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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_2SiO (D) chain building units (or only mers MeHSiO), and terminal groups $Me_3SiO_{0.5}$ (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, ^1H- 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 $Me_3SiOSiMe_3$, towards phosphonitrile catalyst $[Cl_3P(NPCl_2)_2PCl_3]^+PCl_6^-$ at elevated temperature [16–20].

A polymerization of 1,3,5,7-tetramethylcyclotetrasiloxane (D^H_4) [$D^H = H(CH_3)SiO$] was carried out in the presence of the non-ionic emulgator $C_{12}H_{25}(OCH_2CH_2)_{23}OH$ and dodecylbenzenesulphonic acid and it was accelerated by ultrasounds [21,22].

Weber and Paulasaari obtained poly(1-hydro-1,3,3,5,5-pentamethyltrisiloxane) with a regular chain structure by the polymerization of a new monomer, pentamethylcyclotrisiloxane c-$(Me_2SiO)_2(MeHSiO)$ [c-D_2D^H; D = $(CH_3)_2SiO$] in tetrahydrofurane (THF), in the presence of $Ph_2Si(OLi)_2$, at −79 °C [23]. The starting monomer c-D_2D^H was prepared by heterocondensation of $MeHSiCl_2$ with $HO(Me_2SiO)_2H$ (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:

$$RMe_2SiO[(Me_2SiO)_m(MeHSiO)_k]_n(Me_2SiO)_mSiMe_2R, \quad (1)$$

(where: R = –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 dimethylsiloxane-α,ω-diols $HO(Me_2SiO)_mH$ with siloxane oligomers of a general formula $Cl(MeHSiO)_{k-1}SiHMeCl$, having chloro(hydro)silyl functionalities, followed by termination reactions with chlorotrimethylsilane Me_3SiCl, when PDMS-*b*-PMHS chains were blocked with $(CH_3)_3SiO_{0.5}$ (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}H- and ^{29}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 ("spherosiloxanes"): T^H_8, T^H_{10}, T^H_{12}, T^H_{14}, and T^H_{16} ($T^H = HSiO_{1.5}$) are solids, which can be prepared by the hydrolytic polycondensation of: (a) trichlorosilane $HSiCl_3$, carried out in the presence of $FeCl_3$ in methanol medium [24,26–28], or (b) trimethoxysilane $HSi(OCH_3)_3$, saturated with anhydrous HCl, in acetic acid solution [29–32], or in the presence of concentrated H_2SO_4 [33,34]. Octakis(dimethylsiloxy)-octasilsesquioxane $[(HMe_2SiO)SiO_{1.5}]_8$ [$Q_8M^H_8$, Q = $SiO_{4/2}$, $M^H = H(CH_3)_2SiO_{0.5}$] can be prepared with high yields in reaction of octakis(tetramethylammonium)octasilsesquioxane with $ClSiMe_2H$ [35–37], up to 85–91% yield [38,39]. Currently a low molecular mass star tetrakis(dimethylsiloxy)silane $Si[OSi(CH_3)_2H]_4$, octahydrosilsesquioxane (T^H_8) and cubic $Q_8M^H_8$ are commercially available [35,40–46].

Recently siloxane-polyhedral silsesquioxane copolymers (soluble in THF) were prepared by the dehydrogenative condensation of T^H_8 with diphenylsilanediol, tetraphenyldisiloxane diol or oligodimethylsiloxane-α,ω-diols in the presence of diethylhydroxylamine, followed by trimethylsilylation [47,48]. T^H_8 was also applied as a precursor of mezoporous silica, which was prepared without using any template or surfactant [49].

An equilibration of octamethylcyclotetrasiloxane [$(Me_2SiO)_4$, D_4] with $Si[OSi(CH_3)_2H]_4$ and trifluoromethanesulphonic acid led to tetraarm star polysiloxane $Si\{[OSi(CH_3)_2]_nOSi(CH_3)_2H\}_4$ [50,51]. Six- and eight-membered silicates: hexakis(dimethylsiloxy)cyclotrisiloxane $[(HMe_2SiO)_2SiO]_3$ and octakis(dimethylsiloxy)cyclotetrasiloxane $[(HMe_2SiO)_2SiO]_4$ were synthesized with low yields, from reactions of pyrolysis products of wollastonite. $[(HMe_2SiO)_2SiO]_3$ was prepared in reaction of chlorodimethylsilane HMe_2SiCl with pseudowollastonite $Ca_3Si_3O_9Cl_6$, while $[(HMe_2SiO)_2SiO]_4$ was prepared by heating octakis(trimethylsiloxy)cyclotetrasiloxane $[(Me_3SiO)_2SiO]_4$ with 1,1,3,3--tetramethyldisiloxane $HMe_2SiOSiMe_2H$ in the presence of trifluoromethanesulphonic acid [52,53]. The equilibration of $[(HMe_2SiO)_2SiO]_3$ with D_4 and triflic acid gave PMHS of the following branched structure: $-\{-OSi[(OSiMe_2O)_nSiMe_2H]_2-\}_6-$ [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 polysilsesquioxanes of a ladder structure, containing units $HSiO_{1.5}$ and $MeSiO_{1.5}$, by hydrolysis of byproducts prepared through condensation of $HSiCl_3$ and $MeSiCl_3$ with *p*-phenylenediamine or ethylenediamine [55–57].

A silicone dendrimer of a third generation with symmetrical structure and the general formula $(CH_3SiO_{1.5})_{22}[(CH_3)_2SiO)]_{162}[H(CH_3)_2SiO_{0.5}]_{24}$ 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, trimethylchlorosilane and methyltriethoxy)-silane or phenyl(triethoxy)silane. These resins were used as crosslinking agents for addition of cured silicone elastomers [59]. Condensation of (triethoxy)silane $HSi(OC_2H_5)_3$, 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 $(PhSiO_{1.5})_8(MeHSiO)_2$, so-called "double-decker-shaped-silsesquioxane", was prepared from reaction of $MeHSiCl_2$ with a byproduct, which was obtained via a condensation of phenyl(trimethoxy)silane and NaOH with 20% yield [61].

Twelve new liquid branched poly(methylhydrosiloxanes) with statistical structures (b-r-PMHS), containing triple branching units $MeSiO_{1.5}$ (T), both Me_2SiO (D) and MeHSiO (D^H) chain building units (or only mers MeHSiO), and two b-r-PMHS containing five different structural units: D, D^H, T and T^H and trimethylsiloxy end groups $Me_3SiO_{0.5}$ (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, ^{1}H- and ^{29}Si-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 $MeSiO_{1.5}$ 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 (D^H) and Me_2SiO (D) chain building units (or only mers MeHSiO), quadruple branching units $SiO_{4/2}$ (Q), and terminal groups $Me_3SiO_{0.5}$, from appropriate organic chlorosilanes and tetraethoxysilane.

2. Materials and Methods

Dichloromethylsilane $MeHSiCl_2$ (MDS, 99%, b.p. 41 °C), dichlorodimethylsilane Me_2SiCl_2 (DDS, b.p. 70–71 °C), tetraethoxysilane $Si(OC_2H_5)_4$ (b.p. 168 °C), (4-dimetylamino)pyridine (DMAP, 99%) were all sourced from Aldrich Chemical Company Inc., USA. Chlorotrimethylsilane Me_3SiCl 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 P_2O_5. Diethyl ether was purified and dried with anhydrous KOH, and distilled over CaH_2.

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 NaCI plates. ^{1}H-NMR and ^{29}Si-NMR (INEPT) spectra were recorded on Bruker DRX 500 machine (Bruker Physik AG, Karlsruhe, Germany) at CBMM PAN in Łódź. Hexamethyldisiloxane $Me_3SiOSiMe_3$ was used as an external standard in ^{29}Si-NMR (δ = 6.98 ppm, in $CDCl_3$).

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 CH_3 signals in ^{1}H-NMR spectra, and compared to theoretical integration ratios of Si-H and CH_3 signals. The content of Si was determined by the gravimetric method with H_2SO_4 (p.a.) [64].

Dynamic viscosities (η^{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 $g \cdot mol^{-1}$. Calibration was made with polystyrene Ultrastyrogel standards with MWs: 10^2, 10^3, and 10^4 $g \cdot mol^{-1}$.

Synthesis of Branched Polymethylhydrosiloxanes (PMHS-Q)

Branched polymethylhydrosiloxanes, containing only units D^H and Q, terminated with $Me_3SiO_{0.5}$ groups, with structures described by a general formula:

$$(SiO_{4/2})_y[CH_3(H)SiO]_n[(CH_3)_3SiO_{0.5}]_p \tag{2}$$

(where: y = 1–3, n = 48–50, p = 2y + 2), and branched poly(dimethyl-*co*-methylhydro)siloxanes, containing both mers D, as well mers D^H, units Q and end $Me_3SiO_{0.5}$ groups, of a general formula:

$$(SiO_{4/2})_y[(CH_3)_2SiO]_m[CH_3(H)SiO]_n[(CH_3)_3SiO_{0.5}]_p \tag{3}$$

(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_2SiCl_2, and chlorotrimethylsilane Me_3SiCl, 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 ***					
		$QD^H_{48}M_4$	$Q_2D^H_{49}M_6$	$Q_3D^H_{50}M_8$	$QD_{52}D^H_{52}M_4$	$Q_2D_{49}D^H_{49}M_6$	$Q_3D_{50}D^H_{50}M_8$
		Amounts of reagents and a solvent					
$Si(OEt)_4$	(mol)	0.01	0.04	0.06	0.01	0.02	0.03
	(cm^3)	2.2	8.9	13.4	2.2	4.6	6.7
$MeHSiCl_2$ (MDS)	(mol)	0.48	0.98	1.0	0.52	0.49	0.50
	(cm^3)	50.0	102.0	104.1	54.1	51.5	52.1
Me_2SiCl_2 (DDS)	(mol)	-	-	-	0.52	0.49	0.50
	(cm^3)	-	-	-	63.1	59.8	60.6
Me_3SiCl (TMCS)	(mol)	0.04	0.12	0.16	0.04	0.06	0.08
	(cm^3)	5.1	15.2	20.3	5.1	7.6	10.2
H_2O	(mol)	9.11	18.94	19.66	19.33	18.38	18.94
	(cm^3)	164	341	354	348	331	341
(4-dimethylamino)-pyridine (DMAP)	(mol)	-	-	0.003	0.0109	0.0108	0.01
	(g)	-	-	0.3665	1.3316	1.3194	1.2217
Et_3N	(mol)	-	-	0.03	0.109	0.108	0.10
	(cm^3)	-	-	4.2	101.2	15.1	13.9
Diethyl ether	(cm^3)	50	80	60	100	80	90
Addition time of chlorosilanes and $Si(OEt)_4$	(min)	50	60	95	80	55	95
Temperature during addition of chlorosilanes and $Si(OEt)_4$	(°C)	−4–−2	−1–3	−1–3	−1–3	−1–6	−2–2
Stirring time after addition of chlorosilanes and $Si(OEt)_4$	(min)	170	130	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 $\mathbf{Q_3D^H{}_{50}M_8}$ and other poly(dimethyl-*co*-methylhydro)siloxanes, containing both mers D and D^H, with a general formula:

$$(SiO_{4/2})_y[(CH_3)_2SiO]_m[CH_3(H)SiO]_n[(CH_3)_3SiO_{0.5}]_p \tag{3}$$

(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_3N. Products untreated with extra amounts of TMCS and DMAP/Et_3N 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.

PMHS-Q			Dynamic viscosity	Evacuation conditions		Volatile products	
Predicted molecular formula (polymer abreviation)	Yield			Bath temp.	Time	B.p./pressure	Mass
	(g)	(wt%)	(cP)	(°C)	(min)	(°C/mm Hg)	(g)
$\mathbf{QD^H{}_{48}M_4}$ **(Q1)**	20.14	62	12.8	152	190	24/16–79/3.5	9.27
$\mathbf{Q_2D^H{}_{49}M_6}$ **(Q2)**	48.70	68	11.0	154	200	23/16–77/3.5	18.14
$\mathbf{Q_3D^H{}_{50}M_8}$ **(Q3)**	52.82	69	13.1	155	190	23/18–70/3.5	16.71
$\mathbf{QD_{52}D^H{}_{52}M_4}$ **(Q1D)**	40.29	55	12.5	150	210	21/21–80/5	34.84
$\mathbf{Q_2D_{49}D^H{}_{49}M_6}$ **(Q2D)**	40.49	56	11.8	155	200	27/19–78/4	31.06
$\mathbf{Q_3D_{50}D^H{}_{50}M_8}$ **(Q3D)**	43.77	58	10.7	155	190	21/16–74/4.5	28.22

3. Results and Discussion

3.1. Synthesis of Branched Polymethylhydrosiloxanes (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_2SiCl_2, and Me_3SiCl, 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:

$$[SiO_{4/2}]_y[CH_3(H)SiO]_n[(CH_3)_3SiO_{0.5}]_p \tag{2}$$

(where: y = 1–3, n = 48–50, p = 2y + 2), containing quadruple branching points $SiO_{4/2}$ (Q), mers D^H and terminal groups $Me_3SiO_{0.5}$. Similarly, branched poly(dimethyl-*co*-methylhydro)siloxanescontaining branching units Q, linear building blocks D, and D^H, and terminal groups M, were synthesized with the general formula:

$$[SiO_{4/2}]_y[(CH_3)_2SiO]_m[CH_3(H)SiO]_n[(CH_3)_3SiO_{0.5}]_p \tag{3}$$

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_2H_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_3N).

Products not treated with additional amounts of TMCS and DMAP/Et_3N 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 (η^{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: $QD_{52}D^H{}_{52}M_4$, $Q_2D_{49}D^H{}_{49}M_6$, and $Q_3D_{50}D^H{}_{50}M_{8.}$ 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].

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		% H		% Si	
					calc.	found	calc.	found	calc.	found
$QD^H{}_{48}M_4$	3271	6310	17,750	2.81	22.03	21.51 21.76	7.03	6.61 6.90	45.50	44.87
$Q_2D^H{}_{49}M_6$	3554	3220	8330	2.59	22.64	22.01 22.11	7.09	6.92 7.01	45.05	45.15
$Q_3D^H{}_{50}M_8$	3836	3840	10,350	2.69	23.16	22.03 22.14	7.14	7.02 6.85	44.65	43.81
$QD_{52}D^H{}_{52}M_4$	7367	2650	6280	2.36	27.39	28.89 28.70	7.60	7.89 8.03	41.55	41.54
$Q_2D_{49}D^H{}_{49}M_6$	7187	2440	5750	2.35	27.57	28.15 28.40	7.63	7.69 7.88	41.42	41.40
$Q_3D_{50}D^H{}_{50}M_8$	7544	5100	10,210	2.00	27.07	27.78 27.92	7.65	8.35 7.98	41.32	41.30

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-CH_3 (2960, 2890, 1440, 1400, 1255, and 830–700 cm^{-1}), Si-O-Si (1010–1110 cm^{-1}), and Si$(CH_3)_3$ (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 $Q_2D_{49}D^H{}_{49}M_6$.

Wave number [cm^{-1}]		Group or bond	Vibration
found	literature data [72]		
2965	2975–2950	CH_3	ν_{asym} C-H
2878	2885–2860	CH_3	ν_{sym} C-H
2164	2300–2100	Si-H	ν Si-H
1450	1470–1420	CH_3	δ_{asym} C-H
1410	1390–1365	CH_3	δ_{sym} C-H
1260	1265–1250	Si-CH_3	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-CH_3	ν_{asym} Si-C
830	910–830	Si-O	ν_{asym} Si-O
800	800	Si-CH_3	δ_{sym} Si-C
759	755	Si-$(CH_3)_3$	δ_{asym} Si-C

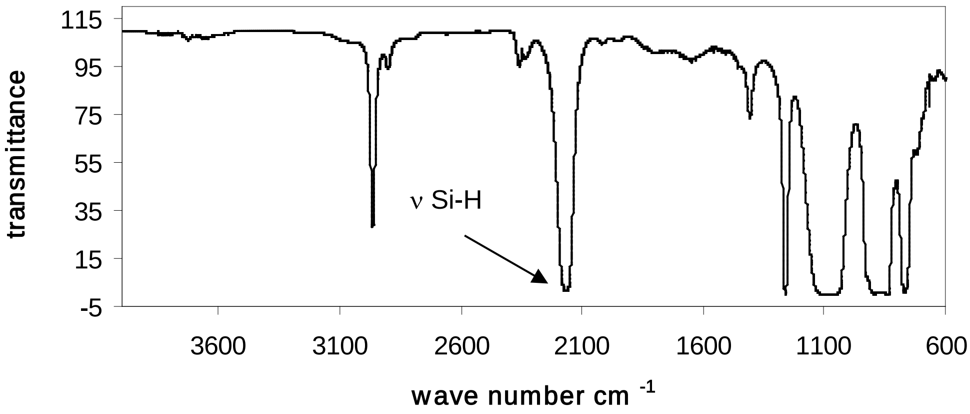


Figure 1. FTIR spectrum of $Q_2D^H{}_{49}M_6$.

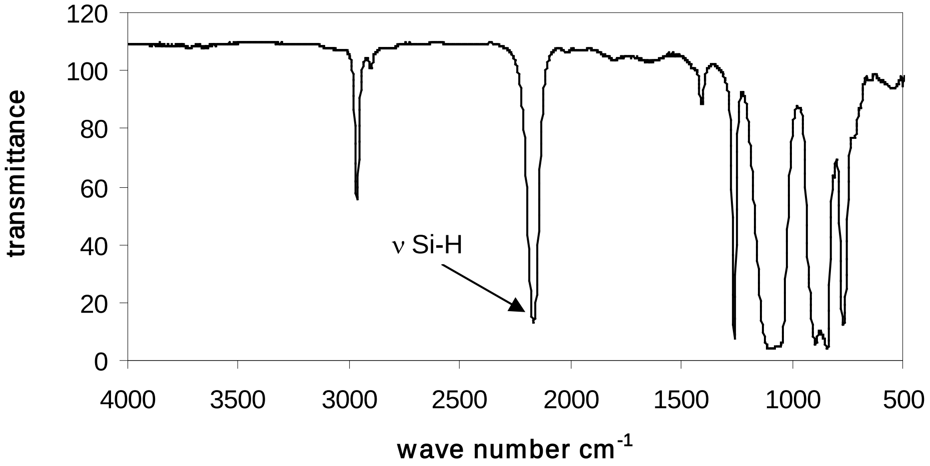


Figure 2. FTIR spectrum of $Q_3D^H{}_{50}M_8$.

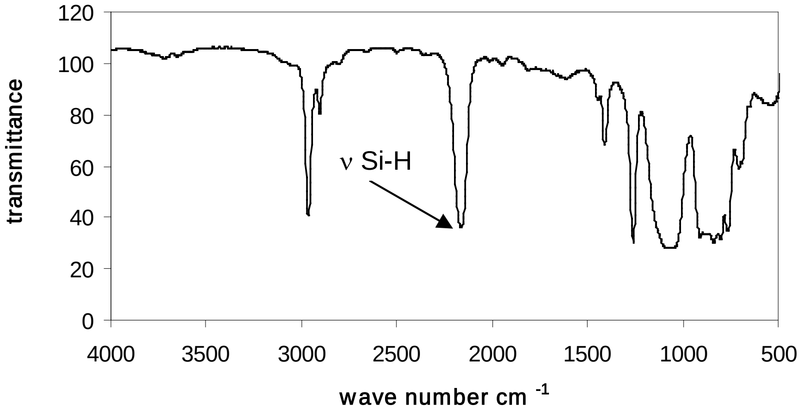


Figure 3. FTIR spectrum of $Q_2D_{49}D^H{}_{49}M_6$.

3.3. Characterization of PMHS-Q by NMR

In ^{1}H–NMR spectra of copolymers, $\mathbf{QD^H{}_{48}M_4}$, $\mathbf{Q_2D^H{}_{49}M_6}$ and $\mathbf{Q_3D^H{}_{50}M_8}$ were present signals at δ 0.01–0.22 ppm, corresponding to hydrogen atoms of Si-CH_3 groups and signals at δ about five parts per million, characteristic for hydrosilane groups Si-H. In the ^{1}H-NMR spectra of copolymers: $\mathbf{QD_{52}D^H{}_{52}M_4}$, $\mathbf{Q_2D_{49}D^H{}_{49}M_6}$, and $\mathbf{Q_3D_{50}D^H{}_{50}M_8}$ were present signals at δ 0.0–0.30 ppm, corresponding to hydrogen atoms of Si–CH_3 groups and signals at δ 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.

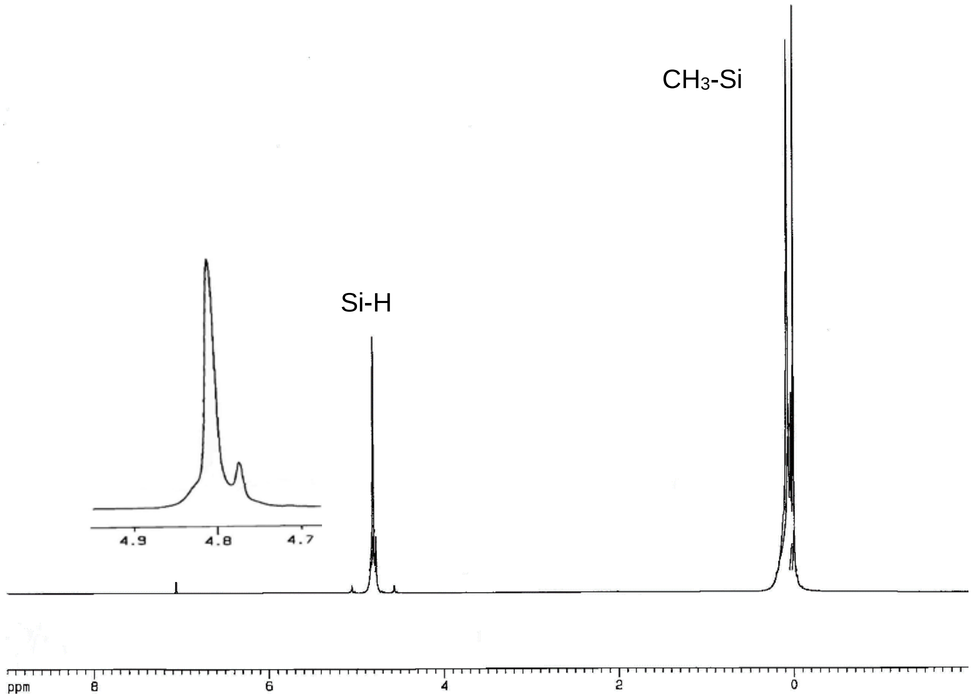


Figure 4. ^{1}H-NMR spectrum (in C_6D_6) of polymethylhydrosiloxane $Q_3D^{H}_{50}M_8$.

In ^{29}Si-NMR INEPT spectra of copolymers $\mathbf{QD^{H}_{48}M_{4}}$, $\mathbf{Q_{2}D^{H}_{49}M_{6}}$ and $\mathbf{Q_{3}D^{H}_{50}M_{8}}$ were present signals at δ −31.62–−39.97 ppm corresponding to silicon atoms of units D^{H} [8,9,54] and at δ 9.40–11.25 ppm corresponding to silicon atoms of end groups $Me_3SiO_{0.5}$ (M). In the range of δ −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 $\mathbf{QD_{52}D^{H}_{52}M_{4}}$ (**Q1D**), $\mathbf{Q_{2}D_{49}D^{H}_{49}M_{6}}$ (**Q2D**), and $\mathbf{Q_{3}D_{50}D^{H}_{50}M_{8}}$ (**Q3D**) existed signals at δ 7.27–9.92 ppm, corresponding to silicon atoms of end groups $Me_3SiO_{0.5}$ and at δ −34.61 to −38.87 ppm, characteristic for mers MeHSiO (D^{H}), and also at δ −18.77–−21.85 ppm from silicon atoms of units Me_2SiO (D) [8,9,52]. It was impossible to observe signals of quadruple silicon atoms of units $SiO_{4/2}$ 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 δ −34.0–−36.0 ppm (for Q1, Q2, and Q3),
at δ −34.0–−37.5 ppm (for Q1D, Q2D, and Q3D),
$(CH_3)_2SiO$ at δ −16.5–−22.0 ppm (for Q1D, Q2D, and Q3D),

and terminal groups $(CH_3)_3SiO_{1/2}$:

at δ 9.5–11.3 ppm (for Q1, Q2, and Q3),

at δ 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 δ:

−100.3–−112.4 ppm,

and they overlapped with very strong ^{29}Si signals of a borosilicate glass.

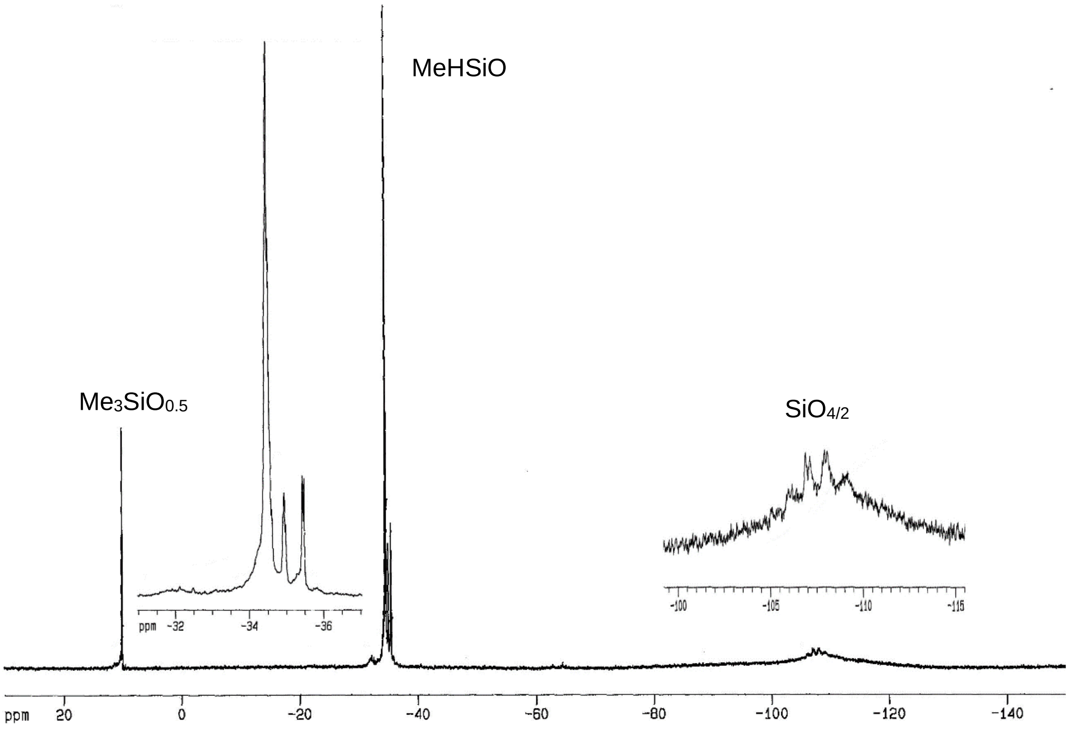


Figure 5. ^{29}Si-NMR spectrum (INVGATE, in C_6D_6) of polymethylhydrosiloxane $Q_3D^H{}_{50}M_8$.

In the ^{29}Si-NMR INVGATE spectra of copolymers: $\mathbf{QD^H{}_{48}M_4}$, $\mathbf{Q_2D^H{}_{49}M_6}$ and $\mathbf{Q_3D^H{}_{50}M_8}$ were present signals at: δ 9.40–11.25 ppm, corresponding to the terminal groups $Me_3SiO_{0.5}$, at δ −31.81–−36.25 ppm, characteristic for units MeHSiO (D^H), and also resonance signals in the range of δ −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 δ −100–−106 ppm.

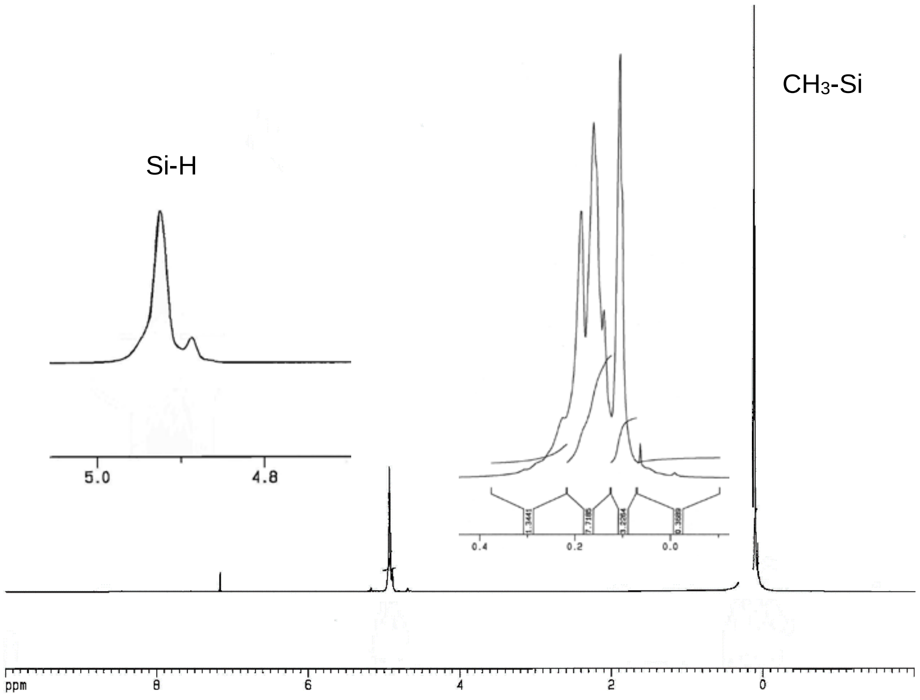
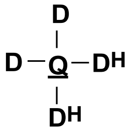


Figure 6. ^{1}H-NMR spectrum (in C_6D_6) of polymethylhydrosiloxane $Q_2D_{49}D^H{}_{49}M_6$.

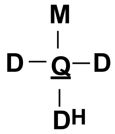
Chemical shifts at δ 9–11 ppm have been assigned to resonances of Si atoms of $Me_3SiO_{0.5}$ (M) groups in the following sequences of the siloxane chain ends: $\underline{\mathbf{M}}D^{H}D^{H}D^{H}$, $\underline{\mathbf{M}}D^{H}D^{H}D$, $\underline{\mathbf{M}}D^{H}DD^{H}$, $\underline{\mathbf{M}}D^{H}DD$, $\underline{\mathbf{M}}D^{H}D^{H}Q$, $\underline{\mathbf{M}}D^{H}QD^{H}$, $\underline{\mathbf{M}}D^{H}DQ$, and $\underline{\mathbf{M}}D^{H}QD$, while chemical shifts at δ 7–8 ppm belong to resonances of Si atoms of end groups M in the sequences: $\underline{\mathbf{M}}DDD$, $\underline{\mathbf{M}}DDD^{H}$, $\underline{\mathbf{M}}DD^{H}D$, $\underline{\mathbf{M}}DD^{H}D^{H}$, $\underline{\mathbf{M}}DDQ$, $\underline{\mathbf{M}}DQD$, $\underline{\mathbf{M}}QDD$, and $\underline{\mathbf{M}}QDD^{H}$. 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: $DD^{H}\underline{\mathbf{D}}D^{H}D$, $DD^{H}\underline{\mathbf{D}}D^{H}D^{H}$, $D^{H}D^{H}\underline{\mathbf{D}}D^{H}D^{H}$, $QD^{H}\underline{\mathbf{D}}D^{H}Q$, $MD^{H}\underline{\mathbf{D}}D^{H}D$, $MD^{H}\underline{\mathbf{D}}D^{H}D^{H}$, $MD^{H}\underline{\mathbf{D}}D^{H}Q$, $MD^{H}\underline{\mathbf{D}}D^{H}D$ (δ of middle silicon atoms of units $\underline{\mathbf{D}}$: −20–−22 ppm), and: $D^{H}D\underline{\mathbf{D}}D^{H}D^{H}$, $D^{H}D\underline{\mathbf{D}}D^{H}D$, $DD\underline{\mathbf{D}}D^{H}D^{H}$, $DD\underline{\mathbf{D}}D^{H}D$ (δ of middle silicon atoms of units $\underline{\mathbf{D}}$: −18–−19.7 ppm).

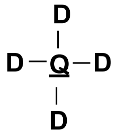
In the ^{29}Si-NMR spectra (recorded by INEPT and INVGATE techniques) in the range of δ −33–−37 ppm exist signals of middle silicon atoms of units $\mathbf{D^{H}}$, which undergo changes in pentades (Table 5). Signals of silicon atoms in the range of δ −102 to −109 ppm, presumably correspond to Si atoms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



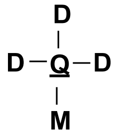
$\begin{array}{c} D \\ | \\ D-\underline{Q}-D^{H} \\ | \\ D^{H} \end{array}$



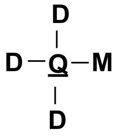
$\begin{array}{c} M \\ | \\ D-\underline{Q}-D \\ | \\ D^{H} \end{array}$



$\begin{array}{c} D \\ | \\ D-\underline{Q}-D \\ | \\ D \end{array}$



$\begin{array}{c} D \\ | \\ D-\underline{Q}-D \\ | \\ M \end{array}$



$\begin{array}{c} D \\ | \\ D-\underline{Q}-M \\ | \\ D \end{array}$

Chemical shifts in the range of 7–11 ppm in the ^{29}Si-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 ^{29}Si-NMR spectra of these three copolymers, probably come from Si atoms of units $MeSiO_{1.5}$ (T), which were formed during syntheses of PMHS-Q from trace hydrolysis of Si-H bonds [74].

Assignments of all ^{29}Si-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	**δ (ppm)**										
	^{1}H-NMR		**^{29}Si-NMR**								
			INEPT	**INVGATE**	**INEPT**	**INVGATE**	**INEPT**	**INVGATE**	**INEPT**	**INVGATE**	
	Si–H	**Si–CH_3**	**$Me_3SiO_{0.5}$**		**Me_2SiO**		**MeHSiO**		**$MeSiO_{3/2}$**		**$SiO_{4/2}$**
$QD^{H}{}_{48}M_4$	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
$Q_2D^{H}{}_{49}M_6$	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	-	−101.37–−112.33
$Q_3D^{H}{}_{50}M_8$	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
$QD_{52}D^{H}{}_{52}M_4$	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
$Q_2D_{49}D^{H}{}_{49}M_6$	4.92	0.01–0.30	9.92–7.26	7.32–9.98	−18.43–−21.85	−18.70–−21.69	−34.54–−37.33	−34.61–−37.03	−62.95–−65.26	−62.35–−66.16	−101.81–−109.71
$Q_3D_{50}D^{H}{}_{50}M_8$	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

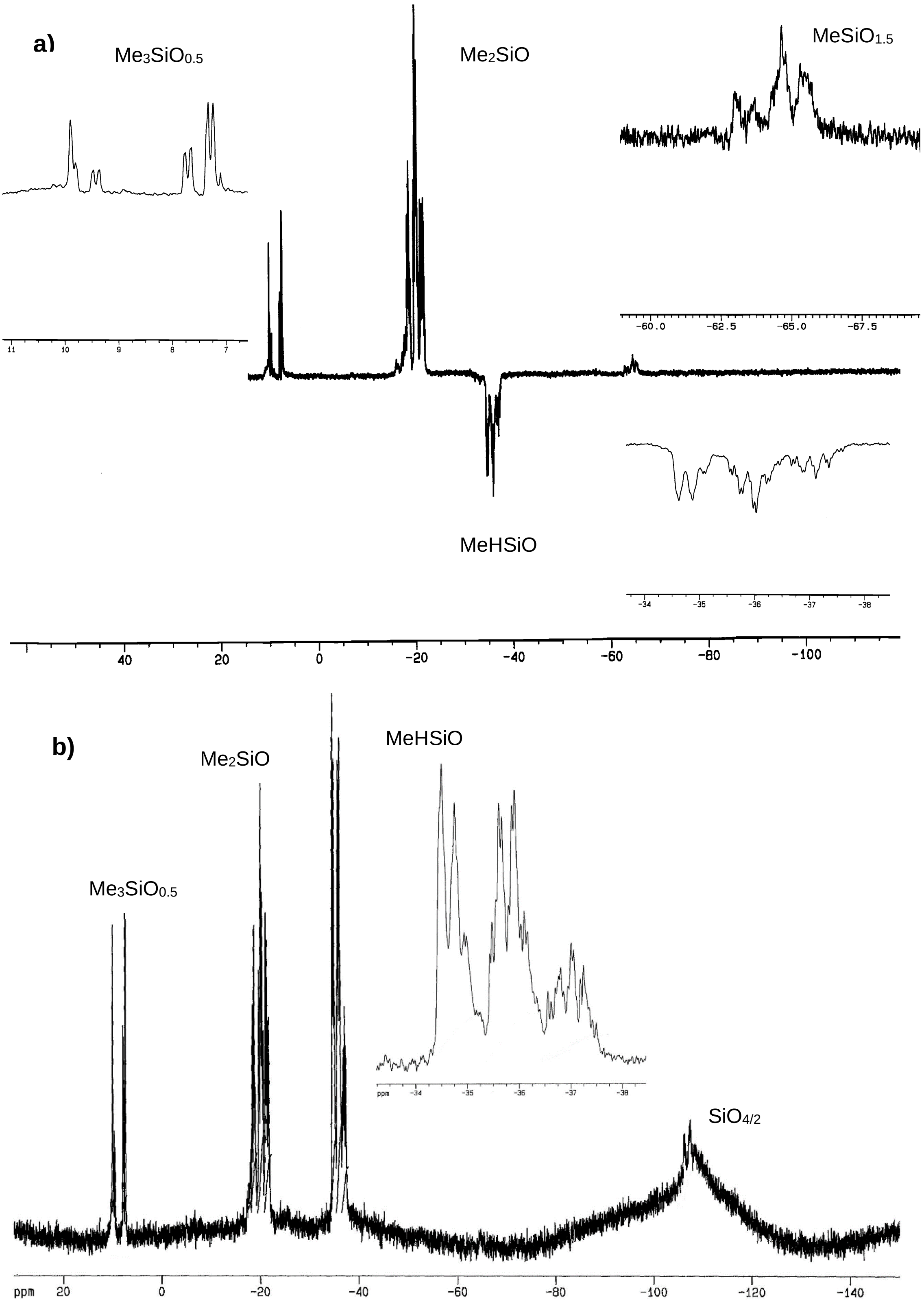


Figure 7. ^{29}Si-NMR spectra (in C_6D_6) of polymethylhydrosiloxane $Q_2D_{49}D^H_{49}M_6$: (**a**) INEPT, (**b**) INVGATE.

Table 6. The microstructure of siloxane chains in PMHS-Q, containing quadruple branching units Q (all possible sequences among tetrads of terminal groups, and linear and star pentads); values of δ concern Si atoms in structural units denoted as bold and underlined.

δ ^{29}Si-NMR (ppm)					
9–11	**7–8**	**−18–−19**	**−20–−22**	**−33–−37**	**−101–−109**
$\underline{\mathbf{M}}\mathrm{D^{H}D^{H}D^{H}}$	$\underline{\mathbf{M}}\mathrm{DDD}$	$\mathrm{DD^{H}}\underline{\mathbf{D}}\mathrm{D^{H}D}$	$\mathrm{D^{H}D}\underline{\mathbf{D}}\mathrm{D^{H}D^{H}}$	$\mathrm{D^{H}D^{H}}\underline{\mathbf{D^{H}}}\mathrm{D^{H}D^{H}}$	D $\mathrm{D}\underline{\mathbf{Q}}\mathrm{D}$ D
$\underline{\mathbf{M}}\mathrm{D^{H}D^{H}Q}$	$\underline{\mathbf{M}}\mathrm{DDD^{H}}$	$\mathrm{DD^{H}}\underline{\mathbf{D}}\mathrm{D^{H}D^{H}}$	$\mathrm{D^{H}D}\underline{\mathbf{D}}\mathrm{D^{H}D}$	$\mathrm{DD^{H}}\underline{\mathbf{D^{H}}}\mathrm{D^{H}D^{H}}$	D $\mathrm{D}\underline{\mathbf{Q}}\mathrm{D}$ M
$\underline{\mathbf{M}}\mathrm{D^{H}QD^{H}}$	$\underline{\mathbf{M}}\mathrm{DD^{H}D}$	$\mathrm{D^{H}D^{H}}\underline{\mathbf{D}}\mathrm{D^{H}D^{H}}$	$\mathrm{DD}\underline{\mathbf{D}}\mathrm{D^{H}D^{H}}$	$\mathrm{D^{H}D}\underline{\mathbf{D^{H}}}\mathrm{D^{H}D^{H}}$	D $\mathrm{D}\underline{\mathbf{Q}}\mathrm{M}$ M
$\underline{\mathbf{M}}\mathrm{D^{H}D^{H}D}$	$\underline{\mathbf{M}}\mathrm{DD^{H}D^{H}}$	$\mathrm{DD^{H}}\underline{\mathbf{D}}\mathrm{D^{H}Q}$	$\mathrm{DD}\underline{\mathbf{D}}\mathrm{D^{H}D}$	$\mathrm{DD^{H}}\underline{\mathbf{D^{H}}}\mathrm{D^{H}D}$	D $\mathrm{D}\underline{\mathbf{Q}}\mathrm{D}$ D
$\underline{\mathbf{M}}\mathrm{D^{H}D^{H}D^{H}}$	$\underline{\mathbf{M}}\mathrm{DDQ}$	$\mathrm{QD^{H}}\underline{\mathbf{D}}\mathrm{D^{H}Q}$	$\mathrm{D^{H}D}\underline{\mathbf{D}}\mathrm{DQ}$	$\mathrm{DD^{H}}\underline{\mathbf{D^{H}}}\mathrm{DD^{H}}$	D $\mathrm{D}\underline{\mathbf{Q}}\mathrm{D^{H}}$ $\mathrm{D^{H}}$
$\underline{\mathbf{M}}\mathrm{D^{H}DD^{H}}$	$\underline{\mathbf{M}}\mathrm{DQD}$	$\mathrm{MD^{H}}\underline{\mathbf{D}}\mathrm{D^{H}D}$	$\mathrm{D^{H}D}\underline{\mathbf{D}}\mathrm{QD}$	$\mathrm{D^{H}D}\underline{\mathbf{D^{H}}}\mathrm{D\ D^{H}}$	M $\mathrm{D}\underline{\mathbf{Q}}\mathrm{D}$ $\mathrm{D^{H}}$
$\underline{\mathbf{M}}\mathrm{D^{H}DD}$	$\underline{\mathbf{M}}\mathrm{QDD}$	$\mathrm{MD^{H}}\underline{\mathbf{D}}\mathrm{D^{H}D^{H}}$	$\mathrm{DD^{H}}\underline{\mathbf{D}}\mathrm{DQ}$	$\mathrm{D^{H}D}\underline{\mathbf{D^{H}}}\mathrm{D^{H}Q}$	
	$\underline{\mathbf{M}}\mathrm{QDD^{H}}$	$\mathrm{MD^{H}}\underline{\mathbf{D}}\mathrm{D^{H}Q}$	$\mathrm{DD^{H}}\underline{\mathbf{D}}\mathrm{QD}$	$\mathrm{D^{H}D^{H}}\underline{\mathbf{D^{H}}}\mathrm{QD^{H}}$	
		$\mathrm{MD^{H}}\underline{\mathbf{D}}\mathrm{D^{H}D}$	$\mathrm{DD}\underline{\mathbf{D}}\mathrm{DQ}$	$\mathrm{DD^{H}}\underline{\mathbf{D^{H}}}\mathrm{D^{H}Q}$	
			$\mathrm{DD}\underline{\mathbf{D}}\mathrm{QD}$	$\mathrm{D^{H}D}\underline{\mathbf{D^{H}}}\mathrm{D^{H}Q}$	
			$\mathrm{QD}\underline{\mathbf{D}}\mathrm{DQ}$	$\mathrm{D^{H}D}\underline{\mathbf{D^{H}}}\mathrm{QD^{H}}$	
			$\mathrm{QD}\underline{\mathbf{D}}\mathrm{QD}$	$\mathrm{DD^{H}}\underline{\mathbf{D^{H}}}{}^{\mathrm{H}}\mathrm{QD^{H}}$	
			$\mathrm{DQ}\underline{\mathbf{D}}\mathrm{QD}$	$\mathrm{DD}\underline{\mathbf{D^{H}}}\mathrm{QD^{H}}$	
			$\mathrm{DQ}\underline{\mathbf{D}}\mathrm{DQ}$	$\mathrm{D^{H}D^{H}}\underline{\mathbf{D^{H}}}\mathrm{DQ}$	
			$\mathrm{MD}\underline{\mathbf{D}}\mathrm{DQ}$	$\mathrm{D^{H}D^{H}}\underline{\mathbf{D^{H}}}\mathrm{QD}$	
			$\mathrm{MD}\underline{\mathbf{D}}\mathrm{QD}$	$\mathrm{DD^{H}}\underline{\mathbf{D^{H}}}\mathrm{DQ}$	
			$\mathrm{MQ}\underline{\mathbf{D}}\mathrm{DD}$	$\mathrm{DD^{H}}\underline{\mathbf{D^{H}}}\mathrm{QD}$	
			$\mathrm{MD}\underline{\mathbf{D}}\mathrm{DQ}$	$\mathrm{D^{H}D}\underline{\mathbf{D^{H}}}\mathrm{DQ}$	
			$\mathrm{MQ}\underline{\mathbf{D}}\mathrm{QD}$	$\mathrm{D^{H}D}\underline{\mathbf{D^{H}}}\mathrm{QD}$	
				$\mathrm{DD}\underline{\mathbf{D^{H}}}\mathrm{D^{H}Q}$	
				$\mathrm{DD}\underline{\mathbf{D^{H}}}\mathrm{DQ}$	
				$\mathrm{MD^{H}}\underline{\mathbf{D^{H}}}\mathrm{D^{H}D^{H}}$	
				$\mathrm{MD^{H}}\underline{\mathbf{D^{H}}}\mathrm{D^{H}\ D}$	
				$\mathrm{MD^{H}}\underline{\mathbf{D^{H}}}\mathrm{DD^{H}}$	
				$\mathrm{MD}\underline{\mathbf{D^{H}}}\mathrm{D^{H}D^{H}}$	
				$\mathrm{MD}\underline{\mathbf{D^{H}}}\mathrm{D^{H}D}$	
				$\mathrm{MD}\underline{\mathbf{D^{H}}}\mathrm{DD^{H}}$	
				$\mathrm{MD^{H}}\underline{\mathbf{D}}\mathrm{^{H}D^{H}Q}$	
				$\mathrm{MD}\underline{\mathbf{D^{H}}}\mathrm{D^{H}Q}$	
				$\mathrm{MD^{H}}\underline{\mathbf{D^{H}}}\mathrm{DQ}$	
				$\mathrm{MD^{H}}\underline{\mathbf{D^{H}}}\mathrm{QD}$	
				$\mathrm{MD^{H}}\underline{\mathbf{D^{H}}}\mathrm{QD^{H}}$	
				$\mathrm{MD}\underline{\mathbf{D^{H}}}\mathrm{QD^{H}}$	
				$\mathrm{MD}\underline{\mathbf{D^{H}}}\mathrm{DQ}$	

Author Contributions: Syntheses and characterization of branched PMHS were carried out by J.J. Chruściel and M. Fejdyś. Moreover, J.J. Chruściel measured dynamic viscosities of PMHS, M. Fejdyś (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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Conflicts of Interest: The authors declare no conflict of interest.

References

1. Eaborn, C. *Organosilicon Compounds*; Butterworth Scientific Publications: London, UK, 1960.
2. Noll, W. *Chemie und Technologie der Silikone*; 2 Auflage; Verlag Chemie: Weinheim Germany; GmbH: Weinheim Germany, 1968.

3. Hardman, B.; Torkelson, A. Chapter Silicones. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Mark, F., Gaylord, N.G., Bikales, N.M., Eds.; J. Wiley & Sons: New York, NY, USA, 1989; Volume 15, pp. 271–289.
4. Rościszewski, P.; Zielecka, M. *Silikony, Właściwości i Zastosowanie*; WNT: Warsaw, Poland, 2002; pp. 26–30, 38.
5. Chauhan, B.P.S. (Ed.) *Hybrid Nanomaterials Synthesis, Characterization, and Applications*; Wiley-VCH: Weinheim, Germany, 2011.
6. Kricheldorf, H.R. (Ed.) *Silicon in Polymer Synthesis*; Springer: Berlin/Heidelberg, Germany; New York, NY, USA, 1996.
7. Brook, M.A. *Silicon in Organic, Organometallic and Polymer Chemistry*; J Wiley & Sons: New York, NY, USA; Chichester, UK; Weinheim, Germany; Brisbane, Australia; Singapore; Toronto, Japan, 2000; ISBN 0-471-19658-4.
8. Chruściel, J. Progress in chemistry of polymethylhydrosiloxanes. *Polimery* **1999**, *44*, 462–474.
9. Chruściel, J. Synthesis and characterization of new liquid, branched and random poly(methyl-hydrosiloxanes). *e-Polymers* **2008**, *8*, 1–23. [CrossRef]
10. Chruściel, J. Crosslinking of polydimethylsiloxane-α,ω-diols with polymethylhydrosiloxanes and some properties of prepared silicone elastomers. *Polimery* **1999**, *44*, 586–596.
11. Devimille, L.; Bresson, B.; Bokobza, L. Synthesis, structure and morphology of poly(dimethyl-siloxane) networks filled with in situ generated silica particles. *Polymer* **2005**, *46*, 4135–4143. [CrossRef]
12. Fejdyś, M.; Chruściel, J.; Miazga, A. Mechanical properties of silicone vulcanizates crosslinked with polymethylhydrosiloxanes containing silica and calcium carbonate. *Polimery* **2006**, *51*, 48–57.
13. Jia, L.; Du, Z.; Zhang, C.; Liu, C.; Li, H. Reinforcement of polydimethylsiloxane through formation of inorganic–organic hybrid network. *Polym. Eng. Sci.* **2008**, *48*, 74–79. [CrossRef]
14. Urayama, K.; Kawamura, T.; Kohjiya, S. Structure–mechanical property correlations of model siloxane elastomers with controlled network topology. *Polymer* **2009**, *50*, 347–356. [CrossRef]
15. Chruściel, J.; Leśniak, E. Preparation of flexible, self-extinguishing silicone foams. *J. Appl. Polym. Sci.* **2011**, *119*, 1696–1703. [CrossRef]
16. Hager, R. Phosphazene catalysis—Basic technology in silicone production. In Proceedings of the XI International Symposium on Organosilicon Chemistry, Montpellier, France, 1–6 September 1996; Universite Montpellier II: Montpellier, France, 1996. Abstracts, LD5.
17. Hager, R.; Schneider, O.; Schuster, J. Process for the Condensation and/or Equilibration of Organosilicon Compounds. U.S. Patent 5,380,902, 1995.
18. Razzano, J.S.; Anderson, P.P.; Perry, R.J. Production of Low Molecular Weight Linear Hydrogen Siloxanes. U.S. Patent 5,670,596, 23 September 1997.
19. Nye, S.A.; Riccio, D.A.; Wutzer, B.S. Process for Preparing Hydrogen Siloxane Copolymers. U.S. Patent 5,698,654, 1997.
20. Liao, W.P.; Nye, S.A. Process for Preparing Self-Curable Alkenyl Hydride Siloxane Copolymers and Coating Composition. European Patent EP 0838547 B1, 1998.
21. Palaprat, G.; Ganachaud, F.; Mauzac, M.; Hemery, P. Cationic polymerization of 2,4,6,8-tetramethylcyclotetrasiloxane processed by tuning the pH of the miniemulsion. *Polymer* **2005**, *46*, 11213–11218. [CrossRef]
22. Maisonnier, S.; Favier, J.C.; Masure, M.; Hemery, P. Poly(methylhydrosiloxane) synthesis in anionic aqueous emulsion. In Proceedings of the XI International Symposium on Organosilicon Chemistry, Montpellier, France, 1–6 September 1996; Universite Montpellier II: Montpellier, France, 1996. Abstracts, PB84.
23. Paulasaari, J.K.; Weber, W.P. Preparation of Highly Regular Poly(1-hydrido-1,3,3,5,5- -pentamethyltrisiloxane) and Its Chemical Modification by Hydrosilylation. *Macromolecules* **1999**, *32*, 6574–6577. [CrossRef]
24. Agaskar, P.A. Facile, High-Yield Synthesis of Functionalized Spherosilicates: Precursors of Novel Organolithic Macromolecular Materials. *Inorg. Chem.* **1990**, *29*, 1603. [CrossRef]
25. Chruściel, J.; Kulpiński, J.; Romanowski, Z. Synthesis of Some Block Polymethylhydrosiloxanes. *Zeszyty Naukowe Politechniki Śląskiej Seria Chemia* **1999**, *140*, 109–114.
26. Agaskar, P.A. New Synthetic Route to the Hydridospherosiloxanes O_h-HSi_80_{12} and D_{5h}-$H_{10}Si_{10}O_{15}$. *Inorg. Chem.* **1991**, *30*, 2707–2708. [CrossRef]
27. Bassindale, A.R.; Gentle, T.E. Siloxane and Hydrocarbon Octopus Molecules with Silsesquioxane Cores. *J. Mater. Chem.* **1993**, *3*, 1319–1325. [CrossRef]

28. Crivello, J.V.; Malik, R. Synthesis and Photoinitiated Cationic Polymerization of Monomers with the Silsesquioxane Core. *J. Polym. Sci. Part A Polym. Chem.* **1997**, *35*, 407–425. [CrossRef]
29. Tsuchida, A.; Bolin, C.; Sernetz, F.G.; Frey, H.; Mülhaupt, R. Ethene and Propene Copolymers Containing Silsesquioxane Side Groups. *Macromolecules* **1997**, *30*, 2818–2824. [CrossRef]
30. Zhang, C.; Babonneau, F.; Laine, R.M.; Soles, C.L.; Hristov, H.A.; Yee, A.F. Highly Porous Polyhedral Silsesquioxane Polymers. Synthesis and Characterization. *J. Am. Chem. Soc.* **1998**, *120*, 8380–8391. [CrossRef]
31. Zhang, C.; Laine, R.M. Hydrosilylation of Allyl Alcohol with $[HSiMe_2OSiO_{1.5}]_8$: Octa(3-hydroxypropyldimethylsiloxy)octasilsesquioxane and Its Octamethacrylate Derivative as Potential Precursors to Hybrid Nanocomposites. *J. Am. Chem. Soc.* **2000**, *122*, 6979–6988. [CrossRef]
32. Constantopoulos, K.; Clarke, D.; Markovic, E.; Uhrig, D.; Clarke, S.; Matisons, J.G.; Simon, G. A new family of POSS monomers suitable for forming urethane polymerizable nanocomposite coatings. *Polym. Prepr.* **2004**, *45*, 668.
33. Frye, C.; Collins, W.T. The Oligomeric Silsesquioxanes, $(HSiO_{3/2})_n$. *J. Am. Chem. Soc.* **1970**, *92*, 5586–5588. [CrossRef]
34. Agaskar, P.A.; Day, V.W.; Klemperer, W.G. A New Route to Trimnethylsilylated Spherosilicates: Synthesis and Structure of $[Si_{12}0_{18}](OSiMe_3)_{12}$, D_{3h}-$[Si_{14}O_{21}](OSiMe_3)_{14}$, and C_{2v}-$[Si_{14}O_{21}](OSiMe_3)_{14}$. *J. Am. Chem. Soc.* **1987**, *109*, 5554–5556. [CrossRef]
35. Hasegawa, I.; Motojima, D. Dimethylvinylsilylation of $Si_8O_{20}{}^{8-}$ silicate anion in methanol solutions of tetramethylammonium silicate. *J. Organomet. Chem.* **1992**, *441*, 373–380. [CrossRef]
36. Majoros, I.; Marsylko, T.M.; Kennedy, J.P. Synthesis and characterization of novel well-defined stars consisting of eight polyisobutylene arms emanating from an octa(dimethylsiloxy)octasilsesquioxane core. *Polym. Bull.* **1997**, *38*, 15–22. [CrossRef]
37. Provatas, A.; Luft, M.; Mu, J.C.; White, A.H.; Matisons, J.G.; Skelton, B.W. Silsesquioxanes: Part I: A key intermediate in the building of molecular composite materials. *J. Organomet. Chem.* **1998**, *565*, 159–164. [CrossRef]
38. Perrin, F.X.; Nguyen, T.B.V.; Margaillan, A. Linear and branched alkyl substituted octakis(dimethylsiloxy)octasilsesquioxanes: WAXS and thermal properties. *Eur. Polym. J.* **2011**, *47*, 1370–1382. [CrossRef]
39. Dutkiewicz, M.; Maciejewski, H.; Marciniec, B.; Karasiewicz, J. New Fluorocarbofunctional Spherosilicates: Synthesis and Characterization. *Organometallics* **2011**, *30*, 2149–2153. [CrossRef]
40. Hasegawa, I. Co-hydrolysis products of tetraethoxysilane and methyltriethoxysilane in the presence of tetramethylammonium ions. *J. Sol-Gel Sci. Technol.* **1993**, *1*, 57–63. [CrossRef]
41. Moran, M.; Casado, C.M.; Cuadrado, I.; Losada, J. Ferrocenyl Substituted Octakis-(dimethylsiloxy)octasilsesquioxanes: A New Class of Supramolecular Organometallic Compounds. Synthesis, Characterization, and Electrochemistry. *Organometallics* **1993**, *12*, 4327–4333. [CrossRef]
42. Sellinger, A.; Laine, R.M. Silsesquioxanes as Synthetic Platforms. 3. Photocurable, Liquid Epoxides as Inorganic/Organic Hybrid Precursors. *Chem. Mater.* **1996**, *8*, 1592–1593. [CrossRef]
43. Laine, R.M. Nanobuilding blocks based on the $[OSiO_{1.5}]_x$ (x = 6, 8, 10) Octasilsesquioxanes. *J. Mater. Chem.* **2005**, *15*, 3725–3744. [CrossRef]
44. Hasegawa, I.; Ino, K.; Onishi, H. An improved procedure for syntheses of silyl derivatives of the cubeoctameric silicate anion. *Appl. Organomet. Chem.* **2003**, *17*, 287–290. [CrossRef]
45. Soh, M.S.; Yap, A.U.J.; Sellinger, A. Methacrylate and epoxy functionalized nanocomposites based on silsesquioxane cores for use in dental applications. *Eur. Polym. J.* **2007**, *43*, 315–327. [CrossRef]
46. Hessel, C.M.; Henderson, E.J.; Veinot, J.G.C. Hydrogen Silsesquioxane: A Molecular Precursor for Nanocrystalline Si-SiO_2 Composites and Freestanding Hydride-Surface-Terminated Silicon Nano-particles. *Chem. Mater.* **2006**, *18*, 6139–6146. [CrossRef]
47. Gunji, T.; Shioda, T.; Tsuchihira, K.; Seki, H.; Kajiwara, T.; Abe, Y. Preparation and properties of polyhedral oligomeric silsesquioxane–polysiloxane copolymers. *Appl. Organomet. Chem.* **2010**, *24*, 545–550. [CrossRef]
48. Shioda, T.; Gunji, T.; Abe, N.; Abe, Y. Preparation and properties of polyhedral oligomeric silsesquioxane polymers. *Appl. Organomet. Chem.* **2011**, *25*, 661–664. [CrossRef]
49. Handke, M.; Kowalewska, A. Siloxane and silsesquioxane molecules—Precursors for silicate materials. *Spectrochim. Acta Part A* **2011**, *79*, 749–757. [CrossRef] [PubMed]

50. Cai, G.; Weber, W.P. Synthesis of terminal Si–H irregular tetra-branched star polysiloxanes. Pt-catalyzed hydrosilylation with unsaturated epoxides. Polysiloxane films by photo-acid catalyzed crosslinking. *Polymer* **2004**, *45*, 2941–2948. [CrossRef]
51. Grunlan, M.A.; Lee, N.S.; Mansfeld, F.; Kus, E.; Finlay, J.A.; Callow, J.A.; Callow, M.E.; Weber, W.P. Minimally Adhesive Polymer Surfaces Prepared from Star Oligosiloxanes and Star Oligofluorosiloxanes. *J. Polym. Sci. Part A Polym. Chem.* **2006**, *44*, 2551–2566. [CrossRef]
52. Sargent, J.R.; Weber, W.P. Telechelic 4 and 6 branch star siloxanes by acid catalyzed incorporation of D4 units into the Si-O-Si bonds of tetra(dimethylsiloxy)silane and hexa(dimethylsiloxy)-cyclotrisiloxane. *Polym. Prepr.* **2000**, *41*, 604.
53. Cai, G.; Sargent, J.R.; Weber, W.P. Preparation and reactivity of polyfunctional six- and eight-membered cyclic silicates. *J. Organomet. Chem.* **2004**, *689*, 689–693. [CrossRef]
54. Saxena, K.; Bisaria, C.S.; Saxena, A.K. Studies on the synthesis and thermal properties of alkoxysilane-terminated organosilicone dendrimers. *Appl. Organomet. Chem.* **2010**, *24*, 251–256. [CrossRef]
55. Zhang, R.; Dai, D.; Cui, L.; Xu, H.; Liu, C.; Xie, P. A glance at the relation of stepwise coupling polymerization to supramolecular chemistry. *Mater. Sci. Eng. C* **1999**, *10*, 13–18. [CrossRef]
56. Wan, Y.; Xu, L.; Ren, L.; Zhang, L.; Xie, P.; Liu, Y.; Zhang, R. Synthesis and mesomorphic properties of fishbone-like liquid crystalline polysilsesquioxanes V. Pd-coordinating, fishbone-like azo-based liquid crystalline polysilsesquioxanes. *Liquid Cryst.* **1998**, *24*, 871–876. [CrossRef]
57. Cao, M.; Li, Z.; Zhang, Y.; Xie, P.; Dai, D.; Zhang, R.; Lin, Y.; Chung, N.T. Synthesis and characterization of ladder-like copolymethyl-epoxysilsesquioxane. *React. Funct. Polym.* **2000**, *45*, 119–130. [CrossRef]
58. Uchida, H.; Kabe, Y.; Yoshino, K.; Kawamata, A.; Tsumuraya, T.; Masamune, S. General Strategy for the Systematic Synthesis of Oligosiloxanes. Silicone Dendrimers. *J. Am. Chem. Soc.* **1990**, *112*, 7077–7079. [CrossRef]
59. Zhao, S.; Feng, S. Hydrogen-Containing Silicone Resin as the Crosslinking Agent of Heat-Curable Silicone Rubber. *J. Appl. Polym. Sci.* **2003**, *88*, 3066–3069. [CrossRef]
60. Su, H.W.; Chen, W.C.; Lee, W.C.; King, J.S. New Photocurable Acrylic/Silsesquioxane Hybrid Optical Materials: Synthesis, Properties, and Patterning. *Macromol. Mater. Eng.* **2007**, *292*, 666–673. [CrossRef]
61. Seino, M.; Hayakawa, T.; Ishida, Y.; Kakimoto, M. Hydrosilylation Polymerization of Double-Decker-Shaped Silsesquioxane Having Hydrosilane with Diynes. *Macromolecules* **2006**, *39*, 3473–3475. [CrossRef]
62. Soraru, G.D.; D'Andrea, G.; Campostrini, R.; Baboneau, F. Characterization of Methyl-substituted Silica Gels with Si-H Functionalities. *J. Mater. Chem.* **1995**, *5*, 1363–1374. [CrossRef]
63. Campostrini, R.; D'Andrea, G.; Carturan, G.; Ceccato, R.; Soraru, G.D. Pyrolysis study of methyl-substituted Si-H containing gels as precursors for oxycarbide glasses, by combined thermo-gravimetry, gas chromatographic and mass spectrometric analysis. *J. Mater. Chem.* **1996**, *6*, 585–594. [CrossRef]
64. Bažant, V.; Chvalovský, V.; Rathouský, I. *Silikony*; PWT: Warsaw, Poland, 1955; p. 153.
65. Morikawa, A.; Kakimoto, M.; Imai, Y. Synthesis and Characterization of New Polysiloxane Starburst Polymers. *Macromolecules* **1991**, *24*, 3469–3474. [CrossRef]
66. Chang, H.T.; Frechet, J.M.J. Proton-Transfer Polymerization: A New Approach to Hyperbranched Polymers. *J. Am. Chem. Soc.* **1999**, *121*, 2313–2314. [CrossRef]
67. Innoue, K. Functional dendrimers, hyperbranched and star polymers. *Prog. Polym. Sci.* **2000**, *25*, 453–571. [CrossRef]
68. Paulasaari, J.K.; Weber, W.P. Synthesis of Hyperbranched Polysiloxanes by Base-Catalyzed Proton-Transfer Polymerization. Comparison of Hyperbranched Polymer Microstructure and Properties to Those of Linear Analogues Prepared by Cationic or Anionic Ring-Opening Polymerization. *Macromolecules* **2000**, *33*, 2005–2010. [CrossRef]
69. Paulasaari, J.K.; Weber, W.P. Base catalyzed proton transfer polymerization of 1-hydroxy-pentamethylcyclotrisiloxane. Comparison of hyperbranched polymer microstructure and properties to those of highly regular linear analogs. *Macromol. Chem. Phys.* **2000**, *201*, 1585–1592. [CrossRef]
70. Jikei, M.; Kakimoto, M. Hyperbranched polymers: A promising new class of materials. *Prog. Polym. Sci.* **2001**, *26*, 1233–1285. [CrossRef]
71. Servaty, S.; Köhler, W.; Meyer, W.H.; Rosenauer, C.; Spickermann, J.; Räder, H.J.; Wegner, G. MALDI-TOF-MS Copolymer Analysis: Characterization of a Poly(dimethylsiloxane)- -*co*-Poly(hydromethylsiloxane) as a Precursor of a Functionalized Silicone Graft Copolymer. *Macromolecules* **1998**, *31*, 2468–2474. [CrossRef]

72. Silverstein, R.M.; Bassler, G.C. *Spektroskopowe Metody Identyfikacji Związków Organicznych*; PWN: Warsaw, Poland, 1969; pp. 72–118.
73. Glaser, R.H.; Wilkes, G.L.; Bronnimann, C.E. *Solid*-state ^{29}Si NMR of TEOS-based multifunctional sol-gel materials. *J. Non-Cryst. Solids* **1989**, *113*, 73–87. [CrossRef]
74. Harris, R.K.; Kimber, B.J. ^{29}Si nuclear magnetic resonance studies of some oligo- and polymeric siloxanes. *J. Organomet. Chem.* **1974**, *70*, 43–49. [CrossRef]