

NEW ROUTES TO SILICIC ACID CONTAINING INORGANIC-ORGANIC HYBRID PRECURSORS AND POLYMERS

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Abstract

In view of the outstanding role that silicic acids (s.a.) play in inorganic materials a survey will be presented regarding the possibilities of the integration of s.a. in organic matrices via chemical reactions. The objective is to combine the advantageous properties of the silicic acid with those of the organic compounds in order to generate novel materials. The reactions of silicic acids with organic molecules, as studied by ^{29}Si NMR spectroscopy, are described using the silicic acid $\text{H}_8\text{Si}_8\text{O}_{20}$ with a defined double four-ring structure as an example. By silylation of the hydrophilic $\text{H}_8\text{Si}_8\text{O}_{20}$ its functional organophilic derivatives were synthesized. The s.a. derivatives with epoxy-, alkoxy-, HSi-, ketoester or unsaturated groups are capable of condensation, polymerization, complexation or additive reactions leading to reactive inorganic-organic precursors or polymers with the defined silicic acid unit. The synthesis and structure of the following s.a. containing precursors and polymers will be reported: (a) inorganic-organic polymers with a high content of silanol groups, (b) microporous polymers free of silanol groups and (c) metal (Al, Zr) alkoxide complexes attached to defined silicic acid units. The model reactions of the double four-ring silicic acid derivatives can be transferred to technical silicic acid solutions prepared from water glass. The presented reaction pathways are a basis for the preparation of a great variety of new inorganic-organic compounds with tailor-made structures and properties which can be used for highly homogeneous and stoichiometric materials.

Introduction

One of the objectives in the development of new materials is the combination of advantageous properties of inorganic and organic compounds into a single material in order to achieve outstanding properties. As an inorganic component in such hybrid materials silica or silicic acids play an important role due to their high reactivity and the great variety of structural types available to produce inorganic polymers [1]. The outstanding properties of inorganic silicate materials are well known from materials such as glasses, ceramics, cements, silica sols, water glass or zeolites. The improvement of the properties of organic materials by silicate fillers such as silica fibers, silica powders or mica has been known for a long time [2]. In these materials the adherence between the inorganic reinforcement and the organic matrix is poor due to insufficient chemical bonding. This work will be concerned solely with hybrid materials with strong chemical bonding. An intensive chemical interaction between silicic acid or silicates and organic compounds has been observed in organic silica sols [1] and organically modified silicates [3, 4]. A strong interaction of hydrolyzable silicic acid esters with functional organic compounds takes place in the sol-gel process, a preferred method for preparation of silicic acid containing

inorganic-organic hybrid materials [5]. Such sol-gel derived hybrid polymers are used for functional and corrosion protective coatings and as precursors for high quality ceramic materials and glasses [6].

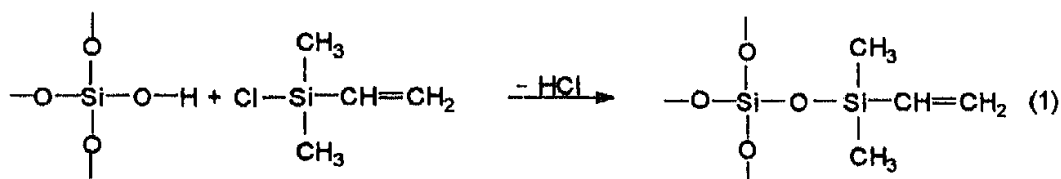
Beside tetraalkoxysilane hydrolyzates, silicic acid solutions from water glass or crystalline silicates can be used as sources for the inorganic component in hybrid polymers. Nevertheless, in the course of hybrid polymer synthesis, polymeric silicic acids with a variety of structures are formed irrespective of the source of silicic acid used [7, 8]. The examination of structures of such inhomogeneous polymeric silicic acid solutions are connected with considerable difficulties. In fact, one of the major difficulties inhibiting the synthesis of inorganic-organic hybrid materials with defined properties is the inability to follow structural changes during reactions of silicic acids with the organic compounds to a sufficient extent.

The objective of this work is to obtain more insight into the fundamental reactions of silicic acid derivatives with organic compounds which yield inorganic-organic hybrid polymers. Silicic acid derivatives with the double four-ring structure were used as model compounds to clarify the reactions and bonds of the silicic acid with the organic component and the relation between the polymer structure and its properties. Detailed descriptions of the synthesis and characterization of the precursors and polymers are given in the cited literature.

Hybrid precursors with defined silicic acid units

Solutions of silicic acids with well defined structures are very rare. However, solutions with the double four-ring (D4R) structure $H_8Si_8O_{20}$ can be prepared by acidification or ion-exchange of the tetramethylammonium silicate $[N(CH_3)_4]_8Si_8O_{20} \times 69H_2O$ [9]. The silicic acid with D4R structure has found importance due to its relatively simple preparation and its unique structure, which is considered as one of the smallest three-dimensional silicic acid polymer or nanosized particle [1]. The D4R structure is known not only as silicic acids but also as silasequioxanes. In both cases this type of structure is often used as a model compound for the simulation of silicate structures and processes and as building blocks for new materials [10-14].

A first step in the preparation of silicic acid containing precursors for hybrid polymers is the stabilization of silicic acids towards hydrolysis and condensation by silylation reaction. Using silylating agents with functional organic groups reactive derivatives of organic silicic acids can be synthesized. A scheme of the silylation reaction is shown in (1).



By silylation of the D4R silicic acid with functional chlorosilanes or disiloxanes its derivatives with vinyl-, allyl-, hydrido- or chloromethylsilyl ligands were synthesized and characterized [15-18]. More recently, D4R silicic acid derivatives have been synthesized by silylation and additive reactions [19-21], whose structure is shown in Fig. 1.

The structure of the silicic acid derivatives was confirmed by NMR spectroscopy, mass spectrometry and X-ray analysis. In every case eight functional organic ligands are attached to one molecule of the precursors. All derivatives are soluble in organic solvents.

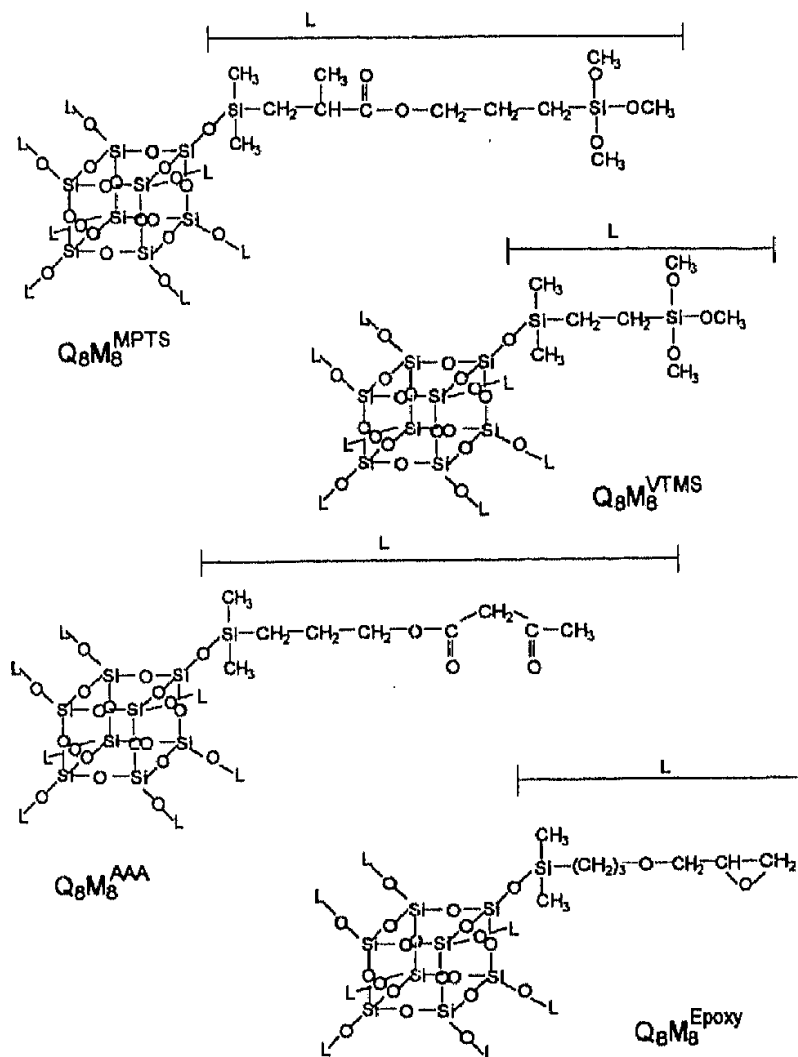


Figure 1: Scheme of functional D4R-silicic acid derivatives

Frequently, the tailor-made synthesis of materials requires a variation in the functionality of the precursors. The number and the types of functional groups on the D4R cage can be varied by silylation with a mixture of silylating reagents with different functionality.

As an example Fig.2 shows a D4R derivative with both vinyl- and hydridosilyl ligands and a derivative with a number of functional groups smaller than eight. From the gas chromatogram it follows that a distribution of both different functional groups on the D4R cage appears. Although it is likely that isomers of the derivatives exist, it is not possible to directly identify their existence on the basis of the gas chromatography and NMR results. However, the main component in the mixtures is adjustable by the ratio of the amounts of the silylating agents [22].

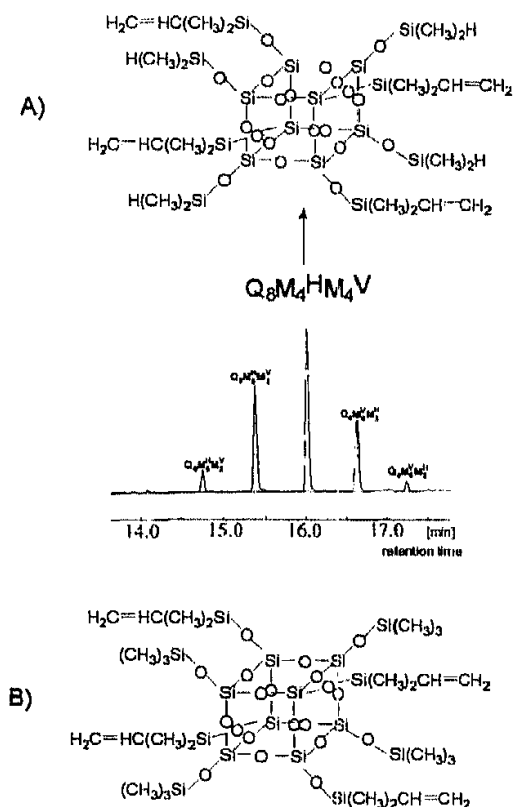


Figure 2: D4R silicic acid derivatives with different functionality: A) the derivatives with two different functional groups and their gas chromatogram and B) the D4R cage with less than eight functional groups

Hybrid polymers with D4R silicic acid units

As precursors of hybrid polymers the D4R derivatives open a wide field for reactions due to the different functional ligands and should be able to undergo the following reactions.

- (i) Additive reactions of hydridosilyl and unsaturated groups leading to Si-CH₂ bonds
- (ii) Hydrolysis/condensation reactions of alkoxy groups leading to Si-O-Si links
- (iii) Polymerization of unsaturated or epoxy groups leading to C-C or C-O-C bonds
- (iv) Complexation of metal (Me) alkoxides resulting in Me-O-C bonds

Polymers derived by complexation

The complexation reaction of the precursor $\text{Q}_8\text{M}_8^{\text{AAA}}$ (Fig. 1) with a Zr-alkoxide yields a reactive silica and zirconia containing organic hybrid precursor [20] (Fig. 3). On the other hand the additive reaction of the H-silylated D4R-precursor $\text{Q}_8\text{M}_8^{\text{H}}$ with allyl acetoacetate (AAA) complexed aluminium alkoxide yields soluble oligomeric precursors or insoluble polymers, depending upon the number of the ligands. The constitution of the reaction products in Fig. 3 is confirmed by ¹³C, ²⁷Al and ²⁹Si NMR measurements.

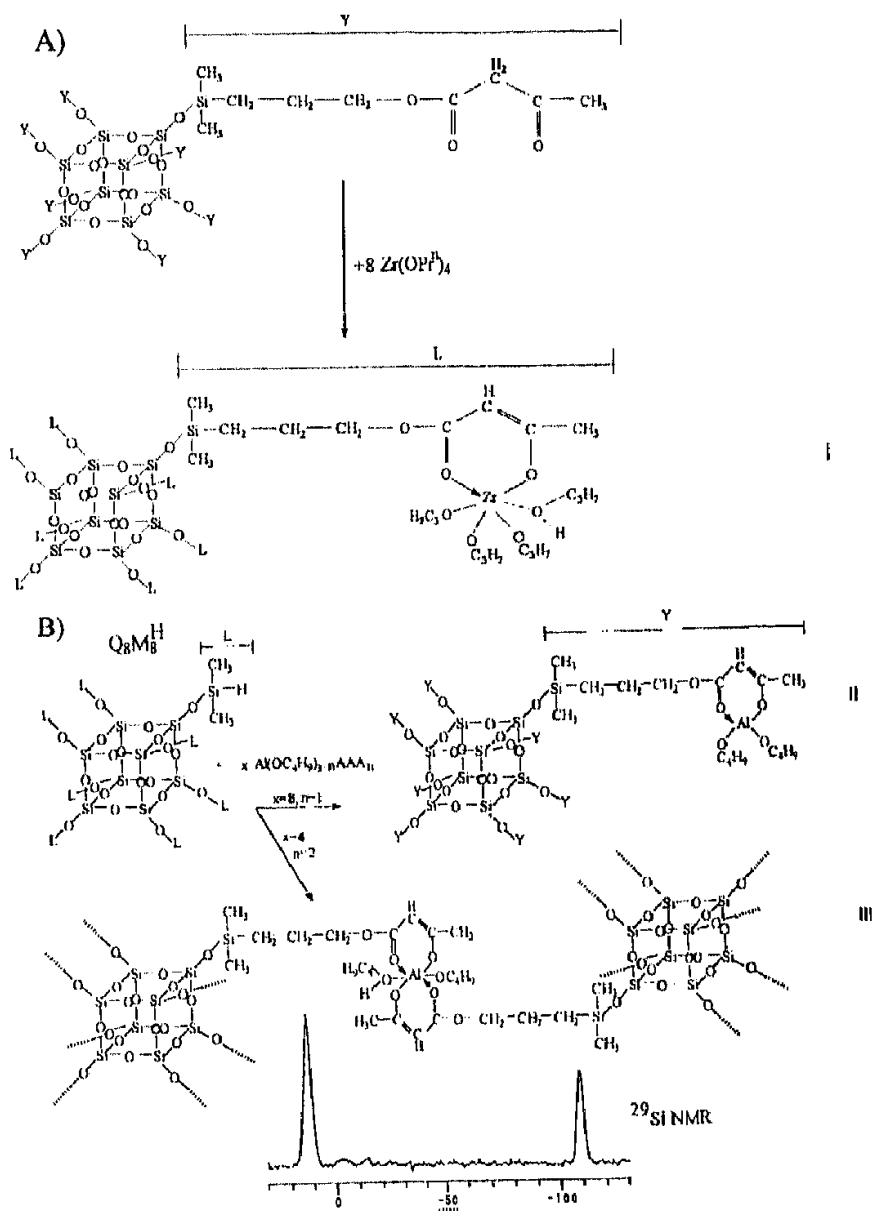


Figure 3: Heterometal precursors and polymers synthesized by complexation (A) and additive reaction (B) and ²⁹Si NMR spectrum of the polymer III.

The symmetrical signal appearing at $\delta = -108.7$ ppm in the ²⁹Si NMR spectrum of the compounds I-III, indicates preservation of the double four-ring structure. The absence of a signal due to hydridosilyl groups ($\delta = \sim 3$ ppm) and the new signal with the chemical shift $\delta = 13.0$ ppm, corresponding to $-O(CH_3)_2Si-C-$ bridges, suggest a complete additive reaction. The heterometal precursors I and II can condense via alkoxide groups to form insoluble heterometal hybrid polymers. For the case of two ketoester ligands per Al atom the complex $Al(OBu^S)(AAA)_2$ is able to link the cage-like silicic acid units to yield polymers with a three dimensional structure (Fig.3,III).

The results show that complexation and additive reactions lead to novel heterometal precursors and polymers with the preserved D4R silicic acid structure. Such alumina or zirconia

containing silicic acid precursors are effective in the preparation of homogeneous and highly stoichiometric inorganic-organic heterometal polymers or ceramic materials.

Hybrid polymers via additive reaction

Hybrid polymers with D4R silicic acid units have been synthesized and characterized by three working groups. Hoebbel et.al. [23] have synthesized polymers by additive reaction of the hydrido- and vinylsilylated D4R derivatives (Fig.4).

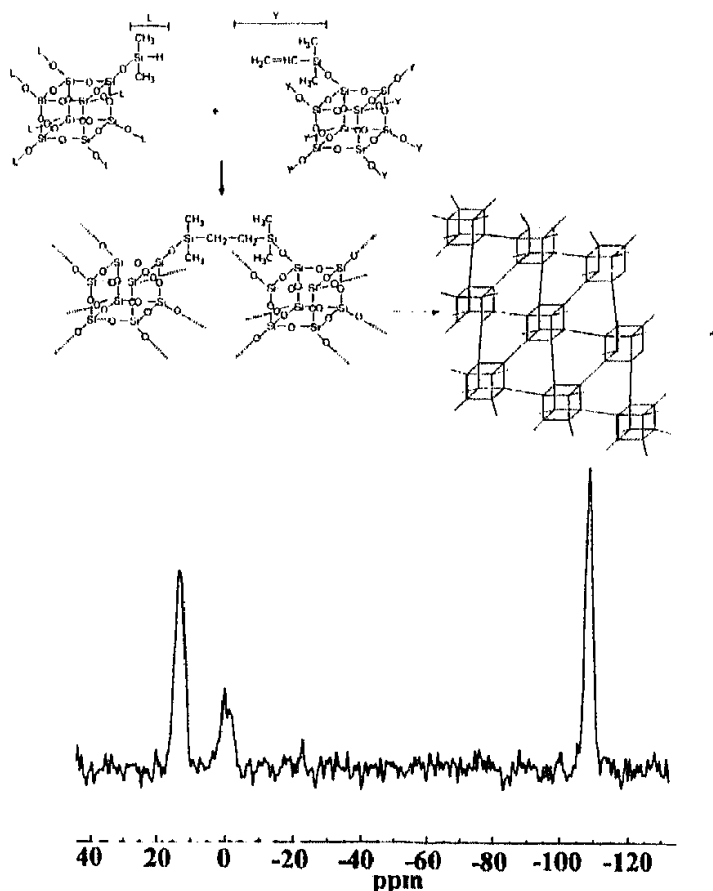


Figure 4: Additive reaction of $Q_8M_8^V$ and $Q_8M_8^H$ to the hybrid polymer 1 and solid state ^{29}Si NMR spectrum of polymer 1

The hydrophobic polymers are insoluble in organic solvents and show microporosity and specific surface area of about $300 \text{ m}^2\text{g}^{-1}$. The porosity results from spaces between the D4R units. The ^{29}Si NMR spectrum indicates that on average two functional groups of the precursors remain unreacted, due to the sterical hindrance as described in the literature [23].

In an attempt to produce new ceramic materials Agaskar [10] also synthesized a hybrid polymer with defined D4R units by means of additive reaction, but with a longer $-\text{O}-\text{Si}-\text{C}-\text{C}-\text{Si}-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4-\text{Si}-\text{C}-\text{C}-\text{Si}-\text{O}-$ bridge between the D4R cages. Heat-treatment of this polymer at 800°C in nitrogen yields a silicon oxycarbide material with low specific surface area. After leaching with hydrofluoric acid the material showed a remarkable specific surface area of $600 \text{ m}^2\text{g}^{-1}$.

Recently, Hasegawa [14] synthesized a hybrid polymer consisting of defined D4R units by silylation of the tetramethylammonium silicate with dichlorodimethylsilane. This hybrid polymer with short $\text{-O-Si(CH}_3\text{)}_2\text{-O-}$ bridges between the D4R units showed a low specific surface area, but heating at 300°C yielded a porous hybrid material with a specific surface area of $300\text{ m}^2\text{g}^{-1}$. It was assumed that tetramethylammonium salts included in the polymer during the synthesis evaporated at higher temperatures leaving holes which led to the porosity. Among the three hybrid polymers described only the polymer 1 synthesized via additive reaction of the hydrido- and vinylsilylated D4R derivatives showed high specific surface area without a post-treatment at high temperatures.

For the examination of the influence of the bridge structure and bridge length on the porosity and structure, hybrid polymers were synthesized with different types of bridging molecules between the D4R cages [24].

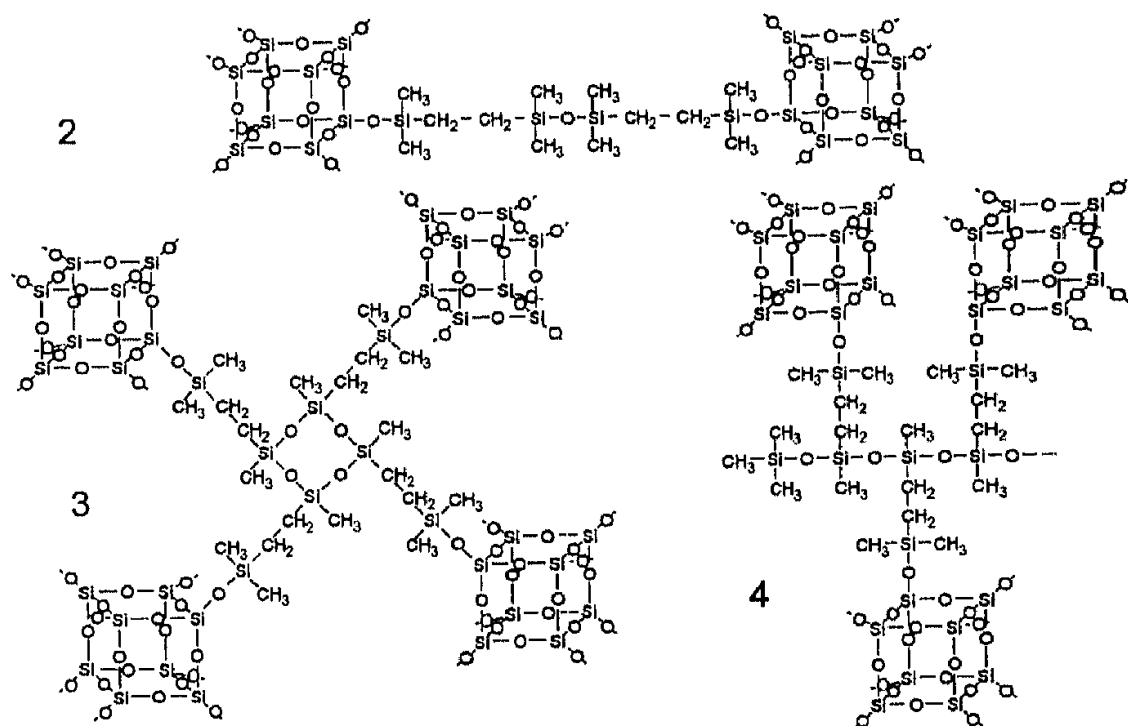


Figure 5: Scheme of hybrid polymers with different types of bridges between the D4R cages

Figure 5 shows hybrid polymers with chain-like (2), cyclic (3) or branched (4) bridges between the D4R cages. Low specific surface area of about $4\text{--}7\text{ m}^2\text{g}^{-1}$ was observed for the polymers from nitrogen adsorption measurements.

To better understand the influence of bridge length on the porosity, two polymers were prepared with shorter four-membered bridges and longer seven-membered bridges between the cages compared to polymer 1 (Fig. 6). By additive reaction of QgMg^{H} with the allyl silylated D4R derivative QgMg^{A} a polymer with seven-membered bridges was derived (polymer 5). In a similar manner, the reaction of QgMg^{V} with a cage-like octahydrosilasesquioxane $\text{H}_8\text{Si}_8\text{O}_{12}$ (T_8^{H}) produced a polymer with short four-membered bridges (polymer 6). The signals at $\delta = -109$ ppm in the solid state ^{29}Si NMR spectra of the polymers 5 and 6 indicate retention of the double four-ring structure of both polymers [22].

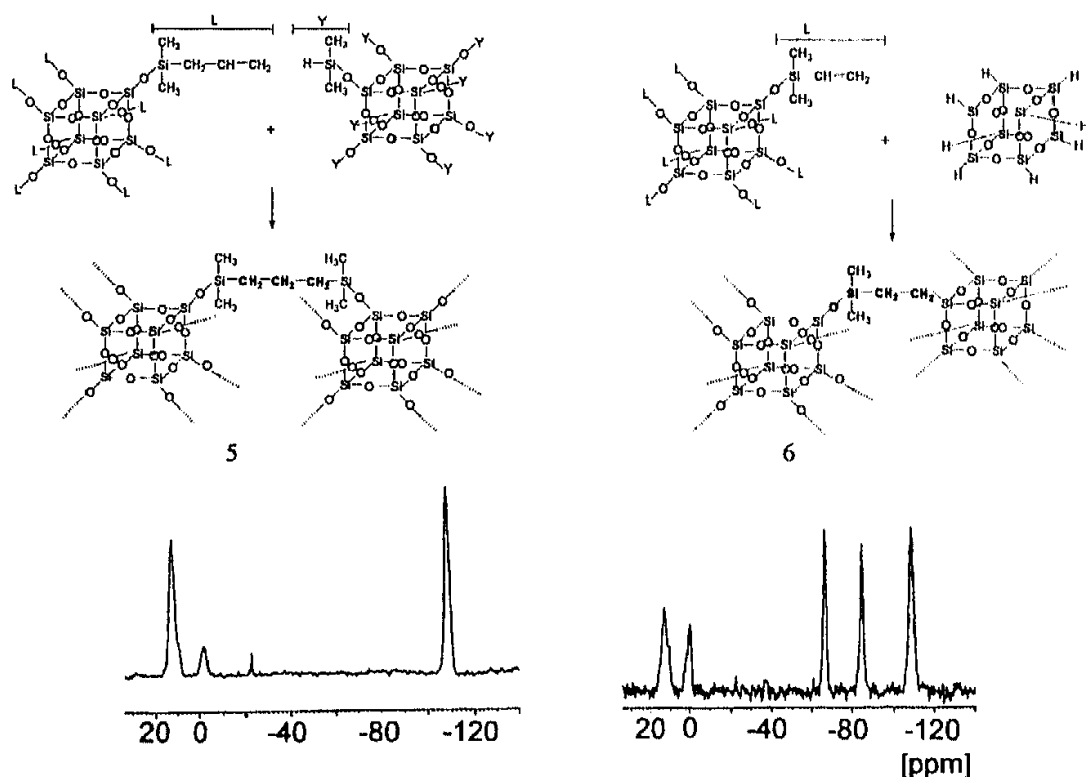


Figure 6: Hybrid polymers with different bridge length between the D4R cages and their ^{29}Si NMR spectra

Also, from the NMR spectra the average polymerization degree of polymer 5 was calculated to be 86% (6.9 of eight functional groups per a D4R unit are reacted) and for polymer 6 to be 66% (5.3 groups reacted). Considering the polymerization degree of polymer 1 (78% = 6.3 groups reacted) it follows that the shorter the bridge between the cages the lower the polymerization degree in the polymer due to sterical hindrance of the high functional D4R precursor. Unlike polymer 1 polymers 5 and 6 do not show significant specific surface area. The small surface area of polymer 6 with the shortest bridges between the cages can be explained by the smaller free space between the silicic acid units which is not accessible to N_2 molecules compared with polymer 1. But for the polymer with a long bridge no sufficient explanation exists for the low surface area. The bridges in this polymer are able to be folded or twisted, leading to an effective shortening of their length which would inhibit access of N_2 molecules into the pores. Another reason is suggested on the basis of the degree of polymerization in polymer 5, which was the highest among the three examined polymers. These results suggest that the six-membered $-\text{O}-\text{Si}-\text{CH}_2-\text{CH}_2-\text{Si}-\text{O}-$ bridge between the cages seems to be a most desirable length for a porous hybrid material consisting of the defined silicic acid unit.

Two compounds, the hydrido- and vinylsilylated D4R derivative were so far used for the synthesis of porous polymer 1. A more optimal synthesis route, however, has been found which starts from the mixed vinyl- and hydridosilylated D4R derivative (see Fig. 2,A) synthesized by a one step silylation of the D4R silicate by using a mixture of corresponding silylating reagents. This derivative itself undergoes an additive reaction to give a hybrid polymer with preserved D4R units and specific surface area of $200 \text{ m}^2\text{g}^{-1}$ [22]. It therefore follows that the porous hybrid polymer can be synthesized easily by a two step reaction: the mixed silylation of the silicate followed by an additive reaction.

To examine the influence of the silicic acid structure on porosity, polymer syntheses were carried out by additive reaction of hydrido- and vinylsilylated inhomogeneous silicic acids derived from water glass solutions. The hybrid polymers show a significant specific surface area of about $500 \text{ m}^2\text{g}^{-1}$. In the solid state ^{29}Si NMR spectrum signals appear due to unreacted hydridosilyl ($\delta = -3.3$ ppm) and vinylsilyl groups ($\delta = 0.1$ ppm) and Si atoms in the bridges between the silicic acid units ($\delta = 12.8$ ppm). A polymerisation degree of 61% is calculated from the spectrum. Similar results were obtained starting from mixed hydrido- and vinylsilylated derivatives of polymeric silicic acids formed from a water glass solution. These results show that the chain-like six-membered bridge between silicic acid units leads to porous hybrid polymers independent of the structure of silicic acid units and the method of polymer preparation.

Thermal stability of the hybrid polymers

The thermal stability and the reactions of the D4R cages which takes place during heat treatments were examined for the porous polymer 1 [25]. The results of the thermal analysis and the solid state ^{29}Si NMR experiments are summarized in Fig. 7

According to the results of the differential scanning calorimetry measurements the polymer is stable in air up to 250°C . After the heat treatment at 342°C signals due to new structural Si units in the D ($(\text{CH}_3)_2\text{Si}(\text{O}_{0.5})_2$) and T ($(\text{CH}_3\text{SiO}_{0.5})_3$) region of the NMR spectrum were detected, indicating thermal degradation of carbon in the bridges and oxidation of the M-silicon units. The thermal oxidation of the methyl groups at about 450°C finally leads to new Q units ($\text{Si}(\text{O}_{0.5})_4$) with different degree of polymerization. Formation of these new Q-units cause the asymmetry of the Q-signal in the NMR spectrum. Due to the asymmetry of the Q signal the NMR spectrum of the sample heated at 450°C does not give reliable information on the preservation of the D4R units at this temperature. Recently wide angle X-ray scattering measurements suggest a partial decomposition of the D4R structure at 450°C [26]. The scattering curve of the polymer after a treatment at 900°C is similar to the curve of a dispersed amorphous silica. Simultaneous measurements of the specific surface area of the polymers after the heat treatment showed a significant decrease with increasing temperature. The decrease of the surface area is caused by the decomposition of the carbon-carbon bridges which act as "distance holders" between the silicic acid units. The results show that it is not possible to obtain silica products with the preserved D4R structure through a burning out of the organic components.

Hybrid polymers via condensation reactions

The inorganic-organic polymers with defined D4R silicic acid units discussed above are hydrophobic materials free of silanol groups. In contrast to these polymers the synthesis of silicic acid containing hybrid polymers with a high content of hydrophilic silanol groups is described in this section. Such polymers could be applied for adsorption or catalytic purposes.

The starting silicic acid derivatives $\text{Q}_8\text{M}_8^{\text{MPTS}}$ and $\text{Q}_8\text{M}_8^{\text{VTMS}}$ (see Fig.1) for silanol group rich polymers are different in the length and structure of the functional ligands, but both derivatives carry the same number of 24 alkoxy groups per molecule. Such a high content of alkoxy groups would lead to remarkable sterical hindrance during the condensation reaction. The objectives of this investigation were :

- (i) to follow the hydrolysis and condensation reaction of the silicic acid derivative.
- (ii) to determine the condensation degree and the silanol content.
- (iii) to examine the influence of the ligand length on the condensation degree.

The hydrolysis/condensation reactions of the precursors in an acidic acetone-water mixture yielded polymers, insoluble in organic solvents. The polymers were dried at 180°C at reduced pressure and examined by ^{29}Si NMR spectroscopy. The NMR spectrum of the reaction products of $\text{Q}_8\text{M}_8^{\text{MPTS}}$ is shown in Fig. 8. In the spectrum signals appear due to OH attached Si atoms in T^1 and T^2 structural units as well as a signal for fully condensed T^3 units.

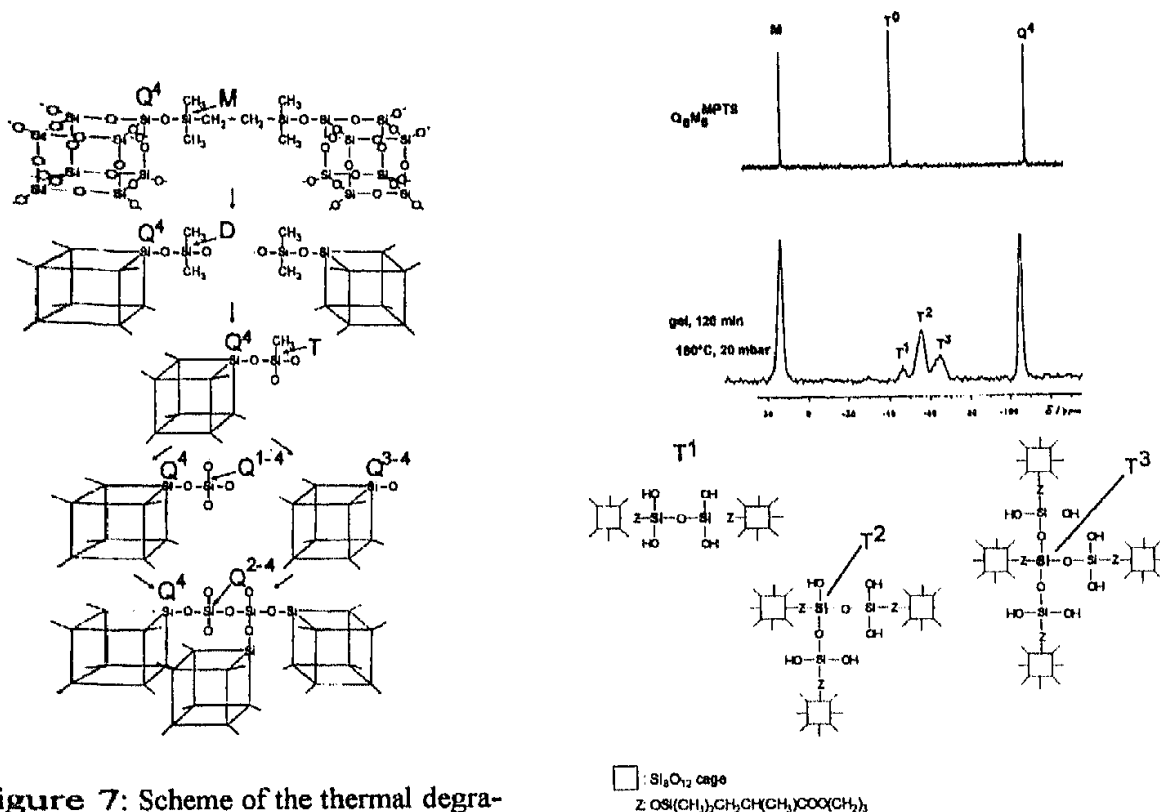


Figure 7: Scheme of the thermal degradation of the hybrid polymer

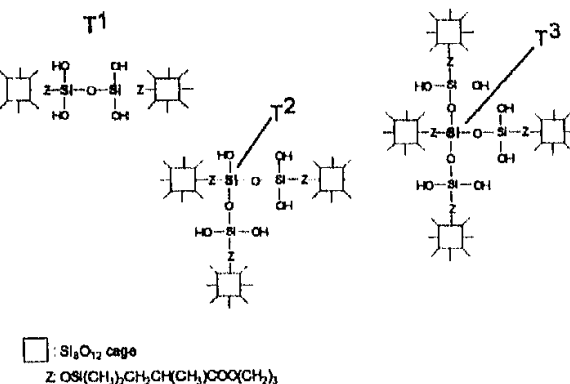
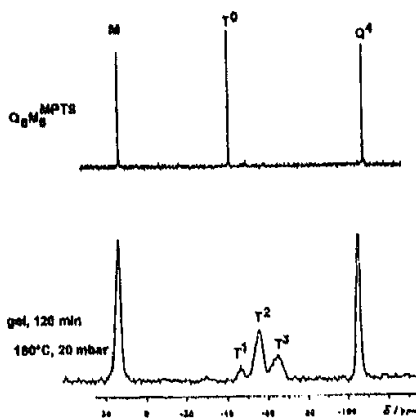


Figure 8: ^{29}Si NMR spectra of the $\text{Q}_8\text{M}_8^{\text{MPTS}}$ and its hydrolysis/condensation product

A quantitative evaluation of the NMR spectra of the $\text{Q}_8\text{M}_8^{\text{MPTS}}$ polymers results in about 9 unreacted OH groups per D4R unit and to 5.6 OH groups after the heat-treatment of the polymer. The content of silanol groups and degree of condensation in the $\text{Q}_8\text{M}_8^{\text{MPTS}}$ polymers with a longer and $\text{Q}_8\text{M}_8^{\text{VTMS}}$ polymers with a shorter bridge length between the D4R cages are summarized in table I.

Table I: Content of silanol groups and degree of condensation in the D4R hybrid polymers: A) derived from $\text{Q}_8\text{M}_8^{\text{MPTS}}$, B) derived from $\text{Q}_8\text{M}_8^{\text{VTMS}}$

Polymer		OH/D4R	Degree of Condensation
A	RT	8.8	63 %
	180°C, 2h	5.6	75 %
B	RT	8.8	63 %
	180°C, 2h	7.2	70 %

These results indicate that, among the heat-treated samples, the highest content of uncondensed silanol groups is found in polymer B with the shortest bridge. Hence it was concluded that the sterical hindrance against condensation is strongest in the synthesis of polymer B so that even at higher temperatures this hybrid polymer showed 7.2 unreacted silanol groups per D4R silicic acid unit.

These polymers with high silanol contents show a low specific surface area. The reason is likely due to the very high functionality of the starting D4R precursor resulting in a compact structure of the polymer. Shea [27] has shown that a relatively low content of 6 silanol groups in organic spacer molecules is sufficient for the synthesis of high porous materials. Therefore, silicic acid precursors were synthesized with a lower functionality than 24 OH groups per D4R by additive reaction of Q_8Mg^H or mixed silylated $Q_8Mg^{M,H}$ derivatives and vinylalkoxysilanes with different contents of alkoxide groups. These D4R silicic acid precursors with on average 8, 12 or 16 OH groups per D4R unit did not yield porous materials, which is possibly due to the fact that the D4R cage is too small for a spacer, or, the length of the bridges between the cages is not optimal. Further work is in progress to clarify this problem.

Conclusions

- The synthesis of highly functional organic silicic acid derivatives without significant degradation of their silicic acid structure is possible.
- The use of defined silicic acid derivatives provide not only a better insight into fundamental reaction of organic silicic acid derivatives to hybrid polymers but also advantageous properties of the hybrid materials.
- The silicic acid precursors are useful for various chemical reactions due to the different functional groups. *Complexation and additive reactions* of the silicic acid derivatives lead to reactive heterometal precursors or hybrid polymers which can serve as sources of homogeneous and highly stoichiometric materials.
- By means of *additive reactions* of vinyl- and H-silylated D4R derivatives microporous, silanol free polymers with the ordered D4R substructure can be synthesized. The bridge length and the bridge structure are responsible for the porosity of silicic acid containing hybrid polymers. The structure of the silicic acid seems to have a lower influence on the porosity.
- The porous hybrid polymers derived by additive reaction are thermally stable up to 250°C. At higher temperatures up to 900°C the oxidation of the C-C bridges occurs followed by that of the methyl groups and finally by degradation and reorganization of the D4R silicic acid structure to a common silica structure.
- Non-porous hybrid polymers with a high content of silanol groups (7.2 OH/molecule) can be synthesized by *hydrolysis/condensation reaction* of alkoxysilylated silicic acid derivatives with 24 alkoxide groups per molecule even at temperatures as high as 180°C. These materials could find applications for separation and catalytic purposes.

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