

SOLID STATE ^{29}Si NMR INVESTIGATION OF INORGANIC-ORGANIC POLYMERS WITH DEFINED SILICIC ACID UNITS

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Abstract

By thermal analysis and ^{29}Si NMR spectroscopy the thermal behaviour and structural changes of two different types of inorganic-organic polymers with defined double four-ring silicic acid units (Si_8O_{20}) were characterized. Polymer 1, prepared from the organic silicic acid precursors $[(\text{CH}_3)_2\text{HSi}]_8\text{Si}_8\text{O}_{20}$ ($\text{Q}_8\text{M}_8^{\text{H}}$) and $[\text{CH}_2=\text{CH}(\text{CH}_3)_2\text{Si}]_8\text{Si}_8\text{O}_{20}$ ($\text{Q}_8\text{M}_8^{\text{V}}$), preserves the double four-ring structure up to 350°C . Higher temperatures lead to structural reorganizations of the SiO_4 tetrahedra forming at 900°C a structure similar to amorphous silica. Polymer 2, synthesized by condensation reaction of the new organic silicic acid precursor $[(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{OC}(\text{O})\text{CH}(\text{CH}_3)\text{CH}_2\text{Si}(\text{CH}_3)_2]_8\text{Si}_8\text{O}_{20}$, shows with 37% uncondensed SiOH groups a remarkable high content of silanol groups caused by sterical hindrances.

1. Introduction

The sol-gel process is an useful procedure for the synthesis of novel inorganic-organic polymers /1/. Such polymers are of technical interest as they combine the advantageous properties of the inorganic-organic components in one polymeric material. Generally, alkoxy silanes are used as silicon source in sol-gel derived inorganic-organic polymers. In this article the synthesis and structural characterization of inorganic-organic oligomer and polymers is described on the basis of silicic acid solutions as silicon source.

A common way for preparation of silicic acid solution is the ion exchange of water glass solution or silicates. Frequently, silicic acids in solution show complicated structures and reactions due to the extensive distribution of different silicic acid units and their high reactivity. Therefore, polymeric silicic acid solutions are unfavourable for use in basic research studies. The use of monomolecular silicic acid species as model compounds is a more advantageous way to provide for better insight into the reactions of the inorganic and organic components to polymers.

One of the rare and relatively stable monomolecular silicic acid species is the so called double four-ring silicic acid $\text{H}_8\text{Si}_8\text{O}_{20}$, prepared from tetramethylammonium silicates /2/. The double four-ring (D4R) silicic acid serves as inorganic component in the described inorganic-organic oligomer and polymers.

2. Experimental

The preparation of polymer 1 by additive reaction of $[(\text{CH}_3)_2\text{HSi}]_8\text{Si}_8\text{O}_{20}$ ($\text{Q}_8\text{M}_8^{\text{H}^a}$) and $[\text{CH}_2=\text{CH}(\text{CH}_3)_2\text{Si}]_8\text{Si}_8\text{O}_{20}$ ($\text{Q}_8\text{M}_8^{\text{V}}$) has been described in the literature /3/. The thermal analysis was carried out with the differential scanning calorimeter SETARAM DSC 92 in aluminium crucibles in flowing air with a heating rate of 1.5 K/min.

The starting organic silicic acid derivative

$[(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{OC}(\text{O})\text{CH}(\text{CH}_3)\text{CH}_2\text{Si}(\text{CH}_3)_2]_8\text{Si}_8\text{O}_{20}$ ($\text{Q}_8\text{M}_8^{\text{MPTS}}$) for polymer 2 was synthesized by additive reaction of $\text{Q}_8\text{M}_8^{\text{H}}$ and 3-methacryloxypropyltrimethoxysilane (MPTS) in molar ratio of 1:8.

$\text{Q}_8\text{M}_8^{\text{MPTS}}$:

1.5 g (1.47 mmol) $\text{Q}_8\text{M}_8^{\text{H}}$ was dissolved in 15 ml toluene. Then 2.98 g (11.9 mmol) MPTS and 1×10^{-5} mol Pt / mol double bond was added. The mixture was stirred for 5 h at 95° C. The solvent was removed under reduced pressure at 65° C to give 3.71 g (yield 84 %) of a colourless oil.

Polymer 2:

A mixture of 2.28 g $\text{Q}_8\text{M}_8^{\text{MPTS}}$ in 3.37 ml acetone, 0.46 ml water and 5×10^{-4} mol HCl was stirred at room temperature. After 10 min the turbid mixture cleared and after a further 60 min the solution became a gel. One part of the gel was dried for 2 h at 180° C at a pressure of 20 mbar.

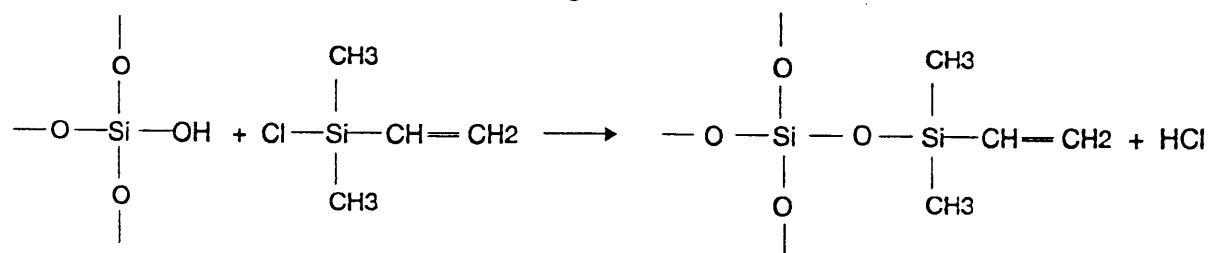
The solid state ^{29}Si NMR spectra of the polymers 1 and 2 were measured on BRUKER MSL 400 instrument at 79.48 MHz and MSL 200 at 39.74 MHz using the MAS technique and inverse gated heteronuclear continuous wave decoupling with the following parameters: pulse width 3 μs , repetition time 60s, number of scans 600, rotation frequency 3KHz.

3. Results and discussion

To make silicic acid solution efficient for inorganic-organic compounds it is essential to

- i. stabilize the silicic acids against hydrolysis and condensation reaction
- ii. build up a more organophilic behaviour
- iii. connect reactive organic groups with the silicic acid.

A usual way to modify unstable silicic acids to form reactive precursors is the silylation with di- or polyfunctional silanes according to the scheme



The silylation of the double four-ring (D4R) silicic acid with different functional silanes leads, partially in combination with additive reactions, to organic silicic acid derivatives, shown in Fig. 1.

a) The abbreviations Q, T, D and M are for different units of silicon corresponding to the literature /3/.

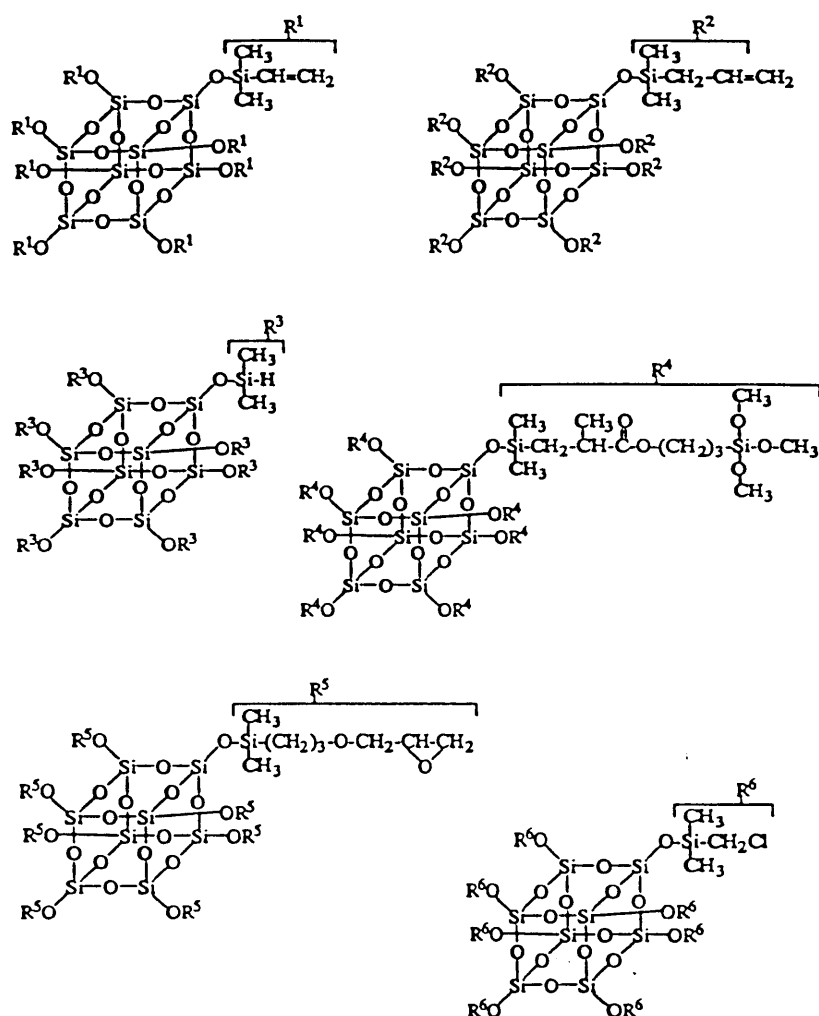


Fig. 1. Functional organic double four-ring silicic acid derivatives

The structure of the derivatives was proved by liquid and solid ^{29}Si NMR spectroscopy and X-ray analysis /5-7/. All molecules are surrounded by 8 functional ligands and represent strong network forming properties.

As precursors, these derivatives open a wide field for reactions with themselves and with other reactive organic compounds /8,9/ via the following reaction types

- i. additive reactions
- ii. polymerization
- iii. condensation reactions.

In the following section the results of synthesis and structural characterization of two inorganic-organic polymers with defined D4R silicic acid units are described.

Polymer 1 has been synthesized on the basis of additive reaction from the vinyl-silylated D4R silicic acid $[\text{CH}_2=\text{CH}(\text{CH}_3)_2\text{Si}]_8\text{Si}_8\text{O}_{20}$ ($\text{Q}_8\text{Mg}^{\text{V}}$) and H-silylated derivative $[(\text{CH}_3)_2\text{HSi}]_8\text{Si}_8\text{O}_{20}$ ($\text{Q}_8\text{Mg}^{\text{H}}$) /3/.

The structural units of the resulting polymer 1, identified by solid state ^{29}Si and ^{13}C NMR spectroscopy, are shown in Fig.2.

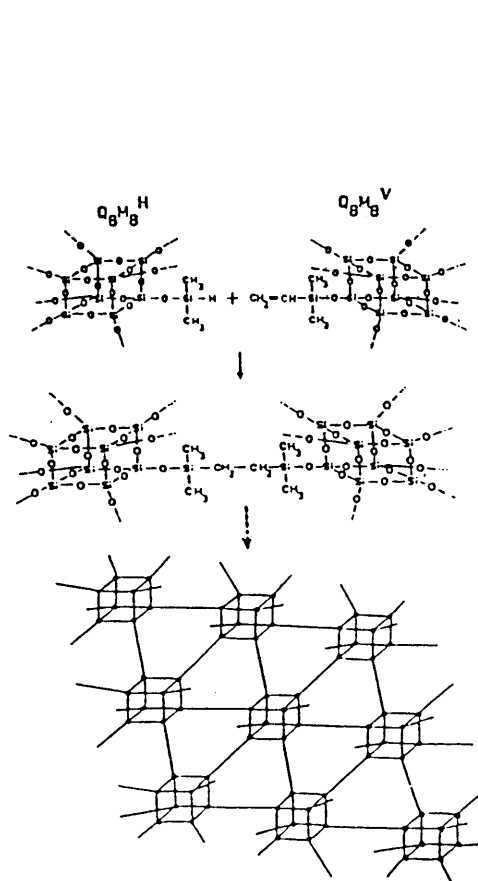


Fig.2. Inorganic-organic polymer 1
from $Q_8M_8^V$ and $Q_8M_8^H$

DSC

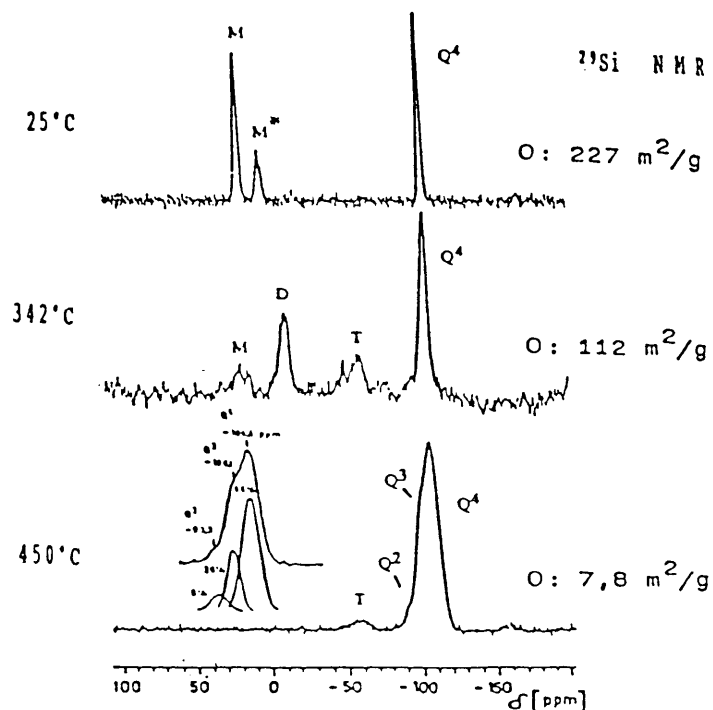
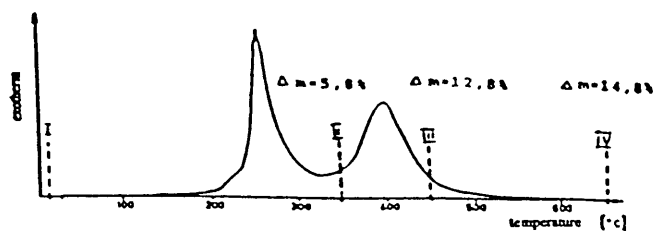


Fig.3. DSC and ^{29}Si NMR spectra
of polymer 1

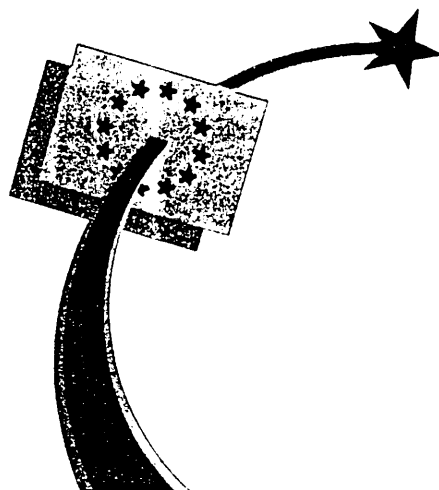
The number of reacted functional groups per D4R cage is about 6.3, this means on average 1.7 functional groups remain unreacted.

Nitrogen-BET measurements on the polymer 1 for characterization of the surface properties shows a surface area of about 230 m²/g and a narrow distribution of the pore diameter with a maxima at 0.8 nm /10/. The active pores for the N₂ molecules are formed by the spaces between the cages, the free diameter of the cages themselves is about 0.2 nm too small for detection by BET methods.

The thermal stability of the D4R cages and the possibility of synthesis of a silica product, consisting of mainly D4R silicic acid units was further examined using thermal analysis techniques. In case of a sufficient thermal stability of the D4R units it should be possible to burn out the carbon atoms while preserving and reorganizing of the D4R silicic acid units to a three-dimensional lattice. The result of the thermal analysis measurements is shown in Fig.3.

In the thermogram two well resolved exothermic peaks with maxima at about 250° and 420°C are visible /11/. For a better insight into the structural changes of the polymer during the heat treatment, ^{29}Si NMR spectra were recorded of samples, heated at 342°C and 450°C (minima after the exothermic peaks).

EUROGEL '92



Practical Applications and Innovative Materials by Sol-Gel
Processing

Proceedings of the Third European Conference on Sol-Gel
Technology
Colmar, France, December 1-4, 1992

Supported by the European Community COMETT

Edited by S. VILMINOT Groupe des Matériaux Inorganiques IPCMS,
23 Rue du Loess 67037 Strasbourg France

The weight losses of the heated samples were determined to be 5.8% (342°C) and 12.8% (450°C). The theoretical weight loss of 14.3% was observed at 662°C.

The ^{29}Si NMR spectra in Fig.3 show clear differences depending upon the heat treatment of the polymer. Three signals appear in the spectrum of the polymer 1 without thermal treatment, characterizing the silicon atoms in the D4R cages (Q^4), in the bridges between the cages (M) and in the unreacted vinyl and H-silyl groups (M^*) of polymer 1. After the heat treatment at 342°C the intensity of the M signals decreased in favour of two new signals in the D and T region of the spectrum. The position of the Q^4 signal is unchanged and shows once more the symmetrical shape with a small line width, characteristic for the D4R units. From this signal it follows that the cagelike D4R structure in the polymer remains stable after a 342°C treatment.

More complicated is the interpretation of the third spectrum. After the sample treatment at 450°C the signals in the M and D region disappear, and only a small signal of T silicon units, possibly overlapped by a rotation side band, remains beside the intense Q signal. The increased intensity of the Q signal and its asymmetry suggests the existence of further Q-Si atoms in the so called Q^2 and Q^3 region of the NMR spectrum. A line simulation of the asymmetrical Q signal gives a more quantitative picture of the different Q-silicon units. From the line simulation follows a molar $Q^4:Q^3:Q^2$ ratio of 66:26:8. Fig.4 presents the results of the NMR experiments.

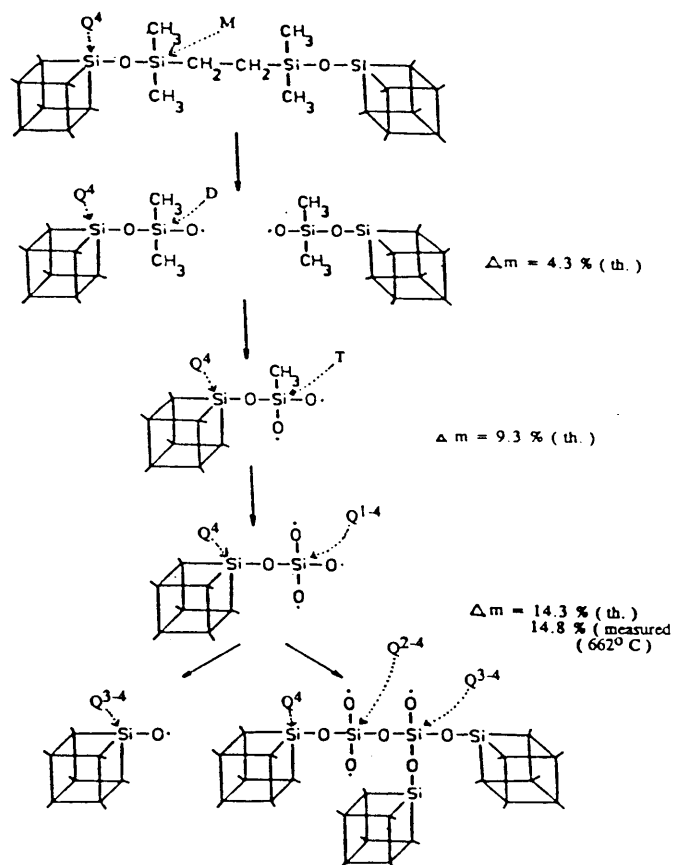


Fig.4. Scheme of the thermal decomposition of polymer 1

After the heat treatment at 342°C new structural units in the D and T region of the NMR spectrum were detected, showing a burning out of carbon in the bridges and oxidation of silicon (D signals). The thermal oxidation of the methyl groups leads primarily to T-silicon atoms and the full oxidation of carbon atoms finally lead to new Q-units with different degrees of polymerisation. 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 450°C sample does not give reliable information about the preservation of the D4R units at this temperature.

Recently published wide angle X-ray scattering of the thermal treated polymers /12/ hints to a partial decomposition of the D4R structure at 450°C. The scattering curve of the polymer after a 900°C treatment shows similarities with the curve of a disperse amorphous silica. Simultaneous measurements of the specific surfaces (O) of the polymers after the heat treatment showed a significant decrease with increasing temperature, as observed in Fig.3. The decrease of the surface area is caused by decomposition of the carbon-carbon bridges as distance holder between the silicic acid cages.

From the results it follows that the D4R units are stable up to 342°C, but at temperatures higher than 450°C a reorganization of the silicon tetrahedra takes place resulting in the usual silica network structure.

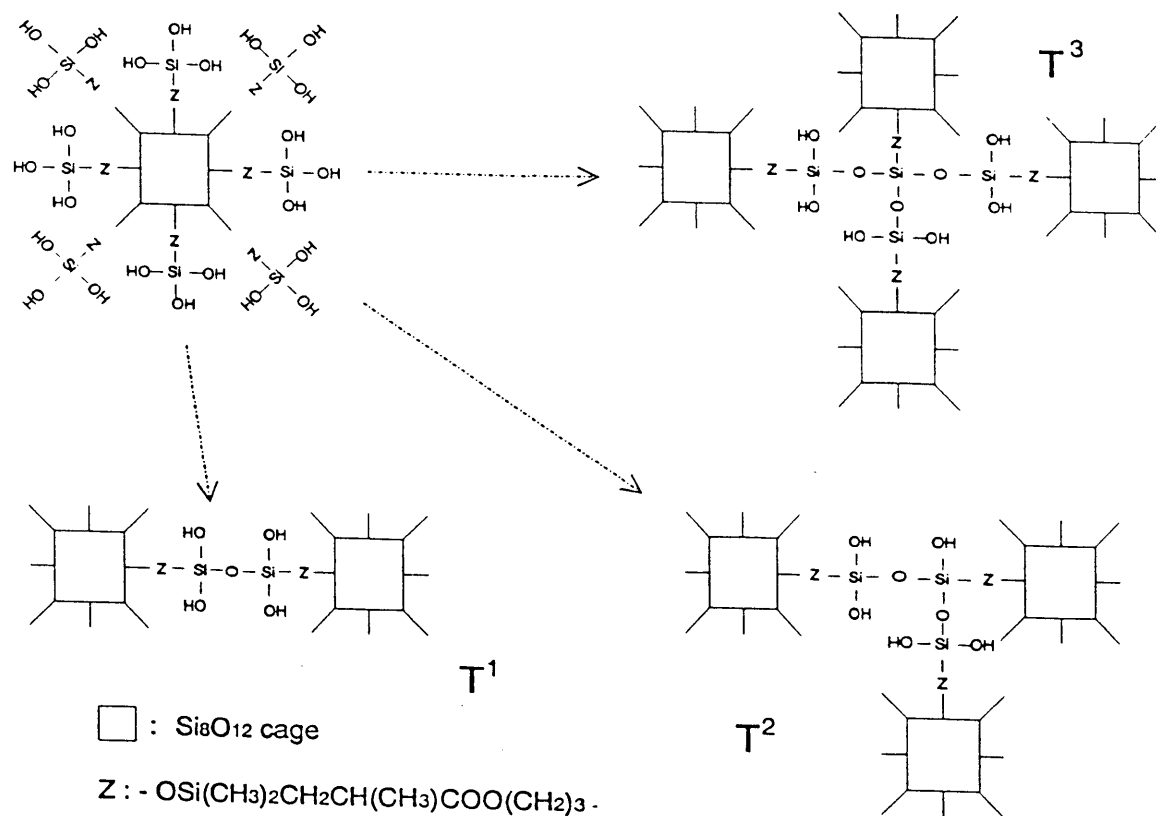


Fig.5. Scheme of condensation reactions of hydrolyzed $\text{Q}_8\text{M}_8\text{MPTS}$

The inorganic-organic polymer 1 discussed above was synthesized by means of additive reaction. The following polymer 2 with defined silicic acid units was prepared via condensation reaction. The starting silicic acid derivative $Q_8M_8^{MPTS}$, the constitution of which is shown in Fig.1(4), is surrounded by 24 alkoxy groups. The aim of this investigation was to follow the hydrolysis and condensation reaction of this polyfunctional silicic acid derivative and to determine the condensation degree and the extent of sterical hindrance in the formed polymer.

The hydrolysis and condensation of the alkoxy silicic acid derivative was carried out in an acidic water-acetone solution. The expected structural units in the condensation process are shown in Fig.5.

The reactions were followed by liquid and solid state ^{29}Si NMR spectroscopy. Fig.6.

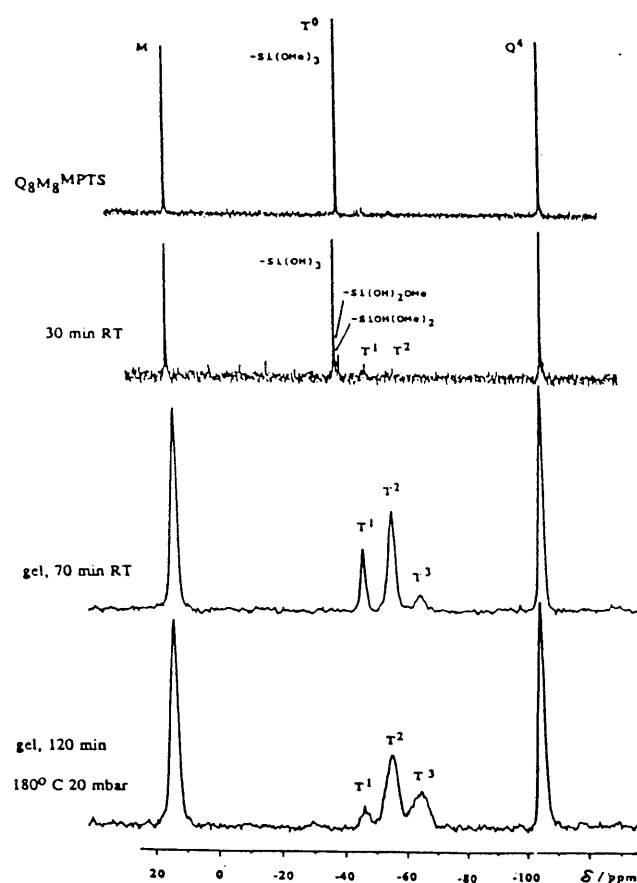


Fig.6. ^{29}Si NMR spectra of the silicic acid derivative $Q_8M_8^{MPTS}$ and of the hydrolysis/condensation products

In the ^{29}Si NMR spectrum of the starting alkoxy derivative $Q_8M_8^{MPTS}$ (Fig.6.) appears three signals corresponding to Q^4 -Si atoms of the silicic acid cage ($\delta = -109.9$ ppm), T^0 -Si atoms in the methoxy silyl groups ($\delta = -43.1$ ppm) and M-Si atoms ($\delta = 11.5$ ppm). Significant changes in the T region of the spectrum are detectable after a hydrolysis time of

about 30 minutes. The signal intensity of trialkoxysilyl groups decreased considerably and a new intense signal at $\delta = -41.4$ ppm appears, caused by fully hydrolyzed $\text{Si}(\text{OH})_3$ groups. Beside small signals of partially hydrolyzed $\text{Si}(\text{OH}, \text{OCH}_3)_3$ groups ($\delta = -41.8$; -42.4 ppm) other signals were detected with low intensity derived from the T^1 and T^2 units of condensed species.

The solid state ^{29}Si NMR spectrum of the gel, formed after a reaction time of 70 min (Fig.6.) shows the two previously known signals of M and Q silicon units, which do not take part in the condensation reaction. Three signals of different intensity appear in the region of T silicon units at $\delta = -48.8$ ppm (T^1), $\delta = -58.3$ ppm (T^2) and $\delta = -67.3$ ppm (T^3), caused by condensation reactions. Uncondensed, monomeric species of the starting silicic acid derivative are not detectable in the spectrum. After drying the gel at 180°C at reduced pressure the NMR spectrum shows in comparison to the original gel a significant shift in the signal intensity from T^1 to T^2 and T^3 units, indicating an increased degree of condensation in the polymer. A quantitative evaluation of the NMR spectra leads to 37% unreacted silanol groups in the gel without heat treatment and 25% in the 180°C heated polymer.

From the data it follows, that in the original gel without heat treatment, 9 of the 24 OH groups of the starting derivative are on average uncondensed. The relatively high content of unreacted silanol groups in the original polymer hints to a remarkable sterical hindrance during the condensation reaction due to the high functionality of the starting silicic acid derivative and the rigid double four-ring cages. Only a 180°C treatment of the polymer decreased the average number of silanol groups per D4R unit to 6.

Using the described processes it is therefore possible to synthesize inorganic-organic polymers with high contents of SiOH groups which could find interest for chromatographic separation processes.

4. Conclusions

The liquid and solid state ^{29}Si NMR spectroscopy is a powerful tool to obtain a better insight in the reactions of organic silicic acid derivatives to polymers and for interpretation of the relation between structure and properties of the inorganic-organic polymers.

Polyfunctional double four-ring silicic acids derivatives react as strong network forming compounds via additive and condensation reactions to inorganic-organic polymers. The microporous polymer 1, free of silanol groups, preserves its double four-ring structure up to 350°C . At higher temperatures a reorganization of the SiO_4 tetrahedra in the double four-ring units takes place leading at 900°C to a structure similar to amorphous silica. Polymer 2 is characterized by a high content of uncondensed silanol groups, due to a sterical hindrance of the condensation reaction.

By variation of size and type of structural units (cages, bridges) in the inorganic-organic polymers a control over the properties of these novel materials should be possible.

The investigation on the organic double four-ring silicic acid derivatives contribute to a better insight in the reaction leading to inorganic-organic polymers and can serve as a model for appropriate reactions of polymeric silicic acid derivatives, which could be more relevant for technical uses.

Acknowledgement

The authors thank Dr.P.Kölsch and Dr.D.Schultze (Berlin) for thermoanalytical measurements and helpful discussions, and Dr. B. Himmel (Universität Rostock) for X-ray

scattering measurements. Dr. H. Jancke (Berlin) and T. Reinert (INM Saarbrücken) are gratefully acknowledged for NMR spectra. The authors thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for the financial support of the work.

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