Inorganic–organic polymers derived from functional silicic acid derivatives by additive reaction

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Abstract

Inorganic–organic polymers were synthesized by additive reaction of vinyl-, allyl-, and H-silylated double four-ring (D4R) silicic acids and polymeric silicic acids. The structure and properties of the hybrid polymers were investigated by means of ^{29}Si NMR spectroscopy, thermoanalysis and BET nitrogen adsorption measurements. Using the defined vinylsilylated D4R silicic acid $[(CH_2=CH)(CH_3)_2Si]_8Si_8O_{20}$ and the corresponding H-silylated compound $[(CH_3)_2HSi]_8Si_8O_{20}$ as precursors, the additive reaction results in a microporous polymer with a ordered Si_8O_{20} substructure. The structural units are connected by six-membered bridges. Shorter (four-membered) or longer (seven-membered) bridges between D4R cages lead to non-porous polymeric materials. The connection of water-glass-derived silicic acid units by six-membered bridges similarly leads to porous polymers with specific surface areas of 500 m^2/g. For the preparation of the porous hybrid polymers a new, simple two-step reaction route is described.

1. Introduction

Silicic acids play an important role in the large-scale production of inorganic materials such as glasses, ceramics, cements or zeolites. The reasons for their importance are the unique properties of silicate-derived materials regarding their hydrolytic, chemical, mechanical, or thermal stability. Attempts were already made a few decades ago to combine the advantageous properties of silicates with organic materials. Well-known examples are the use of silica fillers or fibers in organic polymers as reinforcing components [1]. In general, the connection between the inorganic reinforcement and the organic matrix is poor only because of insufficient chemical bonding. A stronger chemical interaction between silicate materials and organic compounds has been observed in organic silica sols [2] and organically modified silicates [3,4]. An intensive interaction of silicic acid esters with functional organic compounds takes place in sol–gel processes, a valuable method for preparation of silicic acid units containing inorganic–organic hybrid materials [5].

Nevertheless, one of the major difficulties is the ability to follow structural changes during the reactions of silicic acids with organic compounds due to the great variety of structural units and reactions of the silicic acid component, although the knowledge of the structure and bond of silicic acid units to organic components is the basis for a controlled

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Table 1
^{29}Si NMR chemical shift (ppm) and relative signal intensity (%) of the starting compounds

	Symbol	s.a.	s.a.^{H}	s.a.^{V}	$Q_8H_4^HM_4^V$	$Q_8M_8^A$	s.a.^{H,V}
$\underline{Si}(OSi)_4$	Q^4	−111.6 (20) −107.5	−109.6 (43) −112.5	−109.6 (38) −112.5	−108.8 (45) −108.4	−109.1 (58)	−110.6 (45)
$(^-O)\underline{Si}(OSi)_3$	Q^3	−102.1 (52)	−100.1 (4)	−104.2 (22) −101.2			−101.4 (13)
$(^-O)_2\underline{Si}(OSi)_2$	Q^2	−92.5 (23)					
$(^-O)_3\underline{Si}(OSi)$	Q^1	−82.8 (5)					
$H(CH_3)_2SiO_{0.5}$	M^H		−3.5 (53)		−0.8 (28) −0.7		−3.7 (28)
$CH_2=CH(CH_3)_2SiO_{0.5}$	M^V			−1.0 (40) (−3.2)	1.4 (27) 1.5		−0.8 (14)
$CH_2=CHCH_2(CH_3)_2SiO_{0.5}$	M^A					9.6 (42)	

synthesis of hybrid materials with tailor-made properties.

The objective of this work is to obtain more insight into fundamental reactions of silicic acid derivatives with organic compounds leading to inorganic–organic hybrid polymers. Well-defined silicic acid derivatives with a monomolecular double four-ring (D4R) structure Si_8O_{20} were used as model compounds to help clarify the reactions and bonds of the silicic acid with the organic component and the relation between the polymer structure and its properties. In the second part, experiments are described showing how the results from the model silicic acid derivatives can be transfered to common inhomogeneous silicic acids prepared from water glass solution.

2. Experimental

The followig abbreviations will be used throughout the remainder of the text: Q: $(SiO_{0.5})_4$; M^H: $(CH_3)_2HSiO_{0.5}$; M^V: $(CH_2=CH)(CH_3)_2SiO_{0.5}$; M^A: $(CH_2=CHCH_2)(CH_3)_2SiO_{0.5}$; T^H: $HSi(O_{0.5})_3$; s.a.: polymeric silicic acid; s.a.^{V}: vinylsilylated s.a.; s.a.^{H}: H-silylated s.a.: All synthesized compounds were characterized by ^{29}Si NMR spectroscopy. The chemical shifts of the silicon building units are summarized in Tables 1 and 2.

2.1. Synthesis of D4R silicic acid derivatives

$Q_8M_8^A$: 4 g (13.6 mmol SiO_2) tetramethylammonium silicate $[N(CH_3)_4]_8Si_8O_{20} \times 69$ H_2O was

Table 2
^{29}Si NMR chemical shift (ppm) and relative signal intensity (%) of the polymers

	C1	C2	D	E	F1	F2
$\underline{Si}(OSi)_4$	−108.4 (42)	−108.1 (48)	−108.5 (45)	−108.5 (32)	−109.0 (43)	−108.1 (43)
$(^-O)\underline{Si}(OSi)_3$					−99.7 (14)	−100.8 (13)
$H(SiO_{0.5})_3$				−84.4 (16)		
$-CH_2(SiO_{0.5})_3$				−66.2 (20)		
$HSi(CH_3)_2O_{0.5}$	−1.8 (9)	−2.4 (3)	−2.1 (8)		−3.3 (4)	−2.5 (10)
$H_2C=CH(CH_3)_2SiO_{0.5}$	0.2 (9)	−0.3 (9)		0.1 (11)	0.1 (13)	0.0 (3)
$-CH_2CH_2(CH_3)_2SiO_{0.5}$	13.4 (40)	13.8 (40)	12.3 (47 incl. M^A)	13.2 (21)	12.8 (26)	12.8 (31)

added at 20–25°C to a stirred silylation mixture of 52 ml heptane, 104 ml DMF and 50 ml (341 mmol) allyldimethylchlorosilane. After 20 min the mixture was cooled to 2°C, hydrolyzed with 60 ml ice water and stirred for 2 min. The organic phase was separated and washed with water until pH = 6. The solvent was removed by distillation at 65°C and 10^{-3} mbar. White crystals were obtained and washed with methanol yielding 747 mg (33%). $Q_8 M_8^V$ and $Q_8 M_8^H$: for the synthesis of both derivatives, the literature [6,7] was followed.

$Q_8 M_4^H M_4^V$ (as main component): 2 g (6.8 mmol SiO_2) tetramethylammonium silicate was added to a stirred silylation mixture of 17 ml i-propanol, 4 ml H_2O, 10 ml HCl, 1.04 ml (5.86 mmol) tetramethyldisiloxane ($M^H M^H$) and 12.5 ml (55 mmol) divinyltetramethyldisiloxane ($M^V M^V$) at 20–25°C. After 30 min the mixture was cooled to 2°C and hydrolyzed with 200 ml ice water. After 2 min the organic phase was separated and washed with water until pH = 6. The solvent was removed by distillation at 60°C and 10 mbar. The solid was washed with heptane yielding 820 mg (86%).

2.2. Synthesis of polymeric silicic acid and its derivatives

Polymeric silicic acid solution (s.a.): a solution of 27 ml sodium water glass (molar ratio SiO_2 : Na_2O = 3.28; SiO_2 : 2M) was added to a mixture of 50 ml ion-exchange resin (Amberlite IR 120, Merck) in 10 ml 0.1 molar HCl cooled to 0°C and stirred for 10 min. After filtration, a 1.2M (SiO_2) silicic acid solution (s.a.) was obtained (pH 2.1) and immediately used for the silylation reaction.

H-dimethylsilylated polymeric silicic acid (s.a.^{H}): 20 ml (24 mmol SiO_2) polymeric silicic acid solution was added dropwise at 20°C to an agitated silylation mixture of 125 ml i-propanol, 50 ml H_2O, 63 ml 32% HCl and 100 ml (564 mmol) tetramethyldisiloxane ($M^H M^H$). After 30 min, the mixture was cooled to 2°C and hydrolyzed with 600 ml ice water. The subsequent procedure was the same as described for $Q_8 M_4^H M_4^V$. The yield amounts to 2.2 g (66%).

Vinyldimethylsilylated polymeric silicic acid (s.a.^{V}): 20 ml (24 mmol SiO_2) s.a. was added at 20°C to a stirred silylation mixture of 125 ml i-propanol, 50 ml H_2O, 63 ml 32% HCl and 100 ml (439 mmol) divinyltetramethyldisiloxane ($M^V M^V$). The following steps are the same as described before and produced a yield of 2.3 g (66%).

H-, vinylsilylated polymeric silicic acid (s.a.^{H,V}): the mixed silylated s.a. was synthesized by adding 25 ml (30 mmol SiO_2) s.a. to a stirred silylation mixture of 188 ml i-propanol, 75 ml H_2O, 75 ml 32% HCl, 126 ml (550 mmol) $M^V M^V$ and 8 ml (45 mmol) tetramethyldisiloxane ($M^H M^H$) at 20°C. The following steps are the same as described above and produced a yield of 3.0 g (84%).

2.3. Synthesis of polymers by additive reactions

Polymer C1 was synthesized according to the literature [15] by additive reaction of $Q_8 M_8^H$ and $Q_8 M_8^V$.

Polymer C2: 1×10^{-4} mol Pt/mol double bond was added to 700 mg (0.63 mmol) $Q_8 M_4^H M_4^V$ (as main component) dissolved in 7 ml toluene. After 35 min at 95°C, a gel was formed, which was heated further for 5 h at the same temperature. The transparent gel was washed three times with toluene and dried for 2 h at 80°C under reduced pressure yielding 531 mg (76%) of a white solid.

Polymer D: the compounds $Q_8 M_8^A$ (670 mg, 0.5 mmol) and $Q_8 M_8^H$ (508 mg, 0.5 mmol) were dissolved in 12 ml toluene and 10^{-4} mol Pt/mol double bond was added. After 20 min at 90°C, a transparent gel was formed. The gel was heated further for 4 h and then washed with toluene. The solid was dried for 2 h at 80°C and 10 mbar yielding 820 mg (70%).

Polymer E: 400 mg (0.326 mmol) $Q_8 M_8^V$ and 138 mg (0.326 mmol) $H_8 Si_8 O_{12}$ (octahydridosilasesquioxane T_8^H) were dissolved in 10 ml cyclohexane containing 10^{-4} mol Pt/mol double bond. After 30 min at 95°C, a transparent gel was formed. The gel was heated for 5 h, washed with cyclohexane and dried for 2 h at 80°C and 10 mbar yielding 289 mg (53%).

Polymer F1: 200 mg s.a.^{H} (1.47 mmol SiH) and 283 mg s.a.^{V} (1.47 mmol Si-vinyl) were dissolved in 5 ml toluene containing 10^{-4} mol Pt/mol double bond. After heating of the solution for 20 min at 100°C, a transparent gel was formed which was treated in the same way as polymer E yielding 370 mg (76%).

Polymer F2: 1×10^{-4} mol Pt/mol double bond was added to 900 mg (1.87 mmol Si-vinyl) s.a.[H,V] dissolved in 3 ml toluene. After 15 min at 90°C, a transparent gel was formed in the same way as polymer E yielding 610 mg (68%).

2.4. Characterization

N$_2$ BET measurements were carried out with a DEN-AR-MAT 1000 (Ströhlein) at 77 K. The pretreatment of the samples was carried out at 90°C and 10^{-3} mbar for 12 h. The gas chromatograms were obtained using a capillary gas chromatograph (Shimadzu GC 14A) (column RTx 50, 30 m, 0.25 mm ID, 0.25 μm; oven temperature 100–300°C 10°C min; injector (PTV) temperature: 280°C; detector (FID) temperature 300°C; carrier gas: N$_2$). Thermogravimetric and differential thermoanalysis (TG/DTA) data were obtained using a STA 501 (Bähr Thermoanalyse) by heating the sample in air to 900°C at a rate of 5 K/min. The NMR spectra were obtained using liquid state (Bruker AC200) and solid state (MSL200) spectrometers operating at a field of 4.7 T. Acquisition parameters: liquid state: ^{29}Si{^{1}H}: inverse gated, standard (st.) SiMe$_4$ or D$_4$ (19.07 ppm), pulse width (p.w.) 11.7 μs (60°), repetition time (r.t.) 10 s with Cr(acac)$_3$, 300–3000 scans. Solid state: ^{29}Si{^{1}H}: single pulse MAS experiment (rotation frequency: 3 kHz), external st. Q$_8$M$_8$, p.w. 3.3 μs (60°), r.t. 60–100 s, 400–1000 scans.

3. Results

3.1. Hybrid polymers via additive reaction

A first step for building up silicic-acid-containing hybrid polymers is the stabilization of silicic acids towards hydrolysis and condensation by the silylation reaction [8]. Using a silylating agent with functional organic groups, reactive organic silicic acid derivatives can be synthesized for, for example, polymerization or polycondensation reactions. The starting compound for silicic acid derivatives with a defined structure is mainly the tetramethylammonium double four-ring (D4R) silicate [N(CH$_3$)$_4$]$_8$-
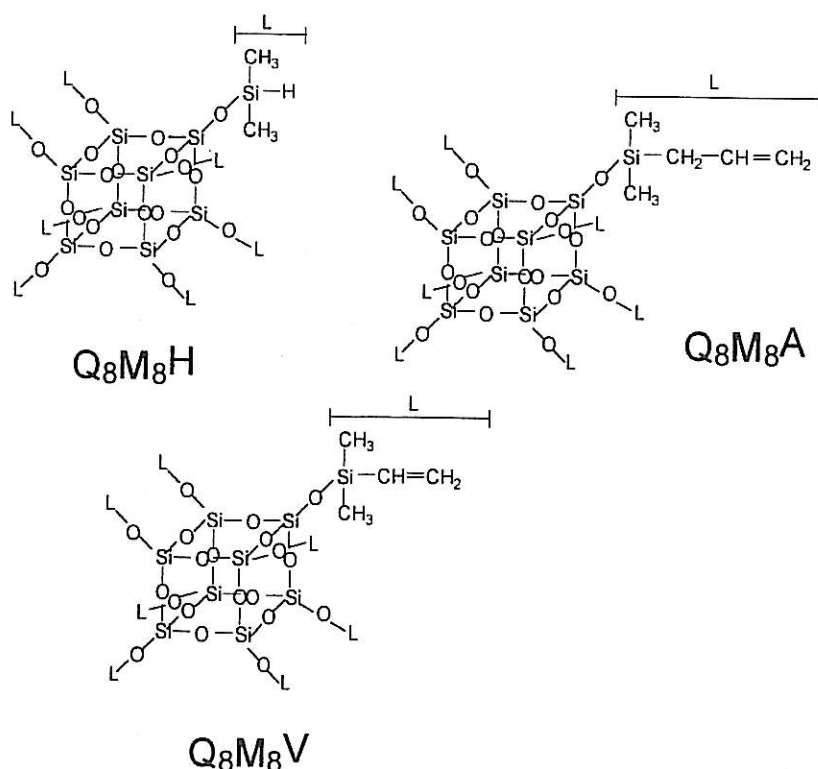

Fig. 1. Schematic representation of the H-, vinyl- and allylsilylated double four-ring silicic acids.

$Si_8O_{20} \times 69\ H_2O$ [9]. By silylation of the silicate or its silicic acid solution with functional chlorosilanes or disiloxanes, functional double four-ring silicic acid derivatives with a defined structure were synthesized [6,7,10,11]. Of interest in this work are three functional silicic acid derivatives which enable the additive reaction (Fig. 1).

By additive reaction of these precursors with themselves or with appropriate functional organic compounds such as dihydridosilanes or unsaturated organic compounds, it is possible to synthesize inorganic–organic hybrid polymers with defined silicic acid units [12,14,15]. Recently, a further D4R silicic acid unit containing hybrid polymer was described,

synthesized by silylation of tetramethylammonium silicate solution with dichlorodimethylsilane [13]. Structural details of the three different hybrid polymers are shown in Fig. 2.

The polymers have different types and lengths of bridge between the silicic acid cages. Heating of polymer A to 300°C results in a porous material [13]. It is assumed that the burning out of incorporated tetramethylammonium groups in the polymer causes the porosity. Polymer B, derived from additive reaction of $Q_8M_8^V$ with a dihydridosilane [12], yields a porous ceramic material after heating to 800°C in a nitrogen atmosphere and treatment with hydrofluoric acid. Polymer C1 was synthesized by additive reac-
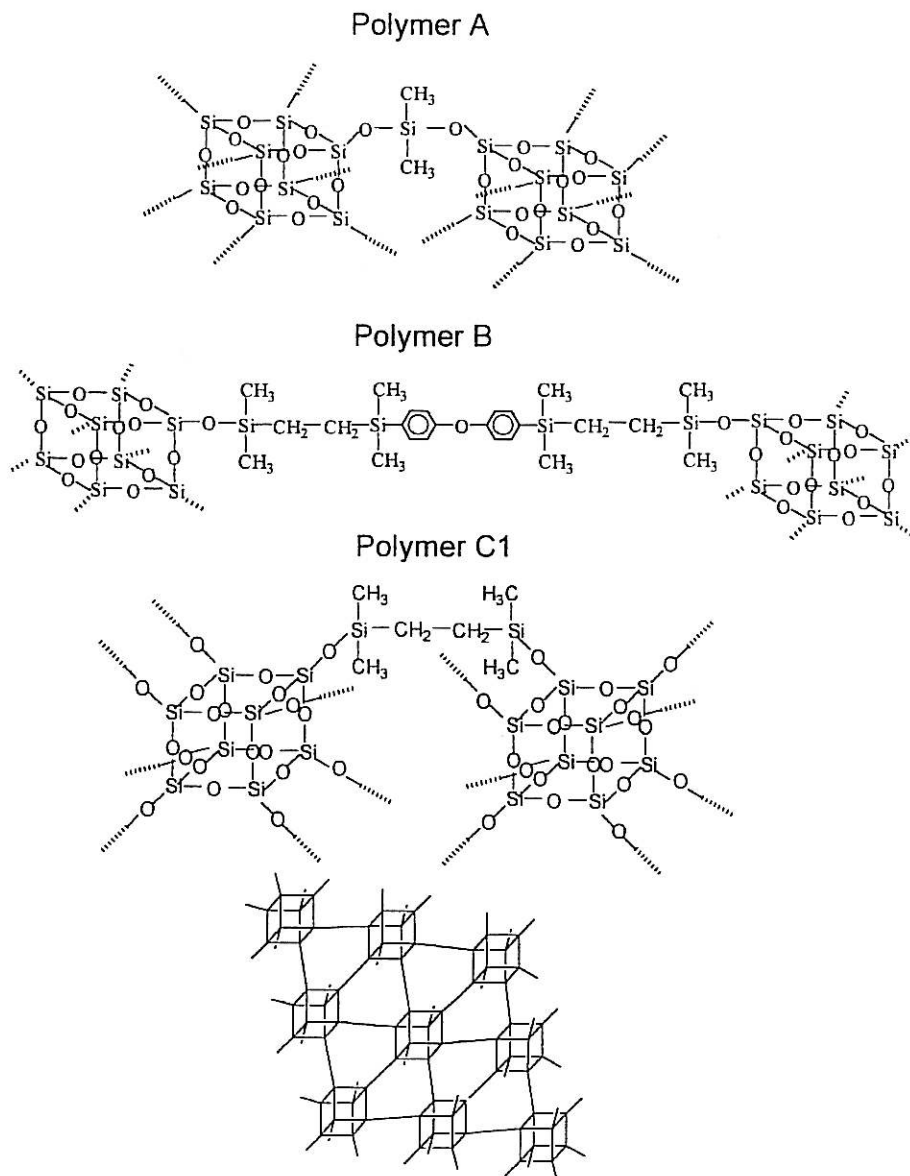

Fig. 2. Types of bridge between D4R silicic acid units in hybrid polymer A [13], B [12] and C1 [15] and scheme of the polymer C1 network.

tion of $Q_8M_8^V$ and $Q_8M_8^H$ and exhibits a microporosity without any heat treatment [16]. The aims of the following experiments on the porous polymer C were:

(1) the optimization of the polymer C synthesis;
(2) the investigation of the influence of the bridge length on the porosity;
(3) the synthesis of hybrid polymers (F) derived from inhomogeneous silicic acids;
(4) the comparison of structure and properties of polymer C and F.

3.2. Optimizing of the polymer C synthesis

For the synthesis of polymer C, two different compounds $Q_8M_8^V$ and $Q_8M_8^H$ are required. The synthesis should be easier by using a D4R silicic acid precursor with both functional groups at one molecule. Such a precursor was synthesized by silylation of D4R silicate with a mixture of H- and vinyl disiloxanes in a defined molar ratio (see Experimental). The ^{29}Si NMR spectrum of the reaction product in Fig. 3 confirms the preservation of the D4R silicic acid cage (Q^4 signal at $\delta = -108.4$ and -108.8 ppm) and the presence of H- and vinylsilyl groups (Table 1). The splitting of the signals is caused by the different types of neighbouring ligands. In accordance with earlier results of mixed silylation experiments [6], it follows from the gas chromatogram that a distribution of both functional ligands exists on the silicic acid cages (Fig. 3).

Under the chosen reaction conditions, four H- and four vinyl groups ($Q_8M_4^HM_4^V$) were found to prevail in the reaction product species (Fig. 3). Although it is likely that isomers of the $Q_8M_4^HM_4^V$ derivative exist, it is not possible to identify directly their
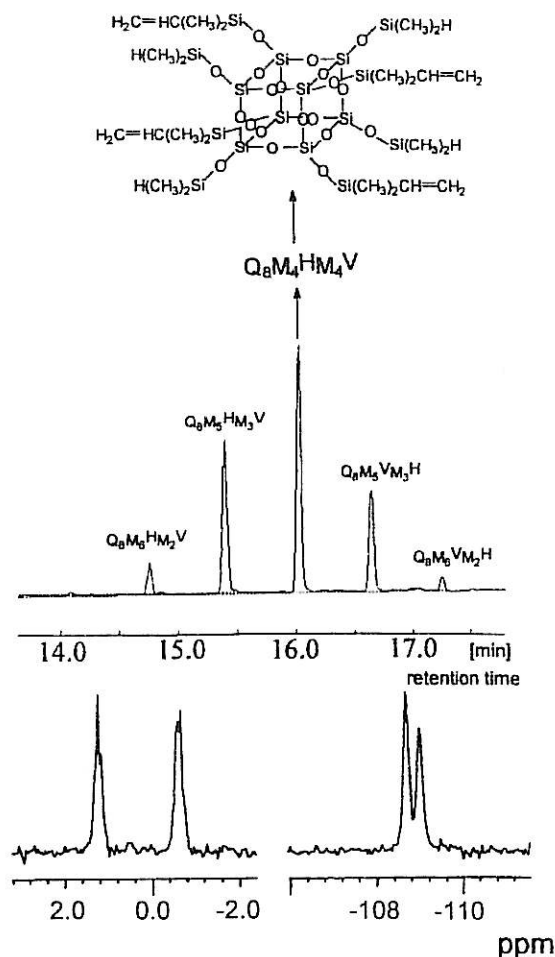

Fig. 3. Gas chromatogram and ^{29}Si NMR spectrum of the mixed H- and vinylsilylated D4R silicic acids and scheme of an D4R isomer.

existence. Since the isolation of the $Q_8M_4^HM_4^V$ is very difficult, the original molecular distribution was used for preparation of a hybrid polymer by a 'one-component' additive reaction. In the solid state ^{29}Si NMR spectrum of the resulting polymer C2, a sharp signal appears at $\delta = -108.1$ ppm, typical for Si

Table 3
Structural characterization and properties of hybrid polymers

Polymer	Components of the additive reactions	Number of bridging atoms	Degree of polymerization	Specific surface area (BET) (m²/g)
E	$Q_8M_8^V + T_8^H$	4	66%	2
C1	$Q_8M_8^V + Q_8M_8^H$	6	78%	300
D	$Q_8M_8^A + Q_8M_8^H$	7	86%	3
C2	$Q_8M_4^VM_4^H$	6	78%	200
F1	s.a.^{V} + s.a.^{H}	6	61%	500
F2	s.a.^{H,V}	6	70%	560

atoms in the D4R cage. The signal at $\delta = 13.8$ ppm is caused by Si atoms in the bridges between cages and the two overlapping signals at $\delta = -2.4$ and -0.3 ppm originate in non-reacted HSi– and $CH_2 = CHSi–$ groups (Table 2). From the signal intensities of the ^{29}Si NMR spectrum it follows that the same polymerization degree of 78% as found in polymer C1 (Table 3) was attained.

A ^{29}Si NMR spectrum was obtained practically identical to that of polymer C1 [15]. By means of the nitrogen BET method a specific area of 200 m^2/g was measured for polymer C2. This value is within the range of specific surface areas of different C1 batches of 190–360 m^2/g [17].

3.3. Hybrid polymers with different bridge lengths

D4R hybrid polymers with different bridge lengths have been described and synthesized via additive reaction of D4R silicic acid derivatives with themselves [15] and of D4R derivatives with difunctional organic molecules of different lengths [12,14]. Difunctional bridging molecules capable of producing non-bridging intramolecular reactions at one and the same molecule as well as intermolecular reactions (bridging of two different cages) complicate the relation between bridge length and properties, e.g., porosity of the polymers. To exclude intramolecular reactions only functional D4R precursors were used as reaction components in the following experiments.

In polymer C1 (Fig. 4) six-membered bridges are present connecting Si atoms of two different cages. By additive reaction of $Q_8M_8^H$ with the allyl silylated D4R derivative $Q_8M_8^A$ polymer D with seven-membered bridges and by reaction of $Q_8M_8^V$ with a cage-like octahydridosilasesquioxane $H_8Si_8O_{12}$ (T_8^H) a short four-membered bridged polymer E was synthesized (Fig. 4).

From the solid state ^{29}Si NMR spectra of polymers D and E (Table 2), a preserved double four-ring structure is observed in both cases. Also, the average degree of polymerization of polymer D was calculated to be 86% (6.9 of eight functional groups per D4R unit are reacted) and for polymer E to be 66% (5.3 groups reacted). Considering the degree of polymerization of polymer C1 (78% = 6.3 groups reacted), it follows that the shorter the bridge between the cages, the lower the degree of polymerization in
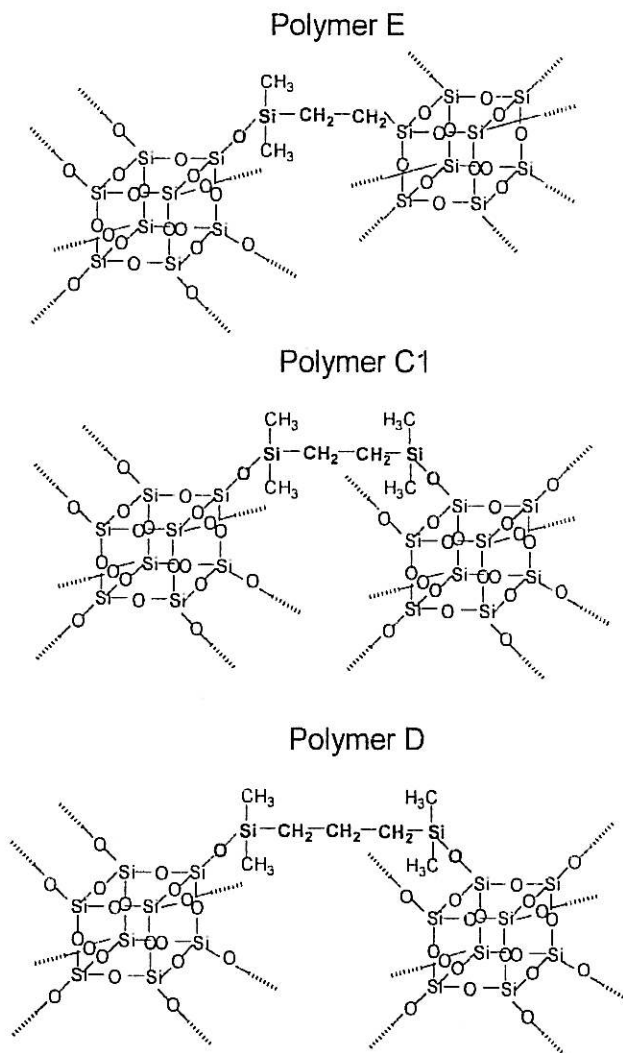

Fig. 4. Variation of the bridge length between D4R silicic acid units.

the polymer due to sterical hindrance of the high functional D4R precursor. Unlike polymer C1, the polymers D and E do not show a significant specific surface area (Table 3).

3.4. Hybrid polymers from polymeric silicic acid solutions

Through the following experiments, the transfer of the results derived from the defined double four-ring silicic acid to instable inhomogeneous silic acid solution was examined. Silicic acid solution prepared by ion exchange of water glass solution have a broad distribution of silicic acids with different molecular masses and structures ranging from monomeric and oligomeric species up to polymeric silicic acids with
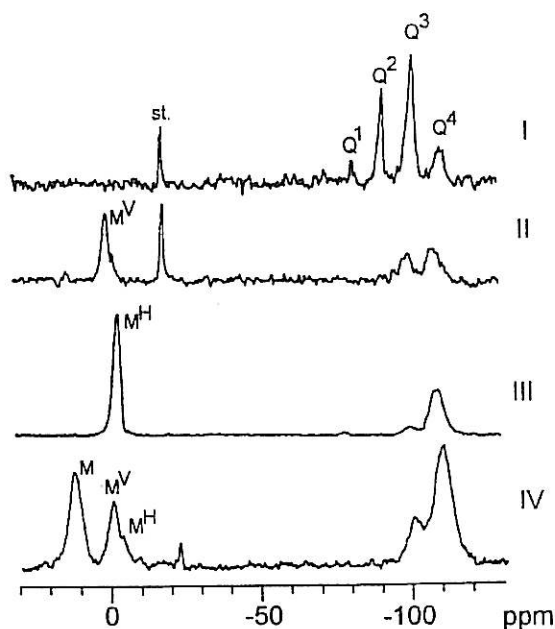
Fig. 5. ^{29}Si NMR spectra of I: polymeric silicic acid (s.a.) solution, II: vinylsilylated s.a., III: H-silylated s.a., IV: hybrid polymer derived from II and III.

branched and cross-linked structures [18]. In the following these solutions are called polymeric silicic acid solutions. The preparation of the H- and vinylsilylated polymeric silicic acids was carried out according to the experimental part.

The ^{29}Si NMR spectra of the starting polymeric silicic acid solution and of both polymeric silicic acid derivatives are shown in Fig. 5. In the spectrum of polymeric silicic acid solution four broad signal groups at $\delta = -82.8, -92.5, -102.1, -111.6$ ppm appear caused by Si atoms in end groups, middle or/and cyclic groups, branched building units and cross-linked units [18] (Table 1). The spectra of the derivatives (Fig. 5, II, III) show two broad signals of Si atoms in branched (Q^3) and crosslinked (Q^4) building units. The Q^3 units prove the presence of unreacted silanol groups due to incomplete silylation reaction. The signals at $\delta = -3.5$ and -1.0 ppm result from the Si atoms in the HSi (M^H) and $CH_2 = CHSi$ (M^V) groups (Table 1).

From the quantitative evaluation of the spectra for the H-silylated silicic acid, a molar ratio HSi:SiO$_2$ of about 0.9:1 and for the vinylsilylated one a $CH_2 = CHSi$:SiO$_2$ ratio of about 0.8:1 is obtained. The comparison of the molar ratio of Si atoms in incomplete silylated Q^3 and Q^4 units in s.a.^{H} and

s.a.^{V} results in a higher Q^3/Q^4 ratio in the case of s.a.^{V} (Fig. 5, III). This ratio is possibly due to a sterical reason whereby the larger dimethylvinylsilyl group reacts with fewer SiOH groups of Q^3 units than the $(CH_3)_2HSi$ group. The additive reaction of s.a.^{H} and s.a.^{V} in a molar ratio HSi:CH$_2$=CHSi nearly 1 results in a polymer F1 insoluble in organic solvents like toluene, acetone and hexane. In the ^{29}Si NMR spectrum of the polymer F1, two overlapping signals of the starting components at $\delta = -3.3$ and 0.1 ppm appear indicating partially unreacted functional groups. The new M signal at $\delta = 12.8$ ppm is caused by the $SiCH_2CH_2Si$ bridges between the silicic acid units. From the signal intensities, a degree of polymerization of 61% is calculated. In analogy to the D4R polymer C2, the additive reaction of a mixed H- and vinyl silylated polymeric silicic acid (s.a.^{H,V}, Table 1) yields a polymer F2 characterized by a degree of polymerization of 70%. Nitrogen BET measurements of polymers F1 and F2 result in a specific surface area between 500 and 560 m^2/g.

3.5. Thermal behaviour of hybrid polymers

The thermal behaviour of hybrid polymers C1, C2 and F1 was examined using simultaneous TG/DTA measurements in an air atmosphere to 900°C. In the thermogram of polymer C1 three exothermic peaks appear (Fig. 6).

The thermal decomposition starts at about 250°C. According to the literature [19], the exothermic peak between 250 and 350°C is caused mainly by the oxidation of unreacted vinylsilyl, H-silyl and bridging CH$_2$–CH$_2$ groups. Both peaks at 484 and 556°C are a result of the oxidation of CH$_3$ groups. It is possible that these two peaks are formed due to a different thermal stability resulting from whether one or two CH$_3$ groups are attached to the Si atoms. The thermogram of polymer C2 synthesized from the mixed silylated precursor shows only two poorly resolved exothermic peaks. The exothermic reaction starts at 150°C and, compared with polymer C1, the first and second exothermic peaks appear at temperatures 40 and 77°C lower, respectively. A third peak is visible as a shoulder only.

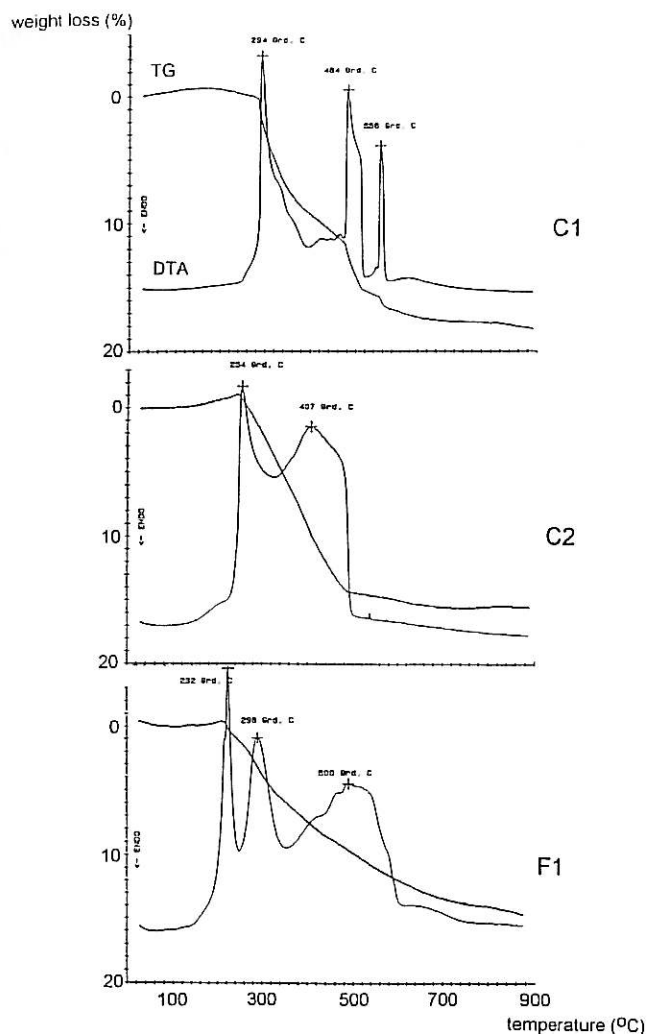Polymer F1 shows a thermogram with three exothermic peaks (Fig. 6). According to the above-

Fig. 6. TG/DTA measurements of the polymers C1, C2 and F1.

mentioned assignment, the exothermic peaks at 232 and 298°C are caused by the oxidation of unreacted functional groups and CH_2–CH_2 bridges. The broad exothermic peak with a maximum at 500°C and shoulders at 430, 480, 530 and 590°C corresponds with the oxidation of Si–CH_3 groups of the polymer. The shoulders hint possibly at separate exothermic reactions of CH_3 groups attached in different positions to the Si atoms. A similar picture of split exothermic peaks was found in the thermogram of a D4R polymer described in the literature [19].

4. Discussion

From the results given in Sections 3.2. and 3.4., it follows that starting from mixed H- and vinyl sily-

lated D4R or polymeric silicic acids an easy two-step reaction route (mixed silylation, additive reaction) for preparation of hydrophobic and porous hybrid polymers from tetramethylammonium silicates or water glass solution has been derived. Both polymers C2 and F2 show a high specific surface area in the range of 200–560 m^2/g. This range is comparable with those of polymers C1 and F1 prepared by the multi-step route (Table 3). Of interest is that hybrid polymers F1 and F2 derived from water glass solution show a surface area higher than polymers with a D4R silicic acid substructure. However the differences in the silicic acid structure of the reaction product do not play a decisive role concerning the porosity. The results show that the bridge length and bridge structure between the silicic acid units are of more interest. Examination of the influence of the bridge length between the D4R cages on the surface area of the polymers indicates that the short four-membered bridge and the longer seven-membered bridge (Fig. 4) do not yield hybrid polymers with a high specific surface area. For polymer E, with the shortest bridges between the cages, the result can be explained by the smaller free space between the silicic acid units which is not accessible to the N_2 molecules as compared with polymer C1. Presently, the low specific surface area of the polymer D, which contains the longest (intermolecular) bridges, is difficult to explain. It is possible that the bridges in his polymer are folded or twisted, leading to an effective shortening of their length which would inhibit access into the pores by N_2 molecules. A further reason could be the degree of polymerization in polymer D, which is the highest of the three polymers examined.

From the results it can be stated that only the polymers C1, C2, F1 and F2 with chain-like six-membered bridges between the silicic acids units have significant porosity. Longer or shorter chain-like bridges or different types of bridges [14] between the silicic acid cages lead to non-porous polymers. Summarizing these results, it follows that chain-like six-membered bridges between silicic acid units seem to be a preferred length for a porous hybrid polymer. The structure of silicic acid units and the method of polymer preparation seems to have a smaller influence on the porosity.

The thermoanalyses of the polymers show a dif-

erent onset of the thermal degradation of the polymers C1, C2 and F1. The highest thermal stability is bserved for polymer C1 (up to 250°C), followed by 2 and F1 (150°C). The maxima of the first exothermic peaks of the polymers at 295, 254 and 232°C aused by the oxidation of unreacted functional ligands and bridging CH_2–CH_2 groups show a similar rder. It is likely that the different thermal behaviour f the polymers is associated with the more inhomogeneous structure of polymers C2 and F1 compared vith polymer C1. The inhomogeneity of polymer 2, caused by the distribution of two different functional groups in the starting precursor, the direct eighbouring vinyl and H groups at one molecule, nd possibly the existence of non-bridging by intramolecular additive reactions, lead to more reactive ompounds with decreased thermal stability. Obviusly, the inhomogeneity of polymer F1 caused nainly by different silicic acid units likewise results n a decreased thermal stability.

;. Conclusions

From silicic acid solution with defined mononolecular Si_8O_{20} and polymeric silicic acid units, I- and vinylsilylated derivates were synthesized as recursors for inorganic–organic hybrid polymers. 'rom the model D4R silicic acid it follows that, under the reaction conditions used, the silicic acid tructure of the starting solution is practically preierved in the organic derivative (precursor) and in he resulting hybrid polymer. The experiments show hat, independent of the structure of the examined ilicic acid units, six-membered bridges between the inits provide a favourable length for formation of porous hybrid polymers. These polymers are thermally stable in air to 250°C. At higher temperatures oxidation of the Si–CH_2–CH_2– and Si–CH_3 bonds appears. A simple two-step pathway is described for he synthesis of porous hybrid polymers by mixed silylation of silicates or silicic acid solutions followed by an additive reaction. The hydrophobic and porous polymers synthesized at low temperatures

are, in the case of D4R silicic acid units containing polymers, free of silanol groups.

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