

not possible to say anything about the preponderance of SiOH vs. TiOH groups present within the sample as the signal due to the titanium content would be very weak in comparison to that for the silicon species. For samples containing higher relative amounts of another metal species it has proved possible to identify the changeover between surface species of one oxide such as silica and surface species of another oxide such as tin (IV) oxide (15, 16) which was not possible in this system.

Conclusions

The addition of titanium atoms to gel glasses at the mixing stage leads to materials in which the majority of the metal ions are found at the surfaces of the fundamental particles making up the bulk phase. These 'foreign' ions affect the densification of the material and the surface chemistry of the resultant phases. It is only at higher temperatures that, for these systems, incorporation of the titanium ions into the matrix occurs fully. The addition of titanium leads to materials that are significantly more hydrophilic than for similar silica gel-glasses and leads to tighter binding of water molecules to silanol groups.

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Inorganic organic polymers with defined silicic acid units

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Abstract

The aim of this work is the synthesis and structural characterization of novel types of inorganic organic polymers consisting of small silicic acid clusters linked via organosiloxane and carbon-carbon bonds. The synthesis is based on additive reactions of silicic acid derivatives with functional siloxanes. Oligomeric silicic acids with defined structure, the double four-ring silicic acids were used to make the polymerization process and the correlation between structure and properties of the polymers more transparent.

1. Introduction

Recently [1,2] the syntheses of functionalized reactive double four-ring (D4R-) silicic acid derivatives, $[(\text{CH}_3)_2\text{HSi}]_8\text{Si}_8\text{O}_{20}$ ($\text{Q}_8\text{M}_8^{\text{H}}$) and $[\text{CH}_2=\text{CH}(\text{CH}_3)_2\text{Si}]_8\text{Si}_8\text{O}_{20}$ ($\text{Q}_8\text{M}_8^{\text{V}}$) were described. The constitution of both derivatives is shown in Figure 1.

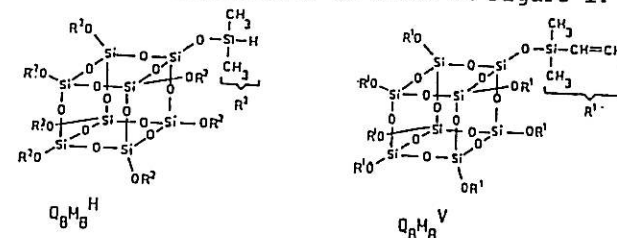


Figure 1. Constitution of the double four-ring silicic acid derivatives $\text{Q}_8\text{M}_8^{\text{H}}$ and $\text{Q}_8\text{M}_8^{\text{V}}$

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The derivatives $Q_8M_8^H$ and $Q_8M_8^V$ were used as starting compounds for additive reactions with three different functionalized methylsiloxanes

- divinyltetramethyldisiloxane (M^{VM^V})
- tetramethylcyclotetrasiloxane (D_4^H)
- polymethylhydrogensiloxane (MD_{25}^{HM})

A fourth polymerization reaction has been carried out by additive reaction of both silicic acid derivatives $Q_8M_8^H$ and $Q_8M_8^V$.

2. Experimental

The syntheses of the four polymers by additive reaction of

1. $Q_8M_8^H + M^{VM^V}$
2. $Q_8M_8^V + D_4^H$
3. $Q_8M_8^V + MD_{25}^{HM}$
4. $Q_8M_8^V + Q_8M_8^H$

follow the same route. Both starting compounds were solved in toluene in a 1:1 ratio of their functional groups. After addition of H_2PtCl_6 as a catalyst, the clear solution is heated to $100^\circ C$ and is held at this temperature for 4 hours. Generally the solutions form a gel after 0.5 h reaction time. After washing with toluene the gels are dried at $50^\circ C$ under vacuum and give white solids, insoluble in organic solvents and water. Further details of synthesis are given in the literature [3,4].

3. Results and Discussion

According to the additive reaction scheme:



the following network structure is expected for the product of the $Q_8M_8^H / M^{VM^V}$ reaction (polymer 1 in Figure 2).

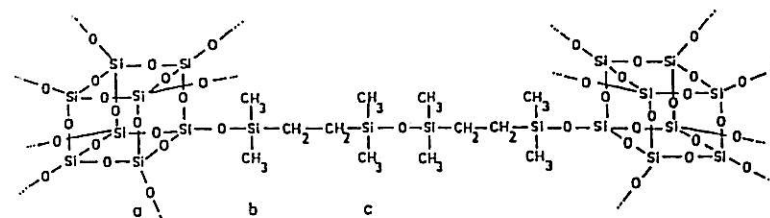


Figure 2. Structural scheme of polymer 1 derived from $Q_8M_8^H$ and M^{VM^V}

The structure of the polymer has been proved by means of ^{29}Si solid state NMR spectroscopy. Figure 3 shows the MAS NMR spectrum of polymer 1, for comparison the spectrum of the starting double four-ring derivative $Q_8M_8^H$ is also given.

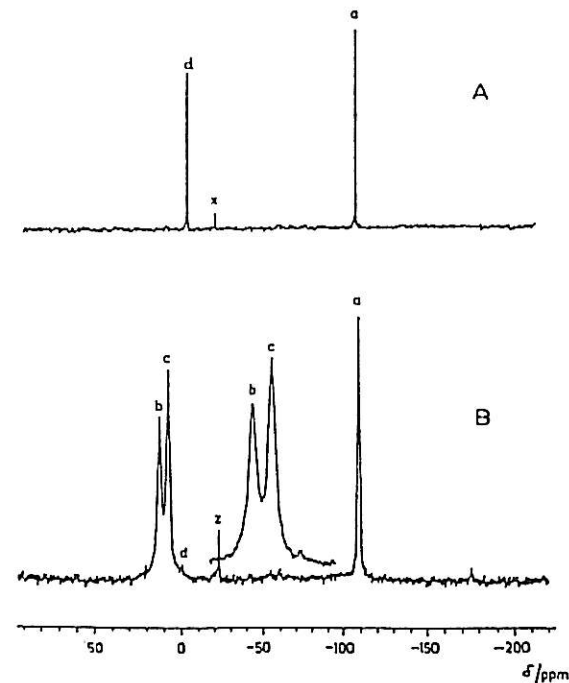


Figure 3. ^{29}Si NMR spectra: $Q_8M_8^H$ (A), polymer 1 (B)

The signal a in the polymer spectrum with a chemical shift $\delta = -108.8$ ppm appears in the shift region typical of Si atoms in Q units of silicic acids. From the identical position of the single signal a in the polymer and in the $Q_8M_8^H$ spectrum follows the existence of double four-ring building units also in the polymer structure. According to reference [3] the signal b ($\delta = +12.7$ ppm) has to be assigned to the Si atoms b and the signal c ($\delta = +7.6$ ppm) to Si atoms c in the structural scheme. A signal d with low intensity at $\delta = -0.18$ ppm originates from unreacted $-OSi(CH_3)_2H$ groups of the starting compound $Q_8M_8^H$. The intensities of signals b and d in the polymer yield $7.8 \approx SiH$ groups per $Q_8M_8^H$ molecule, indicating a practically complete reaction. ^{29}Si MAS NMR investigations of polymers 2-4 confirmed the existence of double four-ring silicic acid units in all of these polymer products. The structural scheme of the polymers 2-4 are shown in Figures 4 and 5.

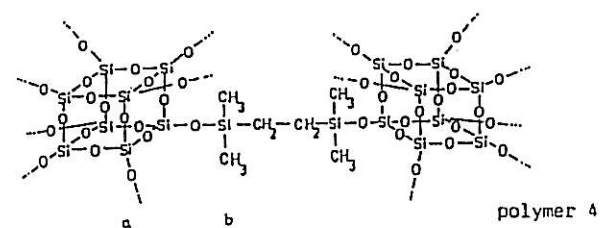
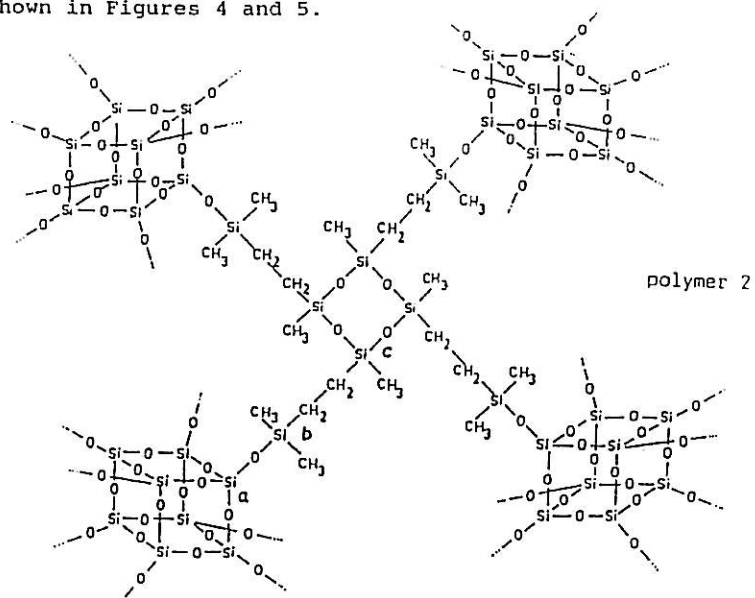


Figure 4. Structural scheme of polymers 2 and 4

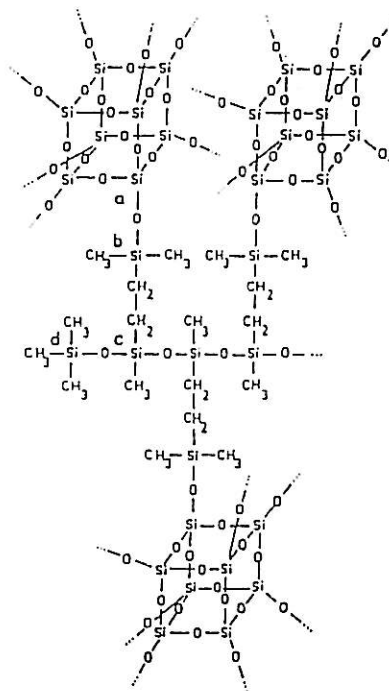


Figure 5. Structural scheme of polymer 3

The quantitative results obtained from the polymer spectra are summarized in Table 1.

Table 1. Degree of polymerization of the silicic acid double four-ring units

Sample	Starting compounds		Nos. of functional groups (II)	Nos. of reacted groups per unit (I)
	I	II		
Polymer 1	$Q_8M_8^H + M^V M^V$		2	7.8
Polymer 2	$Q_8M_8^V + D_4^H$		4	7.4
Polymer 3	$Q_8M_8^V + MD_{23}^H M$		25	5.5
Polymer 4	$Q_8M_8^H + Q_8M_8^V$		8	6.3

The data reveal different extents of polymerization in the reaction products in dependence on the functionality of the starting compounds and the type of bridges between the D4R units. The highest degree of polymerization is observed for polymer 1 containing long (9-membered) chains between the D4R units. Shorter bridges (polymer 4) give a lower degree of polymerisation corresponding to 6.3 reacted functional groups per D4R due to higher sterical hindrance [4] in the polymer. The lowest polymerization of 5.5 groups per D4R, i.e. the highest sterical hindrance is observed in polymer 3, synthesized from highly functionalized organosilicon compound.

The aim of future investigations is the correlation of the polymer structure with physical-chemical properties (adsorption, specific surfaces, porosity e.g.). First results by means of BET adsorption show remarkable differences in the specific surface of the polymers. The highest surface (250 m²/g was found for polymer 4,

containing the shortest chain-like bridges between the D4R units. The polymers 1-3 show smaller specific surfaces between 4 and 8 m²/g.

4. Conclusions

The defined double four-ring silicic acid derivatives with different functional groups serve as model for a detailed investigation of the reactions of silicic acid derivatives with organic compounds to inorganic organic polymers. Due to their eight-fold functionality the double four-ring derivatives are suitable precursors for the synthesis of highly cross-linked polymers via additive reactions.

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