Synthesis, Characterization and Microstructure of New Liquid Poly(methylhydrosiloxanes) Containing Branching Units SiO$_{4/2}$

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Abstract: Six liquid branched poly(methylhydrosiloxanes) of new random structures (PMHS-Q), containing quadruple branching units SiO$_{4/2}$ (Q), both MeHSiO (D$^H$) and Me$_2$SiO (D) chain building units (or only mers MeHSiO), and terminal groups Me$_3$SiO$_{0.5}$ (M) were prepared by a hydrolytic polycondensation method of appropriate organic chlorosilanes and tetraethyl ortosilicate (TEOS), in diethyl ether medium at temperature below 0 °C. Volatile low molecular weight siloxanes were removed by a vacuum distillation at 150–155 °C. Yields of PMHS-Q reached from 55–69 wt%. Their dynamic viscosities were measured in the Brookfield HBDV+IIcP cone-plate viscometer and ranged from 10.7–13.1 cP. Molecular weights (MW) of PMHS-Q ($M_n = 2440–6310$ g/mol, $M_w = 5750–10,350$ g/mol) and polydispersities of MW ($M_w/M_n = 2.0–2.8$) were determined by a size exclusion chromatography (SEC). All polymers were characterized by FTIR, $^1$H- and $^{29}$Si-NMR, and an elemental analysis. A microstructure of siloxane chains was proposed on a basis of $^{29}$Si-NMR results and compared with literature data.

Keywords: hyperbranched poly(methylhydrosiloxanes); hydrolytic polycondensation; $^{29}$Si-NMR; topology of polysiloxane chains

1. Introduction

Poly(methylhydrosiloxanes) (PMHS) are inorganic–organic hybrid polymers with inorganic backbone, composed of alternatively bound silicon and oxygen atoms. Hydrogen atoms and methyl groups are the main substituents of silicon atoms in PMHS; however, other organic groups may be attached to silicon atoms in their structures as well. Most PMHS are colorless oils, though some of them are solids [1–9]. Linear, star, hyperbranched and dendritic poly(methylhydrosiloxanes), as well as spherical hydrosilicates, are important classes of functional silicones. Many methods of their preparation were described in our previous publication, concerning synthesis and characterization of branched PMHS containing triple branching units MeSiO$_{1.5}$ (T) [9]. PMHS find numerous practical applications. Most often they are used as cross-linking agents in a technology of silicone elastomers [9–15].

One of the newer synthetic methods used for the preparation of poly(dimethylsiloxanes-co-methylhydrosiloxanes) (PDMS-co-PMHS) is based on an equilibration polymerization of poly(dimethylsiloxanes) with linear hydrosiloxane polymer and hexamethyldisiloxane Me$_3$SiOSiMe$_3$, towards phosphonitrile catalyst [Cl$_3$P(NPCl$_2$)$_2$PCl$_3$]$^+PCl$_6^-$ at elevated temperature [16–20].
A polymerization of 1,3,5,7-tetramethyldisiloxane \( (D^H_4) \) [\( D^H = \text{H(CH}_3\text{SiO)} \)] was carried out in the presence of the non-ionic emulsifier \( \text{C}_12\text{H}_{25}(\text{OCH}_2\text{CH}_2)_2\text{OH} \) and dodecylbenzenesulphonic acid and it was accelerated by ultrasounds [21,22].

Weber and Paulasaari obtained poly(1-hydro-1,3,5,5-pentamethyltrisiloxane) with a regular chain structure by the polymerization of a new monomer, pentamethyldisiloxane \( \text{c-} \) \( (\text{Me}_2\text{SiO})_2 \text{MeHSiO} \) \( c-\text{D}_2 \text{D}^H \); \( \text{D} = (\text{CH}_3)_2\text{SiO} \) in tetrahydrofuran (THF), in the presence of \( \text{Ph}_2\text{Si(O)} \text{Li}_2 \), at \( -79^\circ \text{C} \) [23]. The starting monomer \( \text{c-} \text{D}_2 \text{D}^H \) was prepared by heterocondensation of MeHSiCl with \( \text{HO(} \text{Me}_2\text{SiO})_2\text{H} \) (yield: 49%). At the same time was elaborated a new sequential polycondensation method (“one-pot”) leading to three homological series of new PDMS-b-PMHS with a general formula:

\[
\text{RMe}_2\text{SiO}[(\text{Me}_2\text{SiO})_m(\text{MeHSiO})_n](\text{Me}_2\text{SiO})_n\text{SiMe}_2\text{R},
\]

(1)

(where: \( \text{R} = \text{–OH or –Me; m = 2, 6, 10, 14, ~50; k = 1–4; n = 5, 10, 15, 20} \), containing single or multiple MeHSiO units in macromolecules [9,24]). This synthetic method is based on a non-stoichiometric polycondensation of appropriate dimethyldimethoxysilane-\( \alpha\),\( \omega\)-diols \( \text{HO(} \text{Me}_2\text{SiO})_n\text{H} \) with siloxane oligomers of a general formula \( \text{Cl(} \text{MeHSiO})_1\text{SiMeCl} \), having chloro(hydro)silyl functionalities, followed by termination reactions with chlorotrimethylsilane \( \text{MeSiCl} \), when PDMS-b-PMHS chains were blocked with \( \text{(CH}_3)_2\text{SiO}_{1.5} \) (M) groups. An isolation and characterization of many model H-siloxanes helped us to establish the regular microstructure of prepared PDMS-b-PMHS, which was further confirmed by \( ^1\text{H-} \) and \( ^29\text{Si-NMR studies} \ [9,25].

In recent years a growing interest has been observed in the field of syntheses of star, highly branched, and dendritic poly(methylhydrosiloxanes). Cage silsesquioxanes (“spheresiloxanes”): \( \text{T}^\text{H}_8, \text{T}^\text{H}_{10}, \text{T}^\text{H}_{12}, \text{T}^\text{H}_{14} \), and \( \text{T}^\text{H}_{16} \) (\( \text{T}^\text{H} = \text{HSiO}_{1.5} \)) are solids, which can be prepared by the hydrolytic polycondensation of: (a) trichlorosilane \( \text{HSiCl}_3 \), carried out in the presence of \( \text{FeCl}_3 \) in methanol medium [24,26–28], or (b) trimethoxysilane \( \text{HSi(OCH}_3)_3 \), saturated with anhydrous \( \text{HCl} \), in acetic acid solution [29–32], or in the presence of concentrated \( \text{H}_2\text{SO}_4 \) [33,34]. Octakis(dimethylsiloxyl)-octasilsesquioxane \( [(\text{HMe}_2\text{SiO})\text{SiO}]_4\) \( \text{Q} = \text{SiO}_4/2, \text{M}^\text{H} = \text{H(CH}_3)_2\text{SiO}_{1.5} \) can be prepared with high yields in reaction of octakis(tetramethyrammonium)octasilsesquioxane with \( \text{ClSiMe}_2\text{H} \) [35–37], up to 85–91% yield [38,39]. Currently a low molecular mass star tetrakis(dimethylsiloxyl)silane \( \text{Si[OSi(CH}_3)_2\text{H}]_4 \), octahydrosilsesquioxane \( \text{T}^\text{H}_8 \) and cubic \( \text{Q} = \text{SiO}_4/2 \) are commercially available [35,40–46].

Recently siloxane-polyhedral silsesquioxane copolymers (soluble in THF) were prepared by the dehydrogenative condensation of \( \text{T}^\text{H}_8 \) with diphenylsilanol, tetraphenyldisiloxane diol or oligodimethylsiloxane-\( \omega\)-diols in the presence of diethylhydroxylamine, followed by trimethoxysilylation [47,48]. \( \text{T}^\text{H}_8 \) was also applied as a precursor of mesoporous silica, which was prepared without using any template or surfactant [49].

An equilibration of octamethyldisiloxane \( [(\text{Me}_2\text{SiO})_4] \), \( \text{D}_1 \) with \( \text{Si[OSi(CH}_3)_2\text{H}]_4 \) and trifluoromethanesulphonic acid led to tetraarm star polysiloxane \( \text{Si[OSi(CH}_3)_2\text{H}]_n\text{OSi(CH}_3)_2\text{H}]_4 \) [50,51]. Six- and eight-membered silicates: hexakis(dimethylsiloxyl)cyclotrisiloxane \( [(\text{Me}_2\text{SiO})_3\text{SiO}]_3 \) and octakis(dimethylsiloxy)cyclotetrasiloxane \( [(\text{HMe}_2\text{SiO})_2\text{SiO}]_4 \) were synthesized with low yields, from reactions of pyrolysis products of wollastonite. \( [(\text{HMe}_2\text{SiO})_2\text{SiO}]_3 \) was prepared in reaction of chlorodimethylsilane \( \text{HMe}_2\text{SiCl} \) with pseudowollastonite \( \text{Ca}_3\text{Si}_2\text{O}_6\text{Cl}_6 \), while \( [(\text{HMe}_2\text{SiO})_2\text{SiO}]_4 \) was prepared by heating octakis(trimethylsiloxy)cyclotetrasiloxane \( [(\text{Me}_2\text{SiO})_2\text{SiO}]_4 \) with 1,1,3,3-tetramethyldisiloxane \( \text{HMe}_2\text{SiOSiMe}_2\text{H} \) in the presence of trifluoromethanesulphonic acid [52,53]. The equilibration of \( [(\text{HMe}_2\text{SiO})_2\text{SiO}]_3 \) with \( \text{D}_1 \) and triflic acid gave PMHS of the following branched structure: \( \text{–}[\text{OSi(} \text{OSiMe}_2\text{O})_n\text{SiMe}_2\text{H}]{1–6} \) [52]. The Si–H terminated multifunctional silicone dendrimer, i.e., tetrakis(dimethylsiloxy)silane, was prepared with 69% yield by the reaction of TEOS and dimethoxysilane [54].

Zhang et al. synthesized polylsilsesquioxanes of a ladder structure, containing units \( \text{HSiO}_{1.5} \) and \( \text{MeSiO}_{1.5} \), by hydrolysis of byproducts prepared through condensation of \( \text{HSiCl}_3 \) and \( \text{MeSiCl}_3 \) with \( p\)-phenylenediamine or ethylenediamine [55–57].
A silicone dendrimer of a third generation with symmetrical structure and the general formula (CH₃SiO)₁₂[(CH₂)₂SiO]₁₀₂[Hi(CH₃)₂SiO]₂₄ was prepared by Masamune et al. [58] in a multistep synthesis from siloxane oligomers containing functional groups: Si-H, Si-Cl, Si-Br and Si-OH. It had 24 terminal functional Si-H groups “on the surface”. Branched resins, containing 10–14 Si-H functional groups in macromolecules were synthesized by the hydrolytic polycondensation of methyldichlorosilane with dimethyldichlorosilane, trimethyldichlorosilane and methylietriethoxysilanes or phenyl(triethoxysilanes). These resins were used as crosslinking agents for addition of cured silicone elastomers [59]. Condensation of (triethoxysilanes) HSi(OC₂H₅)₃, towards HCl solution, in the mixture of THF and methylisobutyl ketone (MIBK), led to soluble multifunctional poly(hydrogensilsesquioxanes) (PHSSQ) of combined cage-like and network-like structures [60]. A solid four-membered silsesquioxane ring compound (PhSiO₁.₅)₃(MeHSiO)₂, so-called “double-decker-shaped-silsesquioxane”, was prepared from reaction of MeHCl₂ with a byproduct, which was obtained via a condensation of phenyl(triethoxysilanes) and NaOH with 20% yield [61].

Twelve new liquid branched poly(methylhydrosiloxanes) with statistical structures (b-r-PMHS), containing triple branching units MeSiO₁.₅ (T), both Me₂SiO (D) and MeHSiO (D¹) chain building units (or only mers MeHSiO), and two b-r-PMHS containing five different structural units: D, D¹, T and T¹ and trimethylsiloxy end groups Me₃SiO₁.₅ (M) were prepared by the hydrolytic polycondensation method of appropriate chlorosilanes in diethyl ether medium at temperature <0 °C. Yields of b-r-PMHS ranged from 57–84 wt% (after removal of low molecular weight oligosiloxanes by a vacuum distillation at 125–150 °C). All polymeric products were characterized by FTIR, ¹H- and ²⁹Si-NMR, and elemental analysis. Their dynamic viscosities were very low and usually ranged from ~8–30 cP, which presumably resulted from their globular structure [9].

Methyl-substituted silica gels with Si-H functionalities were prepared by hydrolysis and condensation reactions of triethoxysilane and methyldiethoxysilane, used in various molar ratios [62]. They gave higher ceramic residue after pyrolysis than gels based only on MeSiO₁.₅ branching units [63].

In the present work, we describe the hydrolytic polycondensation synthetic route to new liquid branched poly(methylhydrosiloxanes) of random structures (PMHS-Q), containing both MeHSiO (D¹) and Me₂SiO (D) chain building units (or only mers MeHSiO), quadruple branching units SiO₄/² (Q), and terminal groups Me₃SiO₁.₅, from appropriate organic chlorosilanes and tetraethoxysilane.

2. Materials and Methods

Dichloromethylsilane MeHCl₂ (MDS, 99%, b.p. 41 °C), dichlorodimethylsilane Me₂Cl₂ (DDS, b.p. 70–71 °C), tetraethoxysilane Si(OC₂H₅)₄ (b.p. 168 °C), (4-dimethylamino)pyridine (DMAP, 99%) were all sourced from Aldrich Chemical Company Inc., USA. Chlorotrimethylsilane Me₃SiCl was obtained from Fluka, Seelze, Germany (TMCS, >99%, b.p. 57 °C). Tetraethoxysilane Si(OEt)₄ was obtained from Unisil, Tarnów, Poland (TEOS, 99%, b.p. 168 °C). Triethylamine (>99%, Fluka) was dried with anhydrous KOH, decanted, and distilled over P₂O₅. Diethyl ether was purified and dried with anhydrous KOH, and distilled over CaH₂.

All products were analyzed by a nuclear magnetic resonance (NMR), infrared spectroscopy (FTIR) and gel chromatography (SEC). FTIR spectra (neat) were done on spectrophotometer IR Bio-Rad 175 C (American Laboratory Trading, East Lyme, CT 06333, USA) for samples placed between NaCl plates. ¹H-NMR and ²⁹Si-NMR (INEPT) spectra were recorded on Bruker DRX 500 machine (Bruker Physik AG, Karlsruhe, Germany) at CBMM PAN in Łódź. Hexamethyldisiloxane Me₃SiOSiMe₃ was used as an external standard in ²⁹Si-NMR (δ = 6.98 ppm, in CDC1₃).

An elementary analysis (% C and % H) was performed at the Centre of Molecular and Macromolecular Studies of the Polish Academy of Sciences in Łódź (CBMM PAN). The content of Si-H groups was calculated from an integration ratio of their signals to CH₃ signals in ¹H-NMR spectra, and compared to theoretical integration ratios of Si-H and CH₃ signals. The content of Si was determined by the gravimetric method with H₂SO₄ (p.a.) [64].
Dynamic viscosities ($\eta^{25}$) of polysiloxanes were measured at 25.0 °C in a Brookfield cone-plate reoviscometer HBDV-II+cP (Brookfield Engineering Laboratories, Inc., Middleboro, MA 02346, USA), using a cone cP40.

The molecular masses and molecular mass distribution of polysiloxanes were analyzed by a size exclusion chromatography (SEC) in toluene solution, using LDC analytical chromatograph (Artisan Technology Group, Champaign, IL 61822, USA) equipped with refractoMonitor and a battery of two phenogel columns covering the MW range $10^2$–$10^5$ g·mol$^{-1}$. Calibration was made with polystyrene Ultrastyrogel standards with MWs: $10^2$, $10^3$, and $10^4$ g·mol$^{-1}$.

**Synthesis of Branched Polymethylhydrosiloxanes (PMHS-Q)**

Branched polymethylhydrosiloxanes, containing only units D and Q, terminated with Me$_3$SiO$_{0.5}$ groups, with structures described by a general formula:

$$\text{(SiO}_{4/2})_y[(\text{CH}_3\text{H})\text{SiO}]_n[(\text{CH}_3\text{Si})_3\text{SiO}]_p$$

(2)

(where: $y = 1$–3, $n = 48$–50, $p = 2y + 2$), and branched poly(dimethyl-co-methylhydrido)siloxanes, containing both mers D, as well mers D$^H$, units Q and end Me$_3$SiO$_{0.5}$ groups, of a general formula:

$$\text{(SiO}_{4/2})_y[(\text{CH}_3\text{Si})_2\text{SiO}]_m[(\text{CH}_3\text{H})\text{SiO}]_n[(\text{CH}_3\text{Si})_3\text{SiO}]_p$$

(3)

(where: $y = 1$–3, $m = n = 49$–52, $p = 2y + 2$), were synthesized by the hydrolytic polycondensation of mixtures of tetraethoxysilane Si(OEt)$_4$ and appropriate chlorosilanes: dichloromethylsilane MeHSiCl$_2$, dichlorodimethylsilane Me$_2$SiCl$_2$, and chlorotrimethylsilane Me$_3$SiCl, in the medium of diethyl ether and water, at temperature ranged from $−10$–$0$ °C, within 3–5 h. Molar ratios of chlorosilanes were changed, depending on expected molecular formula of polysiloxane. Amounts of substrates used in syntheses of branched PMHS-Q and times of additions of chlorosilanes are presented in Table 1.

In the hydrolytic polycondensation reactions were used such amounts of distilled water, which were sufficient for a formation of hydrochloric acid with a final concentration about 20 wt%.

**Table 1.** Amounts of substrates and a solvent, reaction time in syntheses of branched PMHS containing quadruple branching points, and methods of drying of products solutions.

| Substrates, solvent, and reaction conditions | Predicted molecular formulas of PMHS-Q * |
|-------------------------------------------|----------------------------------------|
|                                          | QD$_{48}$M$_4$ | QD$_{49}$M$_6$ | QD$_{50}$M$_8$ | QD$_{52}$M$_{4}$ | QD$_{52}$M$_{6}$ | QD$_{52}$M$_{8}$ |
| Si(OEt)$_4$                               | 0.01          | 0.04          | 0.06          | 0.01          | 0.02          | 0.03          |
| (mol)                                      |              |              |              |              |              |              |
|                                          | 2.2           | 8.9           | 13.4          | 2.2           | 4.6           | 6.7           |
| (cm$^3$)                                   |              |              |              |              |              |              |
| MeHSiCl$_2$ (MDS)                          | 0.48          | 0.98          | 1.0           | 0.52          | 0.49          | 0.50          |
| (mol)                                      |              |              |              |              |              |              |
|                                          | 50.0          | 102.0         | 104.1         | 54.1          | 51.5          | 52.1          |
| (cm$^3$)                                   |              |              |              |              |              |              |
| Me$_2$SiCl$_2$ (DDS)                       | -             | -             | -             | 0.52          | 0.49          | 0.50          |
| (mol)                                      |              |              |              |              |              |              |
|                                          | -             | -             | -             | 63.1          | 59.8          | 60.6          |
| (cm$^3$)                                   |              |              |              |              |              |              |
| Me$_2$SiCl$_2$ (TMCS)                      | 0.04          | 0.12          | 0.16          | 0.04          | 0.09          | 0.08          |
| (mol)                                      |              |              |              |              |              |              |
|                                          | 5.1           | 15.2          | 20.3          | 5.1           | 7.6           | 10.2          |
| (cm$^3$)                                   |              |              |              |              |              |              |
| H$_2$O                                     | 9.11          | 18.94         | 19.66         | 19.33         | 18.38         | 18.94         |
| (mol)                                      |              |              |              |              |              |              |
|                                          | 164           | 341           | 354           | 348           | 331           | 341           |
| (cm$^3$)                                   |              |              |              |              |              |              |
| (4-dimethylamino)-pyridine (DMAP)          | -             | -             | 0.003         | -             | 0.0109        | 0.0108        |
| (mol)                                      |              |              |              |              |              |              |
|                                          | -             | -             | 0.3665        | -             | 1.3106        | 1.2417        |
| (g)                                       |              |              |              |              |              |              |
| Et$_3$N                                    | -             | -             | 0.03          | -             | 0.109         | 0.108         |
| (mol)                                      |              |              |              |              |              |              |
|                                          | -             | -             | 0.136         | -             | 1.169         | 1.139         |
| (cm$^3$)                                   |              |              |              |              |              |              |
| Diethyl ether                              | 50            | 80            | 60            | 50            | 80            | 90            |
| (cm$^3$)                                   |              |              |              |              |              |              |
| Addition time of chlorosilanes and Si(OEt)$_4$ | -4–2     | -1–3          | -1–3          | -1–3          | -1–6          | -2–2          |
| Temperature during addition of chlorosilanes and Si(OEt)$_4$ | -4–2     | -1–3          | -1–3          | -1–6          | -2–2          | -2–2          |
| Stirring time after addition of chlorosilanes and Si(OEt)$_4$ | 130        | 120           | 130           | 130           | 120           | 120           |
| Drying of products: with anhydrous MgSO$_4$ by cooling in a fridge |

* Average molecular composition of polymers, based on a stoichiometry of monomers. PMHS-Q: liquid branched poly(methylhydrosiloxanes) of random structures.
Reaction mixture was allowed to warm to room temperature within 120–170 min, acid layer was separated, and organosilicon layer was washed with water until neutral, transferred to an Erlenmayer flask, and dried at ~4 °C with anhydrous magnesium sulfate overnight. Magnesium sulfate was filtered through Schott funnel G-3 and washed with ether. Alternatively, instead of drying with anhydrous MgSO\(_4\) traces of water were removed from products by cooling their ether solution in a refrigerator overnight, warming up the content of the flask to room temperature, and the ether solution of products was decanted from drops of water. The solvent was distilled off. In order to remove volatile cyclic and linear low molecular weight siloxane oligomers, the prepared products were heated at temperature 150–155 °C under reduced pressure (16–21 mm Hg, 2128–2793 Pa), and subsequently under a vacuum (3–5 mm Hg, 400–665 Pa).

In a second step of syntheses of Q\(_3\)D\(_{70}\)M\(_6\) and other poly(dimethyl-co-methylhydro)siloxanes, containing both mers D and D\(_{\text{H}}\), with a general formula:

\[
\left(\text{SiO}_{4/2}\right)_{y}\left[(\text{CH}_3)_{2}\text{SiO}\right]_m[\text{CH}_3(\text{H})\text{SiO}]_n[\text{(CH}_3)_3\text{SiO}_{0.5}]_p
\]

(where: \(y = 1–3\), \(m = n = 49–52\), \(p = 2y + 2\)), so called “extra blocking” of unreacted silanol groups Si-OH was applied: in reactions with (chloro)trimethylsilane, in the presence of triethylamine, which was used as an acceptor of hydrogen chloride with ~5% excess with respect to a stoichiometric amount. (4-Dimethylamino)pyridine (DMAP) was used as a nucleophilic catalyst in 1:10 mole ratio with respect to Et\(_3\)N. Products untreated with extra amounts of TMCS and DMAP/Et\(_3\)N showed increase of their viscosity after few months and a presence of small drops of water from a homo-condensation reaction of residual Si-OH groups.

The “extra blocking” reactions of silanol groups were carried out after drying step of ether solutions of products of the hydrolytic polycondensation, at room temperature within few hours. Precipitates of amines hydrochlorides were dissolved in diluted solution (5–10 wt%) of hydrochloric acid, a water layers were discarded and washed with distilled water until neutral, dried with anhydrous MgSO\(_4\), and filtered. Ether was distilled off under atmospheric pressure and final products were evacuated under vacuum at temperature 150–155 °C (Table 2). A chemical composition of volatile siloxanes was not analyzed.

### Table 2. Yields of PMHS-Q, conditions of removal of volatile products, and results of measurements of dynamic viscosity of branched PMHS, containing quadruple branching units Q.

| Predicted molecular formula (polymer abbreviation) | Yield (g) | Yield (wt%) | Dynamic viscosity (cP) | Evacuation conditions | Volatile products (C/mm Hg) (g) |
|--------------------------------------------------|-----------|-------------|------------------------|-----------------------|---------------------------------|
| QD\(_{18}\)M\(_6\) (Q1)                        | 20.14     | 62          | 12.8                   | 152                   | 190                             | 24/16–79/3.5                   | 9.27                           |
| Q\(_2\)D\(_{18}\)M\(_6\) (Q2)                   | 48.70     | 68          | 11.0                   | 154                   | 200                             | 23/16–77/3.5                   | 18.14                          |
| Q\(_3\)D\(_{18}\)M\(_6\) (Q3)                   | 52.82     | 69          | 13.1                   | 155                   | 190                             | 23/18–70/5                    | 16.71                          |
| QD\(_{20}\)D\(_{18}\)M\(_4\) (Q1D)              | 40.29     | 55          | 12.5                   | 150                   | 210                             | 21/21–80/5                    | 34.84                          |
| Q\(_2\)D\(_{20}\)D\(_{18}\)M\(_4\) (Q2D)        | 40.49     | 56          | 11.8                   | 155                   | 200                             | 27/19–78/4                    | 31.06                          |
| Q\(_3\)D\(_{20}\)D\(_{18}\)M\(_4\) (Q3D)        | 43.77     | 58          | 10.7                   | 155                   | 190                             | 21/16–74/4.5                 | 28.22                          |

### 3. Results and Discussion

#### 3.1. Synthesis of Branched Poly(methylhydrosiloxanes) (PMHS-Q)

Syntheses of poly(methylhydrosiloxanes) with statistical and branched structures containing quadruple branching points SiO\(_{4/2}\) were carried out in the medium of diethyl ether at temperature below 0 °C. Solutions of chlorosilanes and Si(OEt)\(_4\) in dry ether were added dropwise to water. In all syntheses were used such amounts of water which were necessary for hydrolysis reactions and dissolution of HCl, allowing to obtain hydrochloric acid with concentrations approximately 20 wt%.

Applying the hydrolytic polycondensation of mixtures of appropriate amounts of (tetraethoxy)-silane Si(OEt)\(_4\) and chlorosilanes: MeHSiCl\(_2\), Me\(_2\)SiCl\(_2\), and Me\(_3\)SiCl, with water, at
temperature from −10–0 °C, within 3–5 h, were prepared branched poly(methylhydrosiloxanes) with SiO$_{4/2}$ branching points and the general formula:

$$[\text{SiO}_{4/2}]_y[\text{CH}_3(\text{H})\text{SiO}]_n[\text{CH}_3\text{SiO}]_p$$ (2)

(where: $y = 1–3$, $n = 48–50$, $p = 2y + 2$), containing quadruple branching points SiO$_{4/2}$ (Q), mers D$^H$ and terminal groups Me$_3$SiO$_{0.5}$. Similarly, branched poly(dimethyl-co-methylhydro)siloxanes containing branching units Q, linear building blocks D, and D$^H$, and terminal groups M, were synthesized with the general formula:

$$[\text{SiO}_{4/2}]_y[(\text{CH}_3)_2\text{SiO}]_m[\text{CH}_3(\text{H})\text{SiO}]_n[(\text{CH}_3)_3\text{SiO}]_p$$ (3)

where $y = 1–3$, $m = n = 49–52$, $p = 2y + 2$. After addition of substrates stirring of obtained reaction mixtures was continued within next 2–3 h, in order to reach full conversion of substrates and full hydrolysis of Si-Cl and Si-OC$_2$H$_5$ groups. In the case of syntheses of Q3, Q1D, Q2D, and Q3D termination reactions (so called “extra blocking” reactions) of unreacted silanol groups Si-OH in reactions with (chloro)trimethylsilane were applied, in the presence of: (1) triethylamine as the acceptor of hydrogen chloride (used with ~5–10% excess with respect to stoichiometric amounts); and (2) (4-dimethylamino)pyridine (DMAP) as the nucleophilic catalyst (used in 1:10 mole ratio with respect to Et$_3$N).

Products not treated with additional amounts of TMCS and DMAP/Et$_3$N showed increase of their viscosity after few months and a presence of traces of water, which could originate from the homocondensation reaction of residual Si-OH groups. However, in the case of syntheses of Q1 and Q2 “extra blocking” was not applied, and no increase of their viscosity was observed during longer storage of these PMHS-Q. Ether solutions of products Q1, Q2, and Q3 were dried with anhydrous MgSO$_4$, while polymers Q1D, Q2D, and Q3D were dried by freezing traces of water in the refrigerator overnight. Yields of prepared PMHS-Q ranged from 55–69 wt% (Table 2). The highest yield was obtained for Q3.

The chemical structures of all PMHS-Q were confirmed by spectroscopic methods: FTIR and NMR ($^1$H and $^{29}$Si) and the elemental analysis (% C, % H, and % Si) (see Table 3).

Dynamic viscosities ($\eta$$_{25}$) of PMHS-Q containing quadruple branching points SiO$_{4/2}$, were very low and ranged from 10.7–13.1 cP. Low viscosities of PMHS-Q in comparison with linear polysiloxanes having similar molecular weights presumably may result from a globular structure of hyperbranched macromolecules. It is commonly known from a literature that dendrimers and hyperbranched polymers in solution and in melt have low viscosities. Their viscosities and molecular weights are much lower than those for linear analogs and depend on a degree of branching, a polarity of a solvent, a kind of functional group on their “surface”, and also on pH of a polymer solution. Dendritic and hyperbranched polymers have a variable hydrodynamic radii depending on the property of solvents; they are smaller than those of their linear analogs with the same molar mass.

The values of molecular weights of prepared PMHS-Q determined by SEC method were lower than calculated values for predicted molecular formulas: QD$_{52}$D$^H_{52}$M$_4$, Q$_2$D$_{49}$D$^H_{49}$M$_6$, and Q$_3$D$_{50}$D$^H_{50}$M$_8$. A polydispersity of molecular weights of PMHS-Q ranged from 2.0 to 2.8. The molecular weights of dendrimers and hyperbranched polymers determined by SEC using polystyrene standards are regarded with some scepticism. The hydrodynamic radii were also susceptible to the polarity of functional groups on the periphery [65–67]. Values of $M_n$ and $M_w$ determined by SEC method with polystyrene standards for hyperbranched polysiloxanes were much lower than MW obtained with application of MALLS detectors [68–70].

Köhler et al. used the SEC, $^1$H- and $^{29}$Si NMR, and MALDI-TOF-MS methods for characterization of a linear poly(dimethylsiloxane)-co-poly(hydromethysiloxane) (PDMS-co-PHMS) copolymer with respect to chain length distribution, heterogeneity of chemical composition, and sequence distribution [71].
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Table 3. Characteristics of polymethylhydrosiloxanes with branched, random structure of siloxane chains, containing branching units Q.

| PMHS-Q  | M_n (calc.) | M_n | M_w | M_w/M_n | % C calc. | % C found | % H calc. | % H found | % Si calc. | % Si found |
|---------|-------------|-----|-----|---------|-----------|-----------|-----------|-----------|------------|------------|
| QD_H4sM4 | 3271        | 6310| 17,750 | 2.81 | 22.03    | 21.51     | 5.06     | 4.98     | 60.45      | 60.07      |
| Q2D_H49M6 | 3554        | 3220| 8,330 | 2.59 | 22.64    | 22.01     | 7.09     | 7.04     | 5.55       | 5.45       |
| Q3D_H50M8 | 3836        | 3840| 10,350 | 2.69 | 23.16    | 22.03     | 7.14     | 7.02     | 4.70       | 4.62       |
| QD2D_H52M4 | 7367        | 2650| 6,280 | 2.36 | 27.39    | 28.89     | 7.60     | 7.89     | 4.15       | 4.54       |
| Q2D50D_H49M6 | 7187      | 2440| 5,750 | 2.35 | 27.57    | 28.40     | 7.63     | 7.88     | 4.14       | 4.40       |
| Q3D50D_H52M8 | 7544       | 5100| 10,210 | 2.00 | 27.07    | 27.78     | 7.65     | 8.35     | 4.13       | 4.30       |

3.2. Characterization of PMHS-Q by FTIR

In all FTIR spectra of studied PMHS-Q containing quadruple branching points Q were present absorption bands in the range 2160 cm⁻¹, corresponding to stretching vibrations of Si-H bonds, and also absorption bands of the remaining groups of atoms: Si-CH₃ (2960, 2890, 1440, 1400, 1255, and 830–700 cm⁻¹), Si-O-Si (1010–1110 cm⁻¹), and Si(CH₃)₃ (750, 690 cm⁻¹) (see data in Table 4). Examples of the FTIR spectra of branched poly(methylhydrosiloxanes) are presented in Figures 1–3.

Table 4. Characteristic absorption bands in FTIR spectra of Q2D_D49M6.

| Wave number [cm⁻¹] | Group or bond | Vibration |
|-------------------|---------------|-----------|
| found             | literature data [72] |          |
| 2965              | 2975–2950     | CH₃       | ν asym C-H |
| 2878              | 2885–2860     | CH₃       | ν sym C-H  |
| 2164              | 2300–2100     | Si-H      | ν Si-H     |
| 1450              | 1470–1420     | CH₃       | δ asym C-H |
| 1410              | 1390–1365     | CH₃       | δ asym C-H |
| 1260              | 1265–1250     | Si-CH₃    | δ asym Si-C|
| 1115–1027         | 1100–1000     | Si-O-Si   | ν asym Si-O|
| 910               | 950–800       | Si-H      | δ Si-H     |
| 864               | 860–750       | Si-CH₃    | ν asym Si-C|
| 830               | 910–830       | Si-O      | ν asym Si-O|
| 800               | 800           | Si-CH₃    | δ sym Si-C |
| 759               | 755           | Si-(CH₃)₃ | δ sym Si-C |

Figure 1. FTIR spectrum of Q2D_H49M6.
3.3. Characterization of PMHS-Q by NMR

In $^1$H–NMR spectra of copolymers, $QDH_{48}M_4$, $Q_2DH_{49}M_6$ and $Q_3DH_{50}M_8$ were present signals at $\delta$ 0.01–0.22 ppm, corresponding to hydrogen atoms of Si–CH$_3$ groups and signals at $\delta$ about five parts per million, characteristic for hydrosilane groups Si–H. In the $^1$H-NMR spectra of copolymers: $QD_{52}DH_{52}M_4$, $Q_2D_{49}DH_{49}M_6$, and $Q_3D_{50}DH_{50}M_8$ were present signals at $\delta$ 0.0–0.30 ppm, corresponding to hydrogen atoms of Si–CH$_3$ groups and signals at $\delta$ about five parts per million, characteristic for Si-H groups. Examples of the $^1$H-NMR and $^{29}$Si-NMR spectra of branched poly(methylhydrosiloxanes) are presented in Figures 4–7.
In $^{29}$Si-NMR INEPT spectra of copolymers $QD_{48}M_4$, $Q_2D_{49}M_6$, and $Q_3D_{50}M_8$ were present signals at $\delta = -31.62$–−$-39.97$ ppm corresponding to silicon atoms of units $D^H$ [8,9,54], and at $\delta$ $9.40$–$11.25$ ppm corresponding to silicon atoms of end groups $Me_3SiO_{0.5}$ (M). In the range of $\delta$ $-63$–−$-68$ ppm in INEPT $^{29}$Si-NMR spectra were present signals of a very low intensity, from Si atoms of branching units $MeSiO_{1,5}$, which could be formed during trace hydrolysis of Si-H bonds. In the INEPT NMR spectra of copolymers $QD_{52}D^H_{52}M_4$ (Q1D), $Q_2D_{50}D^H_{49}M_6$ (Q2D), and $Q_3D_{50}D^H_{50}M_8$ (Q3D) existed signals at $\delta$ $7.27$–$9.92$ ppm, corresponding to silicon atoms of end groups $Me_3SiO_{0.5}$ and at $\delta$ $-34.61$ to $-38.87$ ppm, characteristic for mers $MeHSiO$ ($D^H$), and also at $\delta$ $-18.77$–$-21.85$ ppm from silicon atoms of units $Me_3SiO$ ($D$) [8,9,52]. It was impossible to observe signals of quadruple silicon atoms of units $SiO_{1/2}$ in $^{29}$Si-NMR spectra, which were registered by the INEPT technique, so it was necessary to run $^{29}$Si-NMR spectra with application of the INVGATE program. A summary of chemical shifts data in the $^1$H- and $^{29}$Si-NMR (INEPT and INVGATE) spectra of all PMHS-Q is presented in Table 5.

In the $^{29}$Si-NMR INVGATE spectra of branched random PMHS were present signals of silicon atoms corresponding to linear mers:

$CH_3(H)SiO$ at $\delta = -34.0$–$36.0$ ppm (for Q1, Q2, and Q3),
$CH_3(OSiCH_3)_2$ at $\delta = -34.0$–$37.5$ ppm (for Q1D, Q2D, and Q3D),
and terminal groups ($CH_3)_3SiO_{1/2}$:

at $\delta$ $9.5$–$11.3$ ppm (for Q1, Q2, and Q3),
$\delta$ $7.3$–$7.9$ and $9.8$–$10.0$ ppm (for Q1D, Q2D, and Q3D).

Resonance signals of Si atoms of branching units Q were present in the range of $\delta$:

$-100.3$–$112.4$ ppm,

and they overlapped with very strong $^{29}$Si signals of a borosilicate glass.
Figure 5. $^{29}$Si-NMR spectrum (INVGATE, in C$_6$D$_6$) of polymethylhydrosiloxane Q$_3$D$_{50}$M$_8$.

In the $^{29}$Si-NMR INVGATE spectra of copolymers: Q$_D$H$_{48}$M$_4$, Q$_2$D$_{49}$M$_6$ and Q$_3$D$_{50}$M$_8$ were present signals at: $\delta$ 9.40—11.25 ppm, corresponding to the terminal groups Me$_3$SiO$_{0.5}$, at $\delta$ −31.81—−36.25 ppm, characteristic for units MeHSiO (D$^D$H), and also resonance signals in the range of $\delta$ −100.3—−112.3 ppm for Si atoms from units Q. According to data in the literature [73] chemical shifts of Si atoms from units Q exist in the range of $\delta$ −100—−106 ppm.

Figure 6. $^1$H-NMR spectrum (in C$_6$D$_6$) of polymethylhydrosiloxane Q$_2$D$_{49}$D$^D$H$_{49}$M$_6$.
Chemical shifts at δ 9–11 ppm have been assigned to resonances of Si atoms of Me₃SiO₁₀₅ (M) groups in the following sequences of the siloxane chain ends: MDHDDH, MDHDQ, MDHDD, MDHDDQ, MDHQD, and MDHQ, while chemical shifts at δ 7–8 ppm belong to resonances of Si atoms of end groups M in the sequences: MDD, MDDDDH, MDDHD, MDDHDH, MDDQ, MQDQ, MQDD, and MQDD. Chemical shifts of middle silicon atoms of units D change in pentades, and magnetic interactions are shifted through four bonds in chain ends.

The sequences of dimethylsiloxane linkages in polymethylhydrosiloxane copolymers might be the following: DDHDD, DDHDDH, DDHDDH, DDHDDH, QDD, MDHDD, MDHDDH, MDHDDQ, MDHDDQ, MDHDDQ, MDHDDQ, and MDHDDQ. Chemical shifts of middle silicon atoms of units D change in pentades (Table 5) [8,9,74].

In the ²⁹Si-NMR spectra (recorded by INEPT and INVGATE techniques) in the range of δ −33 to −37 ppm exist signals of middle silicon atoms of units D, which undergo changes in pentades (Table 5). Signals of silicon atoms in the range of δ −102 to −109 ppm, presumably correspond to Si atoms in the central units Q, in the following sequences of siloxane structures:

Chemical shifts in the range of 7–11 ppm in the ²⁹Si-NMR spectra (INEPT and INVGATE) correspond to silicon atoms of the end groups M and change in tetrads (Table 5) [8,9,74].

Signals at δ −64 ppm of a very low intensity, registered both in INVGATE and INEPT ²⁹Si-NMR spectra of these three copolymers, probably come from Si atoms of units MeSiO₁₀₅ (T), which were formed during syntheses of PMHS-Q from trace hydrolysis of Si-H bonds [74].

Assignments of all ²⁹Si-NMR signals resulting from the microstructure of siloxane chain of branched polymethylhydrosiloxanes are summarized in Table 6.
Table 5. Chemical shifts of PMHS-Q in their $^1$H- and $^{29}$Si-NMR spectra (in C6D6).

| PMHS-Q    | $^1$H-NMR                | $^{29}$Si-NMR          | δ (ppm)            |
|-----------|--------------------------|------------------------|--------------------|
|           | Si-H Si-CH$_3$ Me$_3$SiO$_{0.5}$ Me$_2$SiO MeHSiO MeSiO$_{2/3}$ MeSiO$_{4/2}$ | INEPT INVGATE INEPT INVGATE INEPT INVGATE INEPT INVGATE INEPT INVGATE INEPT INVGATE INEPT INVGATE INEPT INVGATE |                   |
| QD$^{31}$$_{a}$M$_4$ | 4.90 0.01–0.22 9.75–11.03 9.98–10.96 - - - -31.51–37.42 -31.85–35.90 -64.51 -64.58 -101.40–108.13 | - - - - - - - - - - - - - - - - - - - - - - - - - - - - - |                   |
| Q$_2$D$^{31}$$_{a}$M$_6$ | 4.80 0.01–0.12 9.40–11.24 9.70–10.32 - - - -31.62–39.97 -31.83–36.25 -62.60–64.61 - - - - - - - - - - - - - - - - - - - - - - - | - - - - - - - - - - - - - - - - - - - - - - - - - - - - - |                   |
| Q$_2$D$^{32}$$_{a}$M$_6$ | 4.80 0.01–0.12 9.40–11.25 9.42–11.28 - - - -37.46–31.16 -32.16–35.87 -62.97–64.56 -64.54 -100.31–110.20 | - - - - - - - - - - - - - - - - - - - - - - - - - - - - - |                   |
| QD$_2$D$^{31}$$_{a}$M$_4$ | 4.92 0.05–0.22 9.92–7.27 7.30–9.96 -18.48–21.74 -18.67–21.44 -33.27–38.87 -34.56–37.30 -63.12–65.39 -63.72–65.89 -102.92–109.92 | - - - - - - - - - - - - - - - - - - - - - - - - - - - - - |                   |
| Q$_2$D$_4$D$^{31}$$_{a}$M$_6$ | 4.92 0.01–0.30 9.92–7.26 7.32–9.98 -18.43–21.85 -18.70–21.69 -34.54–37.53 -34.61–37.03 -62.95–65.26 -62.35–66.16 -101.81–109.71 | - - - - - - - - - - - - - - - - - - - - - - - - - - - - - |                   |
| Q$_2$D$^{31}$$_{a}$D$^{31}$$_{a}$M$_6$ | 4.83 0.01–0.23 9.91–7.27 7.32–9.98 -18.77–21.75 -18.72–21.29 -34.61–37.57 -34.54–36.10 -64.73 -63.35–65.16 -102.84–109.61 | - - - - - - - - - - - - - - - - - - - - - - - - - - - - - |                   |
Figure 7. $^{29}$Si-NMR spectra (in C$_6$D$_6$) of polymethylhydrosiloxane Q$_2$D$_{49}$H$_{49}$M$_6$: (a) INEPT, (b) INVGATE.
Table 6. The microstructure of siloxane chains in PMHS-Q, containing quadruple branching units Q (all possible sequences among tetrad of terminal groups, and linear and star pentads); values of $\delta$ concern Si atoms in structural units denoted as bold and underlined.

| $\delta^{29}$Si-NMR (ppm) | 9–11 | 7–8 | −18——19 | −20——22 | −33——37 | −101——109 |
|---------------------------|------|-----|---------|---------|---------|-----------|
| $\text{MD}^{H}H^{H}H^{H}$ | $\text{M}D\text{DD}$ | $\text{DD}^{H}H^{H}H^{H}$ | $\text{DD}^{H}H^{H}H^{H}$ | $\text{DD}^{H}H^{H}H^{H}$ | $\text{DD}^{H}H^{H}H^{H}$ | $\text{DD}^{H}H^{H}H^{H}$ |
| $\text{MD}^{H}H^{Q}H^{Q}$ | $\text{M}D\text{D}D^{H}$ | $\text{DD}^{H}H^{H}H^{H}$ | $\text{DD}^{H}H^{H}H^{H}$ | $\text{DD}^{H}H^{H}H^{H}$ | $\text{DD}^{H}H^{H}H^{H}$ | $\text{DD}^{H}H^{H}H^{H}$ |
| $\text{MD}^{Q}Q^{Q}D^{Q}$ | $\text{MD}^{H}H^{H}D^{H}$ | $\text{DD}^{H}H^{H}H^{H}$ | $\text{DD}^{H}H^{H}H^{H}$ | $\text{DD}^{H}H^{H}H^{H}$ | $\text{DD}^{H}H^{H}H^{H}$ | $\text{DD}^{H}H^{H}H^{H}$ |
| $\text{MD}^{Q}D^{Q}Q^{Q}$ | $\text{MD}^{H}H^{H}D^{H}$ | $\text{DD}^{H}H^{H}H^{H}$ | $\text{DD}^{H}H^{H}H^{H}$ | $\text{DD}^{H}H^{H}H^{H}$ | $\text{DD}^{H}H^{H}H^{H}$ | $\text{DD}^{H}H^{H}H^{H}$ |
| $\text{MD}^{H}D^{Q}Q^{Q}$ | $\text{MD}^{H}D^{Q}Q^{Q}$ | $\text{MD}^{H}D^{Q}Q^{Q}$ | $\text{MD}^{H}D^{Q}Q^{Q}$ | $\text{MD}^{H}D^{Q}Q^{Q}$ | $\text{MD}^{H}D^{Q}Q^{Q}$ | $\text{MD}^{H}D^{Q}Q^{Q}$ |
| $\text{MD}^{H}H^{D}D^{D}$ | $\text{MD}^{H}H^{D}D^{D}$ | $\text{MD}^{H}H^{D}D^{D}$ | $\text{MD}^{H}H^{D}D^{D}$ | $\text{MD}^{H}H^{D}D^{D}$ | $\text{MD}^{H}H^{D}D^{D}$ | $\text{MD}^{H}H^{D}D^{D}$ |
| $\text{MD}^{D}D^{Q}Q^{Q}$ | $\text{MD}^{D}D^{Q}Q^{Q}$ | $\text{MD}^{D}D^{Q}Q^{Q}$ | $\text{MD}^{D}D^{Q}Q^{Q}$ | $\text{MD}^{D}D^{Q}Q^{Q}$ | $\text{MD}^{D}D^{Q}Q^{Q}$ | $\text{MD}^{D}D^{Q}Q^{Q}$ |
| $\text{MD}^{D}Q^{Q}D^{Q}$ | $\text{MD}^{D}Q^{Q}D^{Q}$ | $\text{MD}^{D}Q^{Q}D^{Q}$ | $\text{MD}^{D}Q^{Q}D^{Q}$ | $\text{MD}^{D}Q^{Q}D^{Q}$ | $\text{MD}^{D}Q^{Q}D^{Q}$ | $\text{MD}^{D}Q^{Q}D^{Q}$ |

Author Contributions: Syntheses and characterization of branched PMHS were carried out by J.J. Chruściel and M. Fejdyš. Moreover, J.J. Chruściel measured dynamic viscosities of PMHS, M. Fejdyš (35% total contribution) recorded FT-IR spectra, and W. Fortuniak (10% contribution) performed measurements of molecular weights of PMHS by the SEC method. A manuscript has been written by J.J. Chruściel (55% total contribution).

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