deactivate the catalyst. The gas chromatography analysis showed that all $^{H}MM^{H}$ and 77% of TMOS were converted. Toluene was distilled off in vacuum and the polymer was heated at 80 °C for 6 h on a high vacuum line. The preparative yield of this reaction was 69%. The final silicone resin was characterized by ^{1}H NMR, ^{29}Si NMR and size exclusion chromatography (SEC). ^{1}H NMR (solvent CDCl$_3$, in ppm): 0.06−0.14, m, SiCH_3; 3.47−3.57, m, OCH_3. ^{29}Si NMR (solvent CDCl$_3$, in ppm): −(6.0−7.5), −(10.5−10.9), m, $Si(CH_3)_2(OSi)OC$; −(19.4−22.1), m, $Si(CH_3)_2(OSi)_2$; −(85.3−86.1), m, $Si(OSi)(OC)_3$; −(92.3−94.4), m, $Si(OSi)_2(OC)_2$; −(100.1−101.6), m, $Si(OSi)_3OC$; −(107.0−109.6), m, $Si(SiO)_4$. SEC (toluene, standard polystyrene PS) weight average molecular weight (M_w) 2.32×10^4 g/mol, polydispersity $M_w/M_n = 7.9$ (M_n is number average molecular weight).

Table 1. Polycondensation of Tetraalkoxysilanes with 1,1,3,3-Tetramethyldisiloxane ($^{H}MM^{H}$) in Toluene Catalyzed by $B(C_6F_5)_3$[a]

no.	tetra-alkoxysilane	variant[b]	$^{H}MM^{H}$/ $(RO)_4Si$	yield [% reacted $(RO)_4Si$]	$M_w \times 10^{-3}$ in g/mol[c]	M_w/M_n[d]	RO/Si total
1	$(MeO)_4Si$	I	1.0	77	23.2	7.9	0.39
2	$(MeO)_4Si$	I	1.2	84	55.5	8.7	0.28
3	$(MeO)_4Si$[e])	I	1.2	95	17.5	3.4	0.42
4	$(MeO)_4Si$	II	1.0	79	16.9	5.3	0.42
5	$(MeO)_4Si$[f])	II	1.0	80	15.3	4.4	0.43
6	$(MeO)_4Si$[g])	II	0.5	73	3.5	3.0	1.06
7	$(EtO)_4Si$	I	1.0	73	14.0	5.9	0.34
8	$(EtO)_4Si$	II	0.8	68	7.0	3.0	0.49
9	$(EtO)_4Si$	II	1.0	80	11.7	3.3	0.43
10	$(EtO)_4Si$	II	1.2	82	18.5	3.9	0.27

[a] Unless stated otherwise, the reaction was performed at room temperature. The rate of addition was 1.5 mL/h; concentration of $(RO)_4Si$ was 1.1 mol/kg of the total mixture. [b] Variant I: $^{H}MM^{H}$ is introduced to toluene solution of $(RO)_4Si$ and catalyst. Variant II: mixture of $^{H}MM^{H}$ and $(RO)_4Si$ is introduced to toluene solution of catalyst. [c] Weight average molecular weight. [d] Polydispersity, M_n is number average molecular weight. [e] Temperature was −25 °C. [f] Concentration of $(RO)_4Si$ was 1.6 mol/kg of the total mixture, and rate of the addition was 1.0 mL/h. [g] Experiment on a larger scale (see description in Experimental Section).

The Experiment at Low Temperature (Table 1, Entry 3). The reactor was charged with TMOS (1.42 g, 9.34×10^{-3} mol), toluene (2.6 g, 3 mL), and $B(C_6F_5)_3$ (final concentration 5.4×10^{-4} mol/kg). The reaction was initiated at room temperature by the addition of a small amount of $^{H}MM^{H}$. Then the reactor was placed in an isopropanol bath at −25 °C. The $^{H}MM^{H}$ (1.50 g, 12.2×10^{-3} mol) was introduced dropwise over a period of 2 h to reach the final $^{H}MM^{H}$/TMOS = 1.19 mol/mol. Then the mixture was allowed to warm up slowly to room temperature and was left for 50 h. After quenching the catalyst most of the solvent was carefully distilled off and the polymer subjected to analyses. No $^{H}MM^{H}$ and less than 5% of TMOS was found. M_w (SEC with PS standard) = 1.75×10^4 g/mol, $M_w/M_n = 3.4$.

Reactions According to Variant II (Table 1, Entries 4 and 5). These reactions were performed in an analogous way to that of TEOS, which is described in the next subsection.

Variant II (Larger Scale, Table 1, Entry 6). The reactor was charged with toluene (57.6 g, 66.6 mL), *n*-dodecane (3.23 g, 1.90 × 10^{-2} mol), and $B(C_6F_5)_3$ (final concentration 3.0×10^{-4} mol/kg). $^{H}MM^{H}$ (0.1 g) was introduced to activate the catalyst, and after 20 min the mixture of TMOS (14.89 g, 9.78×10^{-2} mol) and $^{H}MM^{H}$ (6.89 g, 5.13×10^{-2} mol) was added slowly (during 6 h) to the stirred reaction mixture. The GC analyses of samples withdrawn during the reaction showed no $^{H}MM^{H}$ and some amount of unreacted TMOS. The post reaction mixture contained 27% of unconverted TMOS. The reaction was quenched by the addition of an excess of 3-ethylpyridine. Solvent, dodecane and TMOS were removed by heating at 80 °C/0.01 Torr for 3 h. The copolymer viscosity was 18 cP, $M_w = 3.5 \times 10^3$ g/mol, $M_w/M_n = 3.0$ (SEC, PS standard), MeSi/Si_{total} = 1.18, OMe/Si_{total} = 1.06, D/Q = 1.42.

Reaction of Tetraethoxysilane (TEOS) with $^{H}MM^{H}$. *The Reaction According to Variant 1 (Table 1, Entry 7).* This reaction was performed in an analogous way to that of TMOS (Table 1, entry 1) described in the previous subsection.

The Reaction According to Variant II. The reactor was purged by nitrogen and charged with toluene (9.3 g, 10.8 mL) and $B(C_6F_5)_3$ (5.7×10^{-3} g, 1.11×10^{-5} mol). Traces of water were removed by the addition of 10^{-2} g of $^{H}MM^{H}$. Then the mixture of TEOS (3.07 g, 1.47×10^{-2} mol) and $^{H}MM^{H}$ (1.95 g, 1.45×10^{-2} mol) was continuously introduced from a B/Braun syringe driven by AP Ascar pump while the reaction mixture was vigorously stirred. The rate of the addition of reactants was 1.5 mL/h. After the addition of reactants was completed, the reaction mixture was stirred for an additional hour. The reaction was stopped by rapid addition of an excess of 3-ethylpyridine. The reaction mixture was analyzed by gas chromatography, which showed that all $^{H}MM^{H}$ and 80% of TEOS were converted. Volatile components were distilled off in vacuum, and polymer was heated at 80 °C for 8 h on a high vacuum line (10^{-3} Torr). The final resin was characterized by ^1H NMR, ^{29}Si NMR and SEC analysis. ^1H NMR (solvent $CDCl_3$, in ppm): 0.11−0.14, m, $SiCH_3$; 1.16−1.25, m, $SiOCH_2CH_3$; 3.72−3.86, m, $SiOCH_2$. ^{29}Si NMR (solvent $CDCl_3$, in ppm): −(6.6−7.1), −(12.0−12.5), m, $Si(CH_3)_2(OSi)OC$; −(18.1−22.5), m, $Si(CH_3)_2(OSi)_2$; −(88.2−89.0), m, $Si(OSi)(OC)_3$; −(94.2−95.9), m, $Si(OSi)_2(OC)_2$; −(100.6−103.1), m, $Si(OSi)_3OC$; −(106.5−109.5), m, $Si(OSi)_4$. SEC: $M_w = 1.72 \times 10^4$ g/mol, $M_w/M_n = 3.0$.

Results and Discussion

Dehydrocarbon Coupling Copolymerization. A variety of silanes and siloxanes having Si−H and Si−OR functional groups may be used as reagents in dehydrocarbon polycondensation reaction. Compounds having both alkoxy and hydrosilane groups are also within the realm of possibility using this synthetic protocol. Thus the method utilized here for the synthesis of silicone resins is versatile and may serve to obtain polymers consisting of various combinations of SiO_2 (Q), $RSiO_{1.5}$ (T), R_2SiO_2 (D) and R_3SiO (M) units. This paper is devoted to polymers composed of Q and D units. The polycondensation of $^{H}MM^{H}$ with TMOS or TEOS catalyzed $B(C_6F_5)_3$ was studied here as a model process leading to highly branched siloxane copolymers composed of D units originating from $^{H}MM^{H}$ and Q units derived from tetraalkoxysilane. $^{H}MM^{H}$ and TMOS or TEOS are commercially available monomers widely used in the silicone and silicate industry and are convenient precursors of DQ silicone resins or silica hybrid materials.

First, we attempted to obtain information on the kinetics of the polycondensation process in order to determine the best reaction conditions for the synthesis of the desired copolymers. Preliminary observations showed that the reaction of TEOS with $^{H}MM^{H}$ in toluene proceeds very fast, and is highly exothermic and thus difficult to control. Relatively low substrate concentrations about 0.3 mol/kg reaction mixture and 3×10^{-5} mol/kg of catalyst were used to minimize the exothermic effect and be able to follow reaction kinetics. After the mixing of substrates with catalyst, samples were withdrawn in a fixed time interval and analyzed by gas chromatography. In the first interval no reaction of TEOS was observed although a slow bubbling occurred and the concentration of $^{H}MM^{H}$ slightly decreased. Violent liberation of gas started after a significant induction period of about 500 s indicating the onset of a rapid polycondensation reaction. The analysis of the sample quenched after 515 s showed no $^{H}MM^{H}$ and about 10% of the initial amount of TEOS. With an increase in catalyst concentration the induction period was significantly reduced and was not seen at the concentration of 10^{-3} mol/kg. The same observation was noted for the reaction with TMOS, which is possibly faster than that with TEOS.

The observed induction period can be explained by the formation of strong complexes between $B(C_6F_5)_3$ and adventitious water (eq 1) and/or other contaminants such as EtOH.[13] $B(C_6F_5)_3$ in these complexes is unable to catalyze the polycondensation. The strong complexes greatly diminish the concentration of the free Lewis acid in the system. However, $B(C_6F_5)_3$ shows a unique ability for the fast self-purification as it very actively catalyzes the reaction of hydrosilanes with contaminants[13] as it is represented by eq 2.

$$B(C_6F_5)_3 + nH_2O \rightleftarrows (BC_6F_5)_3{\cdot}nH_2O \quad n = 1-3 \tag{1}$$

$$H_2O + 2H{-}Si\equiv \xrightarrow{B(C_6F_5)_3} \equiv Si{-}O{-}Si\equiv + 2H_2 \tag{2}$$

Since the equilibrium of the complex formation lies strongly to the right-hand side of eq 1,[18] the concentration of free $B(C_6F_5)_3$ may be very small in the presence of contaminants, which in our system was expected to be at the level of 10^{-3} mol/kg of H_2O or its equivalence of ROH. Thus, it may result in a long induction period of polycondensation when a small amount of catalyst is used.

Taking into account the unusual course of this reaction, i.e. its enormously high rate, high exothermic effect, inhibition by water at low catalyst concentrations and sensitivity of catalyst to impurities, the synthesis of copolymers was performed using a higher concentration of catalyst and a slow introduction of hydrosilane to the solution of alkoxysilane and catalyst in toluene (variant I) or slow addition of a mixture of both substrates to the solution of the catalyst in toluene (variant II). The series of the polycondensation runs were done using both modes of the experiment and changing experimental conditions. Results are shown in Table 1.

In variant I the relative concentrations of reactants are changed as the reaction proceeds to a much larger extent than in variant II. Thus, the latter leads to a more uniform composition of units in the macromolecules and to narrower molecular weight distribution (compare entries 1, 2 with 4, 5 and 7 with 8−10 in Table 1).

The molar ratio of substrates is the main factor, which controls the structure of the polymeric product. In variants I and II molecular weight and polydispersity are increasing with an increase in the $^{H}MM^{H}$ to $(RO)_4Si$ molar ratio (Table 1). A considerable excess of the alkoxy over hydrosilane group prevents the formation of gels. Other important factors are concentration of reactants and temperature. A lower reaction temperature allows for an achievement of higher tetraalkoxysilane conversion and a lower polydispersity of the resin (entry 3, Table 1). In the case where the reaction is performed neat, gel formation may occur at an early stage of the process due to inefficient mixing of reagents. Low temperature and dilution favor the formation of soluble polymer. It was found that TEOS reacts equally readily as TMOS, although a considerable amount of these monomers remain unreacted in the postreaction mixture. This occurs particularly when the ratio of $^{H}MM^{H}/(RO)_4Si$ in the feed is low (Table 1).

The process proceeded to full conversion of the SiH groups as determined by ^1H NMR, see Figure 3AB in the Supporting Information. In a separate series of experiments the reaction was followed by sampling and gas chromatography analysis of the reaction mixture. Figures 1 and 2 show respectively how TMOS and TEOS are converted as a function of added $^{H}MM^{H}$. $^{H}MM^{H}$ was not detected in the samples withdrawn during reaction, indicating that $^{H}MM^{H}$ is immediately converted as it is added to the reaction mixture. When the process is performed according to variant II, tetraalkoxysilanes tend to enter the

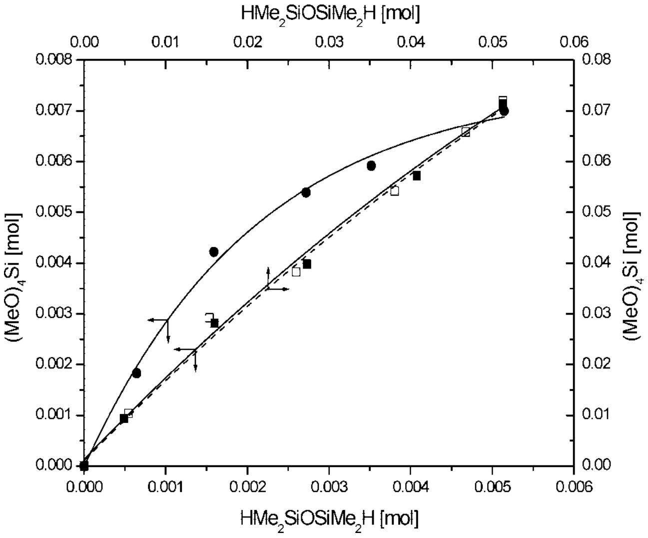


Figure 1. The conversion of tetramethoxysilane (TMOS) as a function of the conversion of 1,1,3,3-tetramethyldisiloxane ($^{H}MM^{H}$) in copolycondensation of these monomers performed using variants I and II. (●) Variant I: $^{H}MM^{H}$ was introduced to 9.5×10^{-3} mol of TMOS and catalyst in 6.7 mL of toluene. (□) Variant II: A mixture of 5.1×10^{-3} mol of $^{H}MM^{H}$ and 9.8×10^{-3} mol of TMOS was introduced to 6.7 mL of toluene containing $B(C_6F_5)_3$. (■) Variant II (scale increased by 10, upper and right-hand side coordinates): A mixture of 9.8×10^{-2} mol of TMOS and 5.1×10^{-2} mol of $^{H}MM^{H}$ was introduced to 67 mL of toluene solution of $B(C_6F_5)_3$. In all experiments the catalyst concentration was 3.0×10^{-3} mol/kg of the final mixture. Experiments were performed at room temperature.

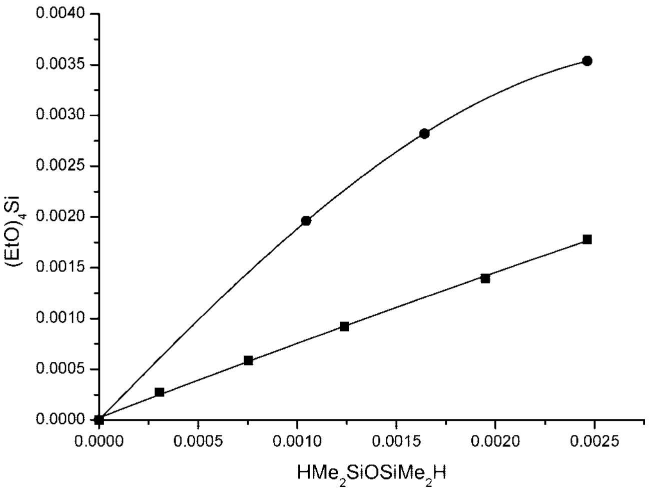


Figure 2. The conversion of tetraethoxysilane (TEOS) as a function of the conversion of 1,1,3,3-tetramethyldisiloxane ($^{H}MM^{H}$) in the copolycondensation of these monomers performed using variants I and II. (●) Variant I: $^{H}MM^{H}$ was introduced to 4.9×10^{-3} mol of TEOS in 1 mL of toluene and $B(C_6F_5)_3$ (concentration 3×10^{-4} mol/kg the final mixture). (■) Variant II: Equimolar mixture of reactants (2.5×10^{-3} mol/2.5×10^{-3} mol) was added to $B(C_6F_5)_3$ (concentration 9.6×10^{-4} mol/kg the final mixture) in 1.5 mL of toluene.

reaction in parallel fashion to $^{H}MM^{H}$, although at slightly lower proportions as compared with the molar ratio of reagents in the feed. In contrast, when $^{H}MM^{H}$ is introduced to a large excess of $Si(OMe)_4$ as in variant I the alkoxysilane is initially consumed in a higher molar proportion to $^{H}MM^{H}$ than the expected 2:1 stoichiometric mole ratio. This observation reflects the importance of the metathetic process leading to the functional group exchange in substrates described in a previous publication,[13] vide infra. The reaction is scalable as demonstrated for reaction variant II, Figure 1.

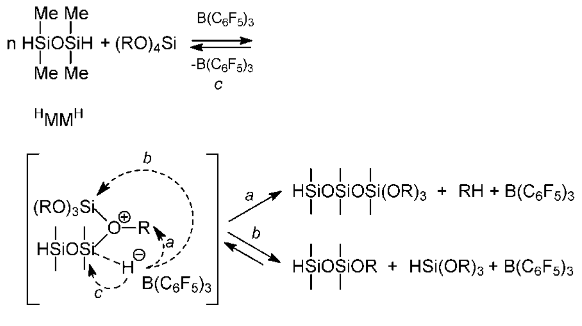
The inspection of the ^{29}Si NMR spectra (Figures 3AB) confirms that the prepared polymers are highly branched. There are four groups of signals originating from TMOS or TEOS. They correspond to Q_1, the $(RO)_3SiO_{1/2}-$ end units; Q_2, the $(RO)_2SiO=$ linear chain extension units; Q_3, the $(RO)SiO_{3/2}\equiv$ fork branching units; and Q_4, the $=SiO_2=$ cross branching units. Signals originating from $^{H}MM^{H}$ belong to D, $-SiMe_2O-$ chain extension units, and to D*, $ROSiMe_2O_{1/2}-$ terminating units. Integration of those signals allows for determination of the relative concentration of different Q and D units in the final macromolecule, e.g., the contribution of various Q units to the total number of Q units was Q_1 0.25, Q_2 0.36, Q_3 0.29, Q_4 0.10 while the ratio Q/D was 0.32 for the TMOS−$^{H}MM^{H}$ resin obtained by variant II at a 1:1 molar monomer ratio (Figure 3A). The TEOS−$^{H}MM^{H}$ copolymer synthesized under similar conditions is somewhat less branched (Figure 4 in the Supporting Information). The respective contributions of Q units were Q_1 0.28, Q_2 0.395, Q_3 0.29, Q_4 0.035 and the ratio Q/D was 0.31. The coefficient of branching of Q units, defined as $(Q_3 + 2Q_4)/(Q_2 + Q_3 + Q_4)$, was 0.66 for the TMOS−$^{H}MM^{H}$ and 0.50 for the TEOS−$^{H}MM^{H}$ copolymers while the respective coefficient of branching of macromolecule defined as $(Q_3 + 2Q_4)/(D + Q_2 + Q_3 + Q_4)$ was 0.136 and 0.095 respectively. The decreased branching of the TEOS−$^{H}MM^{H}$ copolymer comes from the lower concentration associated with Q_4 units, resulting from the greater steric contribution from the TEOS ethoxy group relative to the TMOS methoxy group.

The Mechanism of the Reaction and the Role of the Metathetic Processes. The overall copolycondensation process is complex, and its general reaction products are summarized in eq 3.

$$m\mathrm{HMe_2SiOSiMe_2H} + n(\mathrm{RO})_4\mathrm{Si} \xrightarrow{\mathrm{B(C_6F_5)_3}}$$
$$[\mathrm{Me_2Si(O_{0.5})}_p(\mathrm{OR})_q]_{2m}[\mathrm{Si(O_{0.5})}_r(\mathrm{OR})_s]_n + x\mathrm{RH}$$
$$p,q = 1,1 \text{ or } 2,0;\ r,s = 1,3 \text{ or } 2,2 \text{ or } 3,1 \text{ or } 4,0;\ x = 2m \quad (3)$$

In order to determine the extent of the metathetic SiH for ROSi group exchange, which accompanies the copolycondensation, several samples were withdrawn during the course of reaction and analyzed by GC−MS for the presence of oligomers (see Supporting Information Figures 1ABC and 2ABC). The gas chromatogram of the reaction mixture taken after the introduction of 12% of the equimolar quantity of $^{H}MM^{H}$ to the quantity of the TMOS being in the reactor is shown in Figure 4. The reaction was performed at −10 °C without solvent. Many oligomers reflecting a competition between condensation and metathesis could be observed at these conditions, thus giving insight into the mechanism of this complex process.

Although the reaction leading to the growth of macromolecule is the dehydrocarbon condensation, the metathetic exchange of reactive SiH and SiOR groups accompanies the condensation. According to the published mechanism[13] both reactions proceed through the same oxonium ion intermediate. The initial step of the process may be represented by eq 4.



(4)

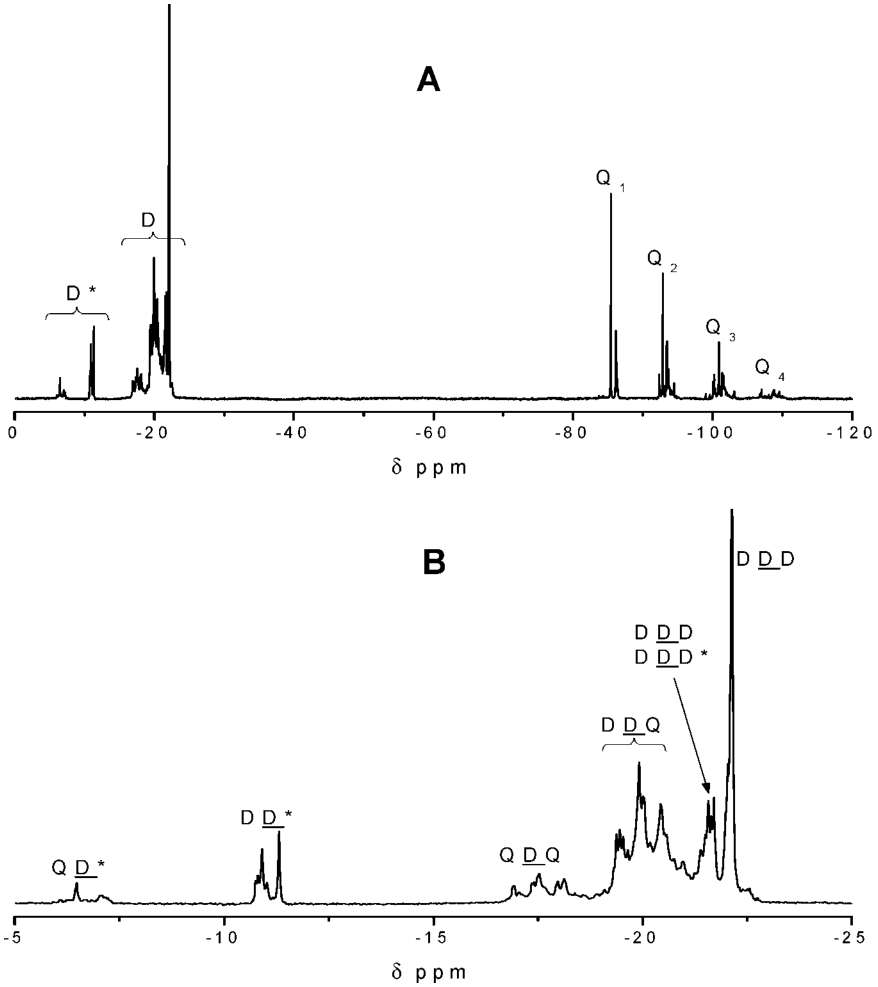
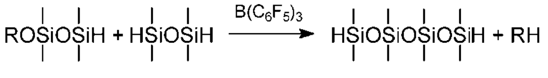


Figure 3. (A) The ^{29}Si NMR spectrum of the copolymer obtained by the copolycondensation of equimolar amounts of tetramethoxysilane (TMOS) and 1,1,3,3-tetramethyldisiloxane ($^{H}MM^{H}$) in toluene catalyzed by $B(C_6F_5)_3$, performed according to variant II (mixture of TMOS and $^{H}MM^{H}$ was added to a toluene solution of $B(C_6F_5)_3$, Table 1 entry 5). (B) The above spectrum expanding upon the region associated with Me_2SiO (D) units. The spectrum was taken in $CDCl_3$ using the inverse gated pulse sequence technique and in the presence of the $Cr(acac)_3$ complex. Signals are denoted by symbols of silicon units in copolymer which correspond to silicon nuclei as follows: D, $Me_2\mathit{Si}(OSi)_2$; D*, $Me_2\mathit{Si}(OSi)(OMe)$; Q_1, $\mathit{Si}(OSi)(OMe)_3$; Q_2, $\mathit{Si}(OSi)_2(OMe)_2$; Q_3, $\mathit{Si}(OSi)_3OMe$; Q_4, $\mathit{Si}(OSi)_4$.

The intermediate oxonium ion complex may decompose choosing one of three possible routes. In route *a,* hydride ion is transferred to the carbon atom of the alkoxy group producing a hydrocarbon and the condensation product. Route *b* involves the attack of hydride ion on the silicon atom of the alkoxysilane leading to metathetic exchange of Si−H for Si−OR. The attack on the silicon atom of the disiloxane, route *c*, is the reverse reaction leading back to the reactants. The dehydrocarbon condensation proceeds irreversibly, while the metathetic SiH for SiOR exchange processes are reversible. The metathetic process leads to formation of new reactants having both functionalities Si−H and Si−OR. The subsequent dehydrocarbon condensation of these compounds with substrates leads to formation of polyhomocondensation products as is presented in eqs 5 and 6.

$$(RO)_3SiH + (RO)_4Si \xrightarrow{B(C_6F_5)_3} (RO)_3SiOSi(OR)_3 + RH \qquad (5)$$



$$ROSiOSiH + HSiOSiH \xrightarrow{B(C_6F_5)_3} HSiOSiOSiOSiH + RH \qquad (6)$$

In order to obtain more information about the metathetic functional group exchange and about the competition between homo- and heterocondensation, the relative intensities of GC peaks of oligomers were followed with conversion for the variant I, see Table 2. The homocondensation of TMOS is particularly important in the initial stage of the reaction when the concentration of TMOS is large. However, since the TMOS to $^{H}MM^{H}$ ratio in the system decreases as the reaction proceeds, the heterocondensation becomes more important. This is reflected in an increase in the ratio between the QD_2 to Q_2 signals. A considerable stationary concentration of $[(MeO)Me_2Si]_2O$, (D_2), was observed until the full conversion of $^{H}MM^{H}$. This observation indicates that $^{H}MM^{H}$ readily enters into the two-step SiH for SiOR group exchange. This could result in the formation of longer sequences of D units in the silicone resin according to eq 6. A detailed inspection of the ^{29}Si NMR spectrum (Figure 3B) shows that the D**D**D triads (signals around −22 ppm) indeed appear but their signals are relatively small compared to those corresponding to **QD**D triads. Thus the homocoupling according to reaction 6 is slower than the heterocoupling. Another reaction that may occur is the metathesis of the 1,2-dihydrodisiloxane involving the cleavage of the siloxane bond, eqs 7 and 8. The mechanism of this reaction, analogous to that presented in eq 4, has been discussed in a prior publication.[14]

Comparison of the rate for the reaction in eq 7[14] with the rate of $^{H}MM^{H}$ conversion indicates that this reaction is slower in this system by at least 3−4 orders of magnitude and it cannot compete with the dehydrocarbon polycondensation. This con-

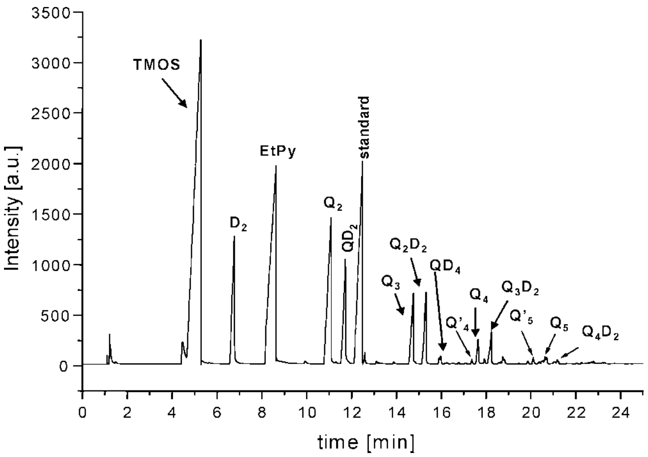
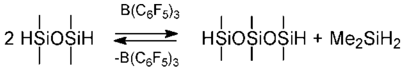


Figure 4. The gas chromatogram of the reaction mixture of the polycondensation of tetramethoxysilane (TMOS) with 1,1,3,3-tetramethyldisiloxane ($^{H}MM^{H}$) catalyzed by $(C_6F_5)_3B$ performed according to variant I ($^{H}MM^{H}$ was added to TMOS and catalyst) at −10 °C. The analysis was made after the introduction of 12% of the equimolar amount of $^{H}MM^{H}$ to TMOS. Chemical structures of the assigned oligomers are as follows: D_2, $MeOSiMe_2OSiMe_2OMe$; Q_2, $(MeO)_3SiOSi(OMe)_3$; QD_2, $(MeO)_3Si[(OSiMe_2)_2OMe]$; Q_3, $Me[OSi(OMe)_2]_3OMe$; Q_2D_2, $(MeO)_3Si[OSiMe_2]_2OSi(OMe)_3$; QD_4, $(MeO)_2Si[(OSiMe_2)_2OMe]_2$; Q'_4, $(MeO)Si[OSi(OMe)_3]_3$; Q_4, $Me[OSi(OMe)_2]_4OMe$; Q_3D_2, presumably $(MeO)_3Si[OSiMe_2]_2[OSi(OMe)_2]_2OMe$; Q'_5, $(MeO)_3SiOSi(OMe)[OSi(OMe)_3]\{[OSi(OMe)_2]_2OMe\}$; Q_5, $Me[OSi(OMe)_2]_5OMe$; Q_4D_2, presumably $(MeO)_3Si[OSiMe_2]_2[OSi(OMe)_2]_2OSi(OMe)_3$.

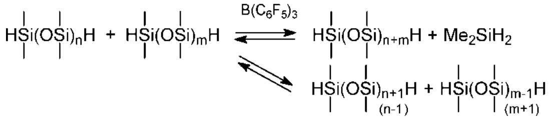
Table 2. The Variation in the Integral Intensity of Peaks of Oligomers (Relative to Standard) in Gas Chromatograms Taken after Different Conversion of 1,1,3,3-Tetramethyldisiloxane ($^{H}MM^{H}$) during the Reaction of $^{H}MM^{H}$ (1.60 g, 11.9 × 10^{-3} mol) with Tetramethoxysilane (TMOS) (1.42 g, 9.34 × 10^{-3} mol) in Toluene (1.42 g) Catalyzed by $B(C_6F_5)_3$[a]

% converted $^{H}MM^{H}$	D_2	Q_2	QD_2	QD_2/Q_2
0	0	0	0	
10	1.0	2.09	1.14	0.55
50	1.7	0.79	0.90	1.14
80	1.57	0.13	0.40	3.1
100	1.43	<0.1	0.32	>3

[a] Temperature −25 °C, variant I ($^{H}MM^{H}$ was introduced to toluene solution of TMOS and catalyst).



$$2\ HSiOSiH \underset{-B(C_6F_5)_3}{\overset{B(C_6F_5)_3}{\rightleftarrows}} HSiOSiOSiH + Me_2SiH_2 \qquad (7)$$



$$HSi(OSi)_nH + HSi(OSi)_mH \overset{B(C_6F_5)_3}{\rightleftarrows} HSi(OSi)_{n+m}H + Me_2SiH_2$$
$$\rightleftarrows HSi(OSi)_{n+1}H_{(n-1)} + HSi(OSi)_{m-1}H_{(m+1)} \qquad (8)$$

clusion was confirmed by the observation that short oligomers having an odd number of D units do not appear in significant amounts by GC analysis (Figure 4). On the other hand, the ^{29}Si NMR spectrum of the copolymer product, see Figure 3B and in the Supporting Information Figure 4B, show small, but significant amounts of the Q**D**Q triad and **D***Q terminating diad. The triad and diad may form by the reaction scheme 8. Hence, the metathesis involving cleavage of the siloxane bond adjacent to SiH, although it does not occur at the monomer and low oligomer level, must take place in copolymer where it involves the SiH chain ends.

The reaction of TEOS with $^{H}MM^{H}$ proceeds in a similar fashion with the homocondensation of TEOS dominated by heterocondensation. Homooligomers of TEOS were not detected in the copolymerization system. On the other hand, the peaks assigned to oligomers having an even number of D units dominate on the chromatogram taken at 50% $^{H}MM^{H}$ conversion (see Supporting Information, Figure 5). Thus alternative arrangements of D_2 sequences and Q units prevail in the copolymer structure derived from TEOS and $^{H}MM^{H}$. The cleavage of the siloxane bond plays a minor role in the TEOS reaction which is reflected in a lower relative intensity of signals of Q**D**Q triad and **D***Q chain end diad (see Supporting Information Figure 4B). A lower reactivity of TEOS compared to TMOS is reflected in higher contribution of the Q_1 end unit to the total chain termini in the $^{H}MM^{H}$−TEOS copolymer (0.65) than in the $^{H}MM^{H}$−TMOS copolymer (0.51).

Conclusions

Dehydrocarbon polycondensation of 1,3-dihydro-1,1,3,3-tetramethylsiloxane, with tetraalkoxysilanes, such as tetramethoxysilane or tetraethoxysilane, in the presence of $B(C_6F_5)_3$ leads to branched alkoxy terminated organosiloxane copolymers composed of D and Q siloxane units. These copolymers may be used as hydrophobic, silanol free silicone resins, thus making them stable and compatible with many organic polymers.

The dehydrocarbon polycondensation is accompanied by metathetic exchange of alkoxysilane and hydrosilane functional groups. Thus the polymer chain growth occurs as a combination of polyheterocondensation and polyhomocondensation processes, leading to various sequences of D and Q units in the final silicone resin.

Another reaction that can occur in the polycondensation sequence is the cleavage of siloxane bonds if the silicon atom is also bonded to hydrogen. This reaction cannot compete with dehydrocarbon coupling on the monomer level but may occur in the copolymer where it leads to a rearrangement of siloxane units.

The dehydrocarbon polycondensation, the metathetic SiH−SiOR exchange and the siloxane bond cleavage occur through a silyloxonium borate intermediate. The borate intermediate is formed by hydride transfer from silicon to the boron atom of the catalyst assisted by nucleophilic attack of alkoxy or silyloxy group on the silicon center.

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Supporting Information Available: Examples of the gas chromatography−mass spectroscopy (GC−MS) spectra of oligomers with their fragmentation schemes and the discussion of structures determined by the chemical ionization GC−MS; ^{1}H NMR spectra of copolymers of 1,1,3,3-tetramethyldisiloxane ($^{H}MM^{H}$) with tetramethoxysilane (TMOS) and with tetraethoxysilane (TEOS); the ^{29}Si NMR spectrum of the copolymer of $^{H}MM^{H}$ with TEOS; the gas chromatogram of the polycondensation system of $^{H}MM^{H}$ with TEOS. This material is available free of charge via the Internet at http://pubs.acs.org.

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