Synthesis and Properties of Perfluoroalkyl Groups Containing Double Four-Ring Spherosilicate (Siloxysilsesquioxane) Precursors

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Abstract. Organically modified cage-like double four-ring spherosilicates have received considerable interest in the construction of nanosized hybrid materials, as well as building units for structural well-defined polymers. This group is extended by perfluoroalkyl ligands containing spherosilicates, synthesized by addition reaction of the octahydridodimethylsiloxyoctasilsesquioxane $[H(CH_3)_2Si]_8Si_8O_{20}$ and heptadecafluorodecyl methacrylate. The resultant liquid spherosilicate substituted with eight terminal perfluoroalkyl groups was characterized by ^{29}Si and ^{13}C NMR spectroscopies and MALDI Time-of-Flight mass spectrometry. Partial substitution of perfluoroalkyl ligands by trimethoxysilyl containing groups provides condensable precursors for the synthesis of hydrophobic and oleophobic materials via the sol-gel process. This new spherosilicate, carrying on average four perfluoroalkyl groups and four trimethoxysilyl groups shows better hydrophobic and oleophobic properties compared with commonly used perfluoroalkyltrialkoxysilanes under identical concentration of perfluoroalkyl chains. In addition a comprehensive literature survey is given on structural well characterized, organically modified cage-like double four-ring spherosilicates.

Keywords: spherosilicate, siloxysilsesquioxane, perfluoroalkylalkoxysilane, ^{29}Si NMR, coatings, hydrophobicity

1. Introduction

Organically modified oligomeric spherosilicates of the formula $R_8Si_8O_{20}$ with a well-defined cage-like double four-ring structure, also called spherical (polyhedral) siloxysilsesquioxanes, find increasing attention in the design of modern hybrid materials. The attractiveness of this class of cage compounds lies in the construction of materials with new and potentially useful properties due to their rigid silica structure in nanomeric dimension and their polyfunctionality (Fig. 1). The synthe-

sis of $[(CH_3)_3Si]_8Si_8O_{20}$, the first member of this new class in 1971 [1] started a remarkable and still ongoing investigation in this area. Over the past decade, synthetic methods have become further elucidated. In this process new double four-ring spherosilicates have been synthesized comprising a great variety of organic functional entities. The organic ligands are connected to the terminal oxygen atoms of the Si_8O_{20} central core mostly via the dimethylsilyl group, but also via metal atoms (Sn, Sb) or directly as methyl or isopropyl groups. Due to the rapid development made in this field [2, 3] an overview on known double four-ring spherosilicates is given first.
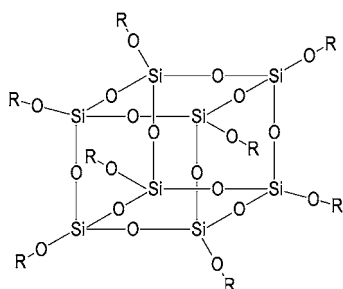
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Figure 1. Scheme of the double four-ring spherosilicate (R: see Table 1).

2. Survey on Organically Modified Spherosilicates $R_8Si_8O_{20}$

Most of the today well characterized double four-ring spherosilicates are summarized in Table 1, excluding compounds barely structurally elucidated in the patent literature [4–6]. The organic ligand R represents not only non-reactive functional groups, e.g. trimethylsilyl or aryldimethylsilyl, but also reactive functional units like methoxy-, methacryl-, hydrido- or epoxy-dimethylsilyl groups. These well defined segments play an essential role in condensation, polymerization or addition reactions. Based on this, spherosilicates show their enormous potential in the construction of nanoscaled hybrid polymers which are characterized by defined inorganic building units and inorganic-organic network structures [21, 25, 28, 32–38]. Furthermore, the spherosilicates together with the cage-like organosilsesquioxanes of the formula $R_8Si_8O_{12}$ act as suitable model for silica derived materials, as source for novel precursors with partially opened double-ring structure [39] and for studies of the relations between structure and properties of hybrid materials [2, 40, 41]. Functional spherosilicates are utilized as crosslinking agents and as precursors for the preparation of materials comprising nanoscaled hybrid polymers [3, 25, 33, 34, 42], dielectrics and liquid crystalline composites for dental applications [13] and nanocomposite coatings [3]. In addition their performance as molecular building blocks for ceramic materials [29, 43], nanoporous hybrid materials [32, 34–36, 44], photonic crystals and precursors for the preparation of catalysts [33], and the application as standard sample for NMR spectroscopy [45] is worth mentioning.

Beside the highly symmetrical species, consisting of eight identical organo-ligands, double four-ring spherosilicates with diverse substitution pattern are well known [20, 21, 36, 43]. Mixtures of both reactive and non-reactive ligands at a single molecule allow a more controlled reaction of the precursor and enable the preparation of materials with tailor-made properties. Spherosilicates with assorted organic groups mostly show no defined numerical ratio of the different ligands but a numerical distribution. Therefore, only an average numeric ratio for the substituents can be given [20].

A synthetic approach of spherosilicates with only one or two reactive functional ligands desirable for the synthesis of defined chain-like polymers is highly complicated. However, first successful methods of preparation have already been described in literature [27, 30, 38, 40].

Until now, there are no works known on the synthesis of double four-ring spherosilicates with extended perfluoroalkyl-substituted chains. In general, perfluoroalkylated materials exhibit low surface energies resulting in an anti-adhesive behaviour of polar as well as non-polar compounds on the surface [46, 47]. The most outstanding property of the perfluoroalkyl chains, e.g. of alkoxysilanes in sol-gel materials, is based on their ability to build up structures in a regular arrangement, perpendicularly oriented to the outermost layer of the hybrid materials/air interface [47, 48].

The objective of the present work is the synthesis and characterization of new perfluoroalkyl groups containing double four-ring spherosilicates and the examination of their potential in the preparation of hydrophobic/oleophobic materials via the sol-gel process. Furthermore, the hydrophobic/oleophobic properties of the spherical precursor in materials synthesis will be compared to commonly used fluoroalkylalkoxysilanes with chain-like structure [49].

3. Experimental

The organically modified spherosilicates are abbreviated according to the usual Q, T and M nomenclature: Q stands for $Si(O_{0.5})_4$, T for $RSi(O_{0.5})_3$ and M for the $R_3SiO_{0.5}$ units. The exponent at M characterizes the type of the organic ligand R. The octahydridodimethylsiloxyoctasilsesquioxane $[H(CH_3)_2Si]_8Si_8O_{20}$ ($Q_8M_8^H$) is used as starting compound for addition reactions with perfluoroalkyl- or trimethoxysilyl-group equipped methacrylates.

Table 1. Organically modified cage-like double four-ring spherosilicates $R_8Si_8O_{20}$.

No.	Ligand (R)	References
1	—$Si(CH_3)_3$	[1, 7–10]
2	—$Si(CH_3)_2(CH_2)_{17}CH_3$	[11]
3	—$Si(CH_3)_2(CH_2)_2C_6H_9$	[11]
4	—$Si(CH_3)_2C_6H_5$	[12]
5	—$Si(CH_3)_2(CH_2)_2C_6H_5$	[11]
6	—$Si(CH_3)_2(CH_2)_3O(CH_2)_3OC_6H_4C(O)OC_6H_4$—$C_6H_5$	[13]
7	—$Si(CH_3)_2(CH_2)_2Si(C_2H_5)_3$	[14]
8	—$Si(CH_3)_2(CH_2)_2SiCH_3(OSi(CH_3)_3)_2$	[14]
9	—$Si(CH_3)_2H$	[9, 10, 15, 16]
10	—$Si(CH_3)_2CH_2Cl$	[12, 17]
11	—$Si(CH_3)_2CH_2CH_2Si(CH_3)_2Cl$	[18]
12	—$Si(CH_3)_2CH_2CH_2Si(CH_3)Cl_2$	[18]
13	—$Si(CH_3)_2Br$	[16]
14	—$Si(CH_3)_2CH_2CH_2Br$	[19]
15	—$Si(CH_3)_2CH$=CH_2	[9, 10, 12, 17, 20, 21]
16	—$Si(CH_3)_2CH_2$—CH=CH_2	[20]
17	—$Si(CH_3)_2CH$=CH—CH_2—O—$C(O)C(CH_3)$=CH_2	[21]
18	—$Si(CH_3)_2CH$=CH—C_6H_5	[22]
19	—$Si(CH_3)_2CH$=CH—$CH_2CH_2CH_3$	[22]
20	—$Si(CH_3)_2(CH_2)_3$—O—$CH_2CH(O)CH_2$	[11, 23]
21	—$Si(CH_3)_2CH(O)CH_2$	[24]
22	—$Si(CH_3)_2CH_2$—CH_2—$Si(OCH_3)_3$	[25]
23	—$Si(CH_3)_2CH_2CH(CH_3)C(O)O(CH_2)_3Si(OCH_3)_3$	[25]
24	—$Si(CH_3)_2CH_2CH_2Si(OC_2H_5)_3$	[18]
25	—$Si(CH_3)_2(CH_2)_3$—O—$C(O)CH_2C(O)CH_3$	[25, 26]
26	—$Si(CH_3)_2CH_2CH(CH_3)C(O)OCH_3$	[11]
27	—$Si(CH_3)_2CH(C(O)OC_2H_5)_2$	[19]
28	—$Si(CH_3)_2CH_2CH_2(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$	[27]
29	—$Si(CH_3)_2CH_2CH_2Si(CH_3)_2(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$	[18]
30	—$Si(CH_3)_2CH_2CH_2(C_5H_3)(CH_3)Mn(CO)_3$	[18]
31	—$Si(CH_3)_2Co(CO)_4$	[16]
32	—$Si(CH_3)_2(CH_2)_3C_2(CH_3)B_{10}H_{10}$	[18]
33	—CH_3	[28, 29]
34	—$CH(CH_3)_2$	[30]
35	—$Sb(CH_3)_4$	[31]
36	—$Sn(CH_3)_3$	[31]

3.1. Synthesis of $Q_8M_8^{F17}$

0.60 g $Q_8M_8^H$ (0.59 mmole) were dissolved in 4 ml 1,4-dioxane under N_2-atmosphere and 2.56 g (4.69 mmole) 1H, 1H, 2H, 2H-heptadecafluorodecyl methacrylate CH_2=$C(CH_3)CO_2CH_2CH_2C_8F_{17}$ ($F_{17}MA$, 98%) were added to the solution together with 9.2 mg Pt-divinyltetramethyldisiloxane complex as catalyst dissolved in 0.5 ml 1,4-dioxane. Two transparent liquid phases were formed at a bath temperature of 100°C after 6 h reaction time. The upper phase mainly consists of 1,4-dioxane, the lower phase contains the

reaction product with traces of dioxane. This product is insoluble in common organic solvents but soluble in petrolether and 2,2-dimethoxypropane.

3.2. Synthesis of $Q_8 M_4^{OMe} M_4^{F17}$

1.282 g (2.36 mmole) $F_{17}MA$ and 0.6 g $Q_8 M_8^H$ (0.59 mmole) were added under N_2 to 3.05 ml 1,4-dioxane. 4.6 mg Pt-catalyst dissolved in 0.5 ml 1,4-dioxane was added to the solution. Two liquid phases resulted after 6 h reaction time (bath temperature 100°C) and cooling to room temperature. 0.56 ml (2.37 mmole) methacryloxypropyltrimethoxysilane (MPTS) and an additional amount of 4.6 mg catalyst in 0.5 ml 1,4-dioxane were added to the first biphasic reaction product. A homogeneous transparent solution was formed after repeated heating for 6 h. When necessary, the solvent was evaporated at 50°C at reduced pressure resulting in a transparent liquid.

3.3. Preparation of Coating Sols

The sols were prepared from methyltriethoxysilane (MTEOS) and tetraethoxysilane (TEOS) at the molar ratio 4:1 and a water content of 0.5 H_2O per alkoxy group. 0.002-1 mole% (F-chain) of the $Q_8 M_4^{OMe} M_4^{F17}$ precursor were added with regard to the sum of MTEOS and TEOS. For comparison identical concentrations of tridecafluoro-1,1,2,2-tetrahydrooctyltriethoxysilane $C_6F_{13}CH_2CH_2Si(OC_2H_5)_3$ ($F_{13}TS$) and 1H, 1H, 2H, 2H-perfluorodecyltriethoxysilane $C_8F_{17}CH_2CH_2Si-(OC_2H_5)_3$ ($F_{17}TS$) were used. The term "mole% F-chain" considers that the $Q_8 M_4^{OMe} M_4^{F17}$ compound contains on average four F-chains per molecule, whereas $F_{13}TS$ and $F_{17}TS$ contain only one. As an example, the preparation is described for a 0.1 mole% (F-chain) $Q_8 M_4^{OMe} M_4^{F17}$ containing coating solution. 0.222 g $Q_8 M_4^{OMe} M_4^{F17}$ (0.054 mmole/0.216 mmole F-chain) were added to 30.66 g (171.96 mmole) MTEOS and 8.96 g (42.99 mmole) TEOS. Then, 6.19 ml 0.1N HCl (344 mmole H_2O) were given to the stirred solution. The primary mixture of the two phases changes into a homogeneous and transparent solution within 15 minutes. The transparent sol was stirred for 24 h at room temperature and filtered through a micro filter before use. Glass substrates were coated with these solutions by dip-coating. The coatings were dried and hardened for 4 h at 130°C.

3.4. Methods

3.4.1. NMR Spectroscopy.
The ^{29}Si and ^{13}C NMR spectra were obtained using a Bruker AC 200 spectrometer (liquid-state) and a Bruker MSL 200 (solid-state) operating at fields of 4.7 T. ^{29}Si NMR: inverse gated sequence, external reference: tetramethylsilane (TMS), pulse repetition time (r.t.): 40 s, pulse angle (p.a.): 63°, number of scans (n.s.): 80–160. ^{13}C NMR: inverse gated sequence, r.t.: 10 s, p.a.: 60°, n.s.: 180. Solid-state ^{29}Si NMR: $^{29}Si\{^1H\}$ sequence, external standard $Q_8 M_8$(M signal = 11.58 ppm related to TMS), MAS 3 kHz, p.a.: 63°, r.t.: 60 s, n.s.: 1200.

3.4.2. Time of Flight Mass Spectrometry.
The MALDI-TOF mass spectra were recorded with a Kratos Kompact MALDI III (Shimadzu Europa GmbH, Duisburg, Germany) using a nitrogen laser source ($\lambda = 337$ nm), a positive polarity and 20 kV acceleration voltage in the reflectron mode. The samples were prepared by mixing of approximately 5 μl of substrate dissolved in 2,2-dimethoxypropane (1 mg/ml) with 5 μl of matrix solution (25 mg/ml THF) before drying on the sample slide. 2,4,6-tri-hydroxyacetophenone was used as matrix. The equipment was calibrated with bovine insulin. For each sample, spectra were averaged over 122 laser shots.

3.4.3. Contact Angle.
Contact-angle measurements were made on six drops of water and hexadecane with a diameter of 2-4 mm at both sides of the coated glass support at 22°C.

3.4.4. Surface Tension.
The surface tension of the coating solutions was measured 24 h after preparation by means of a Krüss K12 tensiometer at 24°C.

4. Results and Discussion

4.1. Synthesis and Structural Characterization

4.1.1. Addition Reaction of $Q_8 M_8^H$ and $F_{17}MA$.
The reaction of $Q_8 M_8^H$ (Table 1, No. 9) with heptadecafluorodecyl methacrylate ($F_{17}MA$) at the molar ratio 1:8 results in two transparent liquid phases. The upper phase mainly consists of the solvent (1,4-dioxane), whereas the lower phase contains the reaction product alongside with small traces of solvent. The ^{29}Si NMR spectrum of the liquid reaction product (Fig. 2(B)) shows two signals (intensity 1:1), one for Si-atoms
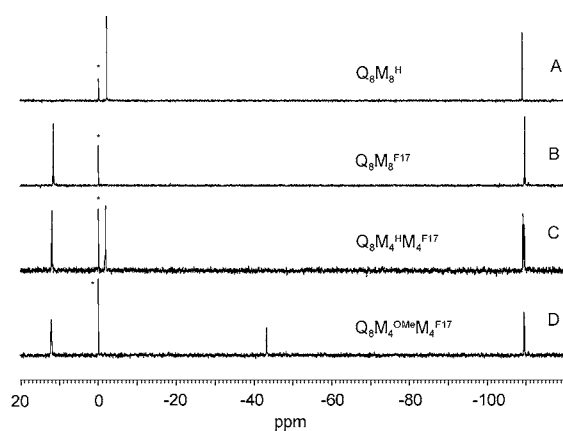
Figure 2. ^{29}Si NMR spectra of different Q_8M_8 precursors (*TMS standard).

Figure 3. Scheme of the $Q_8M_4^{OMe}M_4^{F17}$ molecule.

in M-units at $\delta = 11.86$ ppm and the second one for Si-atoms in Q-units at $\delta = -109.71$ ppm. Quantity and intensity of the signals and magnitude of their chemical shifts, especially the significant low-field shift of M-Si-units compared to that of the $H(CH_3)_2Si$ groups of $Q_8M_8^H$ (Fig. 2(A)), undoubtedly indicate an extensive reaction to a perfluoroalkyl group carrying double four-ring spherosilicate.

In addition, the absence of the signals for C-atoms in double bonds in the ^{13}C NMR spectrum confirms the complete addition of the methacryl groups of $F_{17}MA$. The MALDI-TOF mass spectrum of the perfluoroalkylated product shows a peak with highest mass and highest intensity at $m/z = 5295$ Da. This mass peak corresponds satisfactorily to the mass of a full perfluoroalkylated double four-ring spherosilicate ($M = 5275$ Da) bonded to a Na^+ ion ($m/z = 23$), vital for the detection of the molecule. The difference of three mass units between the theoretical and experimental results is attributed to the measurement error of 0.1% in the region of high masses. The result strongly confirms the preservation of the double four-ring structure and the existence of the perfluoroalkyl group modified spherosilicate of the formula $[CF_3(CF_2)_7(CH_2)_2OC(O)CH(CH_3)CH_2Si(CH_3)_2]_8$-$Si_8O_{20}$, in the following: $Q_8M_8^{F17}$. The schematic structure of $Q_8M_8^{F17}$ arises from Fig. 3 by insertion of eight R_1 groups.

Low solubility in polar solvents resulting in phase separations diminishes the applicability of $Q_8M_8^{F17}$ in sol-gel processes. By taking advantage of this property, the $Q_8M_8^{F17}$ precursor with a total number of 136 F-atoms per molecule might be established as
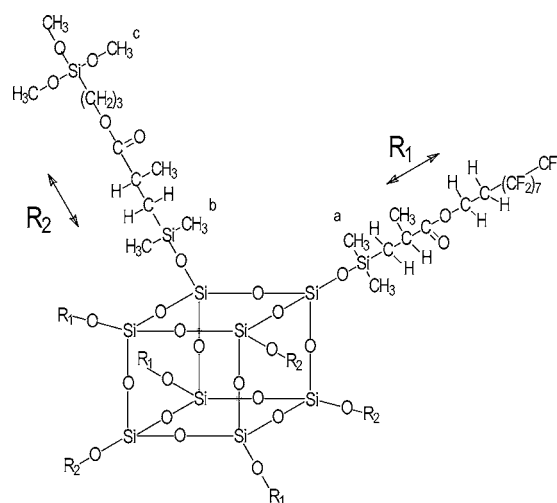
nanoscaled, high F-containing filler in apolar systems. To achieve perfluoroalkyl substituted spherosilicates favorably qualified for sol-gel derived materials adjustments regarding reactivity and solubility are crucial. This will be outlined in the following section.

4.1.2. Addition Reaction of $Q_8M_8^H$, $F_{17}MA$ and MPTS. A promoted reactivity of the spherosilicate is accomplished by partial replacement of perfluoroalkyl units at the silica core by e.g. alkoxysilyl-groups. These entities facilitate hydrolysis and homo-, respectively, co-condensation reactions with the sol-gel matrix. Syntheses and reactions of spherosilicates containing condensable trimethoxysilyl substituents only (Table 1, No. 22, 23) have been described previously [25]. These compounds are prepared by addition reaction of $Q_8M_8^H$ with unsaturated trimethoxysilanes.

In the first step, $F_{17}MA$ is added to $Q_8M_8^H$ at a molar ratio of 4:1 in 1,4-dioxane. Methacryloxypropyltrimethoxysilane (MPTS) is added in a second step at the molar ratio 4:1 regarding to $Q_8M_8^H$ for completion of the addition reaction of the SiH groups. A transparent homogeneous liquid is formed as reaction product.

Figure 2 depicts the ^{29}Si NMR spectra of the reaction products of $Q_8M_8^H$ after the first addition reaction with $F_{17}MA$ (C) and after the second reaction with MPTS (D). Spectrum C shows two signals with comparable intensities in the region of M-Si-atoms at $\delta = 11.94$ and -1.90 ppm deriving from the dimethylsilyl group (Si-atom "a" in Fig. 3) of the perfluoroalkyl ligand and from the non-reacted

H(CH$_3$)$_2$Si-group of the Q$_8$M$_8^H$. The corresponding Q-Si-atoms of the core bonded to H(CH$_3$)$_2$Si-groups and to perfluoroalkyl groups R$_1$ (Fig. 3) respectively, show signals with similar intensities at $\delta = -109.30$ and -109.68 ppm (Fig. 2(C)). Both tightly adjacent signals are slightly split which might have been caused by an irregular distribution of the two different ligands at the silica core. Spectrum C reveals that about 50% of the SiH groups of Q$_8$M$_8^H$ have reacted with the F$_{17}$MA corresponding to the employed molar ratio of both components. The ^{29}Si NMR spectrum D after the second addition reaction with MPTS shows two signals with identical intensities at $\delta = 12.28$ and 12.09 ppm which are assigned to the M-Si-atoms of the dimethylsilyl-group of the R$_2$ ligand ("b" in Fig. 3) and of the dimethylsilyl-group (a) of the perfluoroalkyl ligand R$_1$. The overlapping signals in spectrum D with two maxima at $\delta = -109.50$ and -109.57 ppm are attributed to the Q-Si-atoms of the core bonded to the perfluoroalkyl-(R$_1$) and trimethoxysilyl-ligands (R$_2$). The additional signal at $\delta = -43.21$ ppm in Fig. 2(D) is caused by the T-Si-atom of the trimethoxysilyl group ("c" in Fig. 3). Complete addition can be assumed due to the absence of signals in the region of $-$SiH groups at -1.90 ppm. Considering all these results together, a spherosilicate structure with the theoretical formula [CF$_3$(CF$_2$)$_7$(CH$_2$)$_2$OC(O)CH(CH$_3$)CH$_2$Si(CH$_3$)$_2$]$_4$-[(CH$_3$O)$_3$Si(CH$_2$)$_3$OC(O)CH(CH$_3$)CH$_2$Si(CH$_3$)$_2$]$_4$-Si$_8$O$_{20}$, in the following Q$_8$M$_4^{OMe}$M$_4^{F17}$, is most likely. The idealized scheme of this Q$_8$M$_4^{OMe}$M$_4^{F17}$ molecule with a regular distribution of the R$_1$ and R$_2$ ligands is shown in Fig. 3.

Probably, a distribution of the R$_1$ and R$_2$ ligands around the average ratio of 4:4 exists due to the results of previous examinations on mixed addition reactions of spherosilicates [20]. Supplementary investigations were carried out by means of MALDI-TOF mass spectrometry to prove the distribution of the ligands. The mass spectrum of Q$_8$M$_4^{OMe}$M$_4^{F17}$ reveals a Gaussian curve-like mass distribution with a maximum intensity at m/z = 4162 Da (Fig. 4). This mass maximum corresponds to the theoretical mass of the Na$^+$ ion supported Q$_8$M$_4^{OMe}$M$_4^{F17}$ molecule (4140 + 23 Da).

Peaks of higher and lower masses are symmetrically arranged around the central peak with decreasing intensities. The difference between single mass peaks (283–284 Da) is caused by the mass difference between the perfluoroalkyl (R$_1$) and the trimethoxysilyl (R$_2$) ligands. From this can be deduced that the lowest detectable mass at m/z = 3310 Da is caused by the
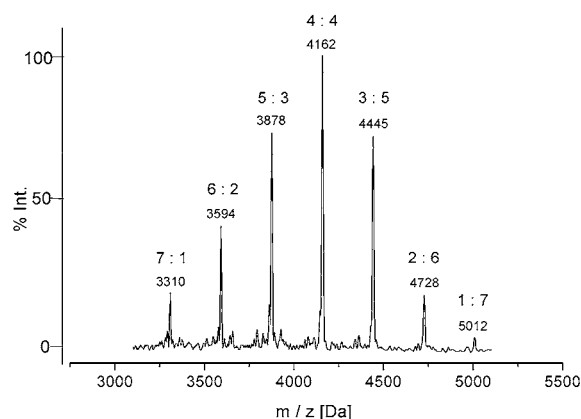

Figure 4. Time-of-flight mass spectrum of the Q$_8$M$_4^{OMe}$M$_4^{F17}$ (ratio of numbers: R$_2$:R$_1$, see Fig. 3).

(Na$^+$) Q$_8$M$_7^{OMe}$M$_1^{F17}$ molecule and the highest mass at 5012 Da by the (Na$^+$) Q$_8$M$_1^{OMe}$M$_7^{F17}$. The mass spectrum confirms the numerical distribution of the two different ligands at the silica cage. Therefore, the formula Q$_8$M$_4^{OMe}$M$_4^{F17}$ represents only the average ratio (4:4) of the two ligands.

In contrast to the Q$_8$M$_8^{F17}$ sample, Q$_8$M$_4^{OMe}$M$_4^{F17}$ is soluble in both polar and apolar solvents e.g. in i-propanol, acetone, 1,4-dioxane, tetrahydrofuran and hexane. This solubility makes possible investigations of hydrolysis and condensation reactions.

4.2. Hydrolysis and Condensation Reactions

The hydrolysis and condensation of the trimethoxysilyl groups of the Q$_8$M$_4^{OMe}$M$_4^{F17}$ precursor were examined in a 1,4-dioxane solution ($C_{SiO2} = 1.26$ M) at the molar ratio H$_2$O/OR = 0.5 by ^{29}Si NMR. For example Fig. 5. A shows the ^{29}Si NMR spectrum of the hydrolyzate after 10 h reaction time.

The signal at $\delta = -43.14$ ppm with highest intensity is caused by the non-hydrolyzed trimethoxysilyl group and the three signals at lower field are attributed to the three different T^0 silanol units. Low condensed T^1 units appear around $\delta = -50$ ppm. Higher condensed T^2 and T^3 units are not detectable. Integration of the total signal intensities after 3.5 h reaction time reveals about 77% unchanged trimethoxysilyl groups. By increasing the reaction time to 10 h this percentage drops to approximately 50%. Accordingly, a low condensation degree (c.d. <10%) is calculated. A gelification of the Q$_8$M$_4^{OMe}$M$_4^{F17}$ hydrolyzate is observed after a reaction
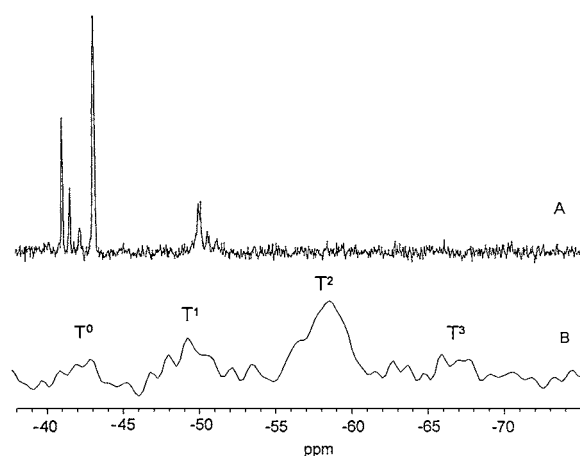
Figure 5. Detail of the ^{29}Si NMR spectra (region of T-units) of the $Q_8M_4^{OMe}M_4^{F17}$ hydrolyzate after 10 h reaction time and of the corresponding gel after heat treatment at 130°C for 5 h.

Figure 6. Surface tension of 4.0 MTEOS-1.0 TEOS-0.5 H$_2$O/OR sols with different amounts of $Q_8M_4^{OMe}M_4^{F17}$, F$_{17}$TS and F$_{13}$TS.

time >50 h. The transparent hydrogel was dried at 130°C for 5 h and examined by solid-state ^{29}Si MAS NMR. Spectrum B in Fig. 5 (detail) shows only a weak signal-noise ratio due to the relatively low concentration of the T-Si-atoms in the sample and the signal broadening. Nevertheless, four significant groups can be detected correlating with Si-atoms in T^0-, T^1-, T^2- and T^3-units. The maximum signal intensity appears for Si-atoms in T^2-units. It has to be mentioned that after thermal treatment small amounts of non-condensed T^0-units can still be detected. Altogether, a c.d. of only about 60% was estimated in the gel. Such relatively low c.d. has previously been observed for gels [25] derived from spherosilicates with eight trimethoxysilyl-ligands ($Q_8M_8^{OMe}$, No. 23 in Table 1). The low c.d. was attributed to the sterical hindrance during condensation of $Q_8M_8^{OMe}$ precursor, containing 24 methoxy groups. Taking the bulkiness of perfluoroalkyl groups into account the same reason could be responsible in the case of $Q_8M_4^{OMe}M_4^{F17}$. The results reveal that the trimethoxysilyl groups in $Q_8M_4^{OMe}M_4^{F17}$ are reactive enough to hydrolyze and condense, forming a gel already at a low condensation degree. Consequently, no significant problems are to be anticipated concerning co-condensation reactions with additional low molecular alkoxysilane components in sol-gel systems.

4.3. Hydrophobic and Oleophobic Properties

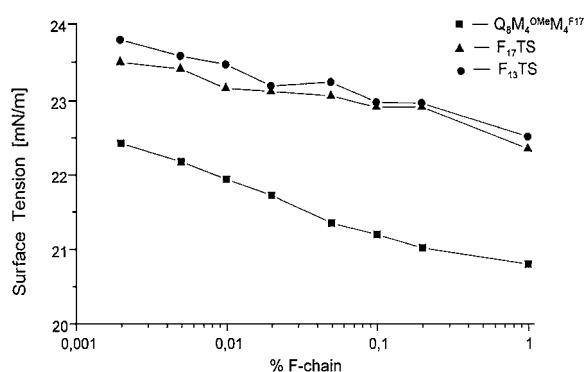For the comparison of hydrophobic and oleophobic properties of the new $Q_8M_4^{OMe}M_4^{F17}$ precursor with those of the perfluoroalkyltrialkoxysilanes F$_{13}$TS and F$_{17}$TS, sols of the composition 4.0 MTEOS-1.0 TEOS-0.5 H$_2$O/OR were chosen for investigation (see experimental). The results of the examination of the surface tension of the MTEOS/TEOS sols with 0.002 to 1 mole% F-chain are depicted in Fig. 6.

Sols with $Q_8M_4^{OMe}M_4^{F17}$ additive possess always significantly lower surface tensions compared to F$_{13}$TS and F$_{17}$TS containing sols at corresponding F-chain concentration. Evaluation of the surface tension of the two perfluoroalkylsilanes F$_{13}$TS and F$_{17}$TS exposes a slightly lower surface tension for F$_{17}$TS containing sols most likely due to the longer perfluoroalkyl chain. However, in the case of $Q_8M_4^{OMe}M_4^{F17}$ and F$_{17}$TS derived sols, the discrepancy in surface tensions is unquestionably not a function of the perfluoroalkyl chain lengths.

Coatings on glass plates were made from sols to examine the influence of the different perfluoroalkyl additives on the surface properties. The hydrophobicity and oleophobicity of the surface were investigated by contact-angle measurements on water and hexadecane droplets. Generally, the results in Fig. 7 show a slight increase in the contact-angles of water and hexadecane droplets on the surface with increasing concentration of the three perfluoroalkyl additives. In both series the $Q_8M_4^{OMe}M_4^{F17}$ additive generates higher contact-angles compared to F$_{13}$TS and F$_{17}$TS. Consequently, the $Q_8M_4^{OMe}M_4^{F17}$ precursor gives rise to coatings with better hydrophobic and oleophobic properties than the perfluoroalkylalkoxysilanes, already at a low F-chain concentration. This property creates an advantageous use of the precursor concerning easy-to-clean and antigraffiti supplied coatings on material surfaces.
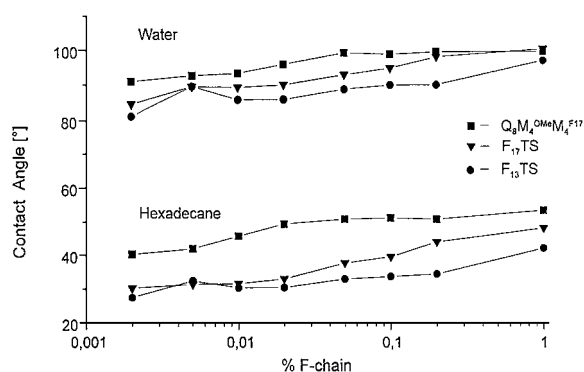
Figure 7. Contact-angle of water and hexadecane dropletts on coatings of the system 4.0 MTEOS-1.0 TEOS-0.5 H$_2$O/OR with different amounts of Q$_8$M$_4^{MeO}$M$_4^{F17}$, F$_{17}$TS and F$_{13}$TS.

The differences in the hydrophobic and oleophobic properties of the Q$_8$M$_4^{OMe}$M$_4^{F17}$ precursor and the perfluoroalkyltriethoxysilanes are surprising. The size, spherical structure and alternating order of the two different types of ligands of the Q$_8$M$_4^{OMe}$M$_4^{F17}$ should cause a more distorted arrangement of perfluoroalkyl ligands at the outermost surface of the coating. According to literature [48] such disorder in fluoroalkyl chains arrangement amplifies the surface energy. Additionally, the adjacent ligand R$_2$ (Fig. 3) enlarges the number of polar bonds (SiOH/OR, C=O, C—O—C) near the surface, further lowering the hydrophobic/oleophobic properties of the surface. The unexpected effect of Q$_8$M$_4^{OMe}$M$_4^{F17}$ in contrast to F$_{17}$TS can only be deduced to its special structure. Probably, a non-regular, cumulative arrangement of the perfluoroalkyl ligands at the silica core contributes to the observed performance of the Q$_8$M$_4^{OMe}$M$_4^{F17}$ precursor.

A more detailed examination of the element distribution of F, O and C in the surface and in the adjacent inner layers of Q$_8$M$_4^{OMe}$M$_4^{F17}$ containing coatings is intended, aiming at a more suitable explanation for the unanticipated properties of this new spherosilicate.

5. Conclusions

The group of organically modified double four-ring spherosilicates is enlarged by highly perfluoralkyl ligands containing species. The double four-ring spherosilicate Q$_8$M$_8^{F17}$, completely equipped with eight perfluoroalkyl groups is available by stoichiometric addition reaction between Q$_8$M$_8^H$ and perfluoro methacrylate. Elevated solubility in polar solvents, essential for sol-gel reactions, is realized by partial substitution of perfluoroalkyl groups by trialkoxysilyl ligands. The trialkoxysilyl groups of the mixed ligand spherosilicate Q$_8$M$_4^{OMe}$M$_4^{F17}$ hydrolyze and condense in water/1,4-dioxane to a transparent hybrid gel showing a relatively low condensation degree. Compared to perfluoroalkylalkoxysilanes this new spherosilicate Q$_8$M$_4^{OMe}$M$_4^{F17}$ generates better hydrophobic and oleophobic properties of sol-gel derived coating materials.

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