

# *s*-Triazine and tri-*s*-triazine based organic–inorganic hybrid gels prepared from chlorosilanes by exchange reactions†

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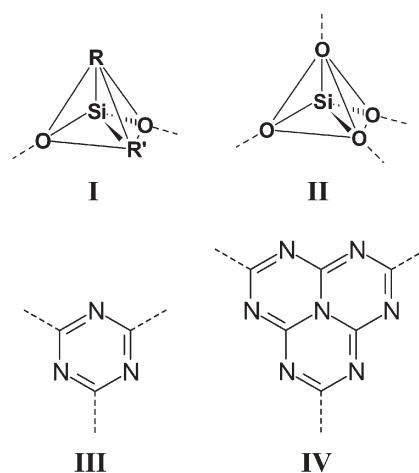
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Hybrid polymers  $[(\Delta\text{O}_3)_4\text{Si}_3]_n$  and  $[(\Delta\text{O}_3)\text{SiMe}]_n$  (where  $\Delta = \text{C}_6\text{N}_7$  or  $\text{C}_3\text{N}_3$ ) have been prepared by a novel sol–gel process based on exchange reactions of  $\text{MeSiCl}_3$  or  $\text{SiCl}_4$  with  $\text{C}_6\text{N}_7(\text{OSiMe}_3)_3$  and  $\text{C}_3\text{N}_3(\text{OSiMe}_3)_3$ .

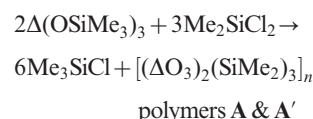
The synthesis of organic–inorganic polymer hybrids has been widely investigated and received considerable attention.<sup>1</sup> This is due to many interesting properties, which arise from the combination of organic and inorganic components. In many cases the classic sol–gel processing has been applied to prepare such hybrid polymers.<sup>2</sup> In this approach, the inorganic part is typically comprised of a metal oxide, which is obtained by hydrolysis of a metal alkoxide or another metal source, although non-hydrolytic<sup>3</sup> as well as non-oxide<sup>4</sup> sol–gel systems have also been reported. The organic component may be introduced by physically mixing, *e.g.* with an organic polymer. An alternative is based on precursors containing the organic functional groups directly bound to the metal. Examples are polysilsesquioxanes  $[\text{R}-\text{SiO}_{1.5}]_n$  with R being an end-group,<sup>5</sup> or bridged systems of the type  $[\text{O}_{1.5}\text{Si}-\text{R}-\text{SiO}_{1.5}]_n$ .<sup>6</sup>

Here we report a novel hybrid type, which may be considered as “trigonally expanded silica, silsesquioxanes and siloxanes”. The synthesis is based on the elimination of  $\text{Me}_3\text{SiCl}$  similar to the formation of  $\text{Si}-\text{C}-\text{N}$  and  $\text{B}-\text{C}-\text{N}$  gels upon reactions of chlorosilanes and trichloroborazine with bis(trimethylsilyl)carbo-diimide.<sup>4</sup> The heterocyclic units **III** and **IV** are combined with the inorganic  $\text{SiO}_4$  units or organometallic  $\text{RSiO}_3$  or  $\text{R}_2\text{SiO}_2$  groups (Scheme 1). We selected *s*-triazines and tri-*s*-triazines as polymer building blocks due to their rigidity. This property might allow the formation of covalent open frameworks, a class of porous crystalline networks which was recently discovered.<sup>7</sup> Besides, the  $\text{C}_3\text{N}_3$  and  $\text{C}_6\text{N}_7$  units show interesting functional properties. The former well known heterocycle has been used as a synthon in supramolecular chemistry.<sup>8</sup> The latter less known tri-*s*-triazine ring (heptazine) has recently attracted increasing attention.<sup>9–15</sup> It shows strong photoluminescence.<sup>14</sup> Besides, the  $\text{C}_6\text{N}_7$  unit is characterised by a very high thermal stability up to  $>500$  °C combined with flame retardant properties. It is considered to be an interesting building block for the still elusive carbon(IV) nitride phases.<sup>15</sup> Furthermore, it has been shown that the peripheral N-atoms of *s*-triazines as well as tri-*s*-triazines can act as ligands for metal coordination and metal incorporation into the polymer.<sup>16</sup>



**Scheme 1** Polymer building blocks used in this study: D<sub>2</sub> or T<sub>3</sub> units **I** (with R = R' = CH<sub>3</sub>) and Q<sub>4</sub> groups **II** are combined with the heterocyclic units *s*-triazine **III** or tri-*s*-triazine **IV** to form “expanded” siloxanes or “expanded” silica.

First, we prepared “expanded dimethylsiloxane” polymers *via* exchange reactions of dichlorodimethyl silane with the trimethylsilyl esters of cyameluric acid  $\text{C}_6\text{N}_7(\text{OSiMe}_3)_3$  **1a** and cyanuric acid  $\text{C}_3\text{N}_3(\text{OSiMe}_3)_3$  **1b**:



Elemental analysis of polymer A (with  $\Delta = \text{C}_6\text{N}_7$ ) indicated that only a small amount of chlorine remained in the product, namely less than 1.5 mass%. This indicates that the reaction is nearly complete. The <sup>29</sup>Si solid state NMR spectrum reveals two overlapping resonance signals at 6.5 and –5.4 ppm. The latter was assigned to the  $-\Delta\text{O}-\text{SiMe}_2-\text{O}\Delta-$  units. The weaker signal at lower field is most likely due to  $-\Delta\text{O}-\text{SiMe}_2-\text{Cl}$  and/or  $-\Delta\text{O}-\text{SiMe}_2-\text{OH}$  end groups. The starting material **1a** (see below) as well as  $-\text{O}-\text{SiMe}_3$  end groups were not detectable.‡

The described results concerning the synthesis of polymer A encouraged us to try to prepare network structures which have stronger cross-links, using  $\text{SiCl}_4$  and  $\text{MeSiCl}_3$  as starting materials. As mentioned above we hoped to obtain potentially crystalline covalent porous network structures. Surprisingly, it turned out that all four reactions generate gels. Dissolving the chlorosilane and the trimethylsilyl esters **1a** or **1b** in THF at room temperature provided clear homogenous reaction mixtures. Concentrations used for the reactions varied between 0.026 and 0.17 mol l<sup>–1</sup>

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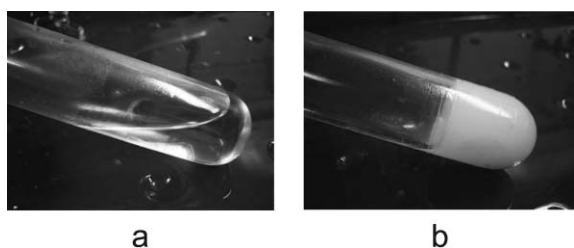
† Tri-*s*-triazine derivatives part 6. For part 5 see ref. 16.

**Table 1** Synthesis parameters for selected polymers **A** and **A'** as well as gels **B** to **E**

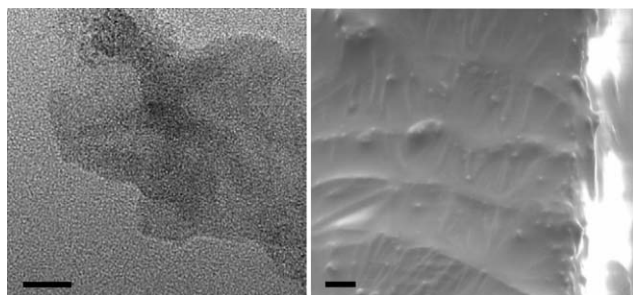
	<i>T</i>	<i>V</i> <sub>(THF)</sub> /ml	<i>c</i> /mol l <sup>-1</sup>	Gelation time
<b>A</b> : Me <sub>2</sub> SiCl <sub>2</sub> - <b>1a</b>	rt	2	0.13	—
<b>B</b> : MeSiCl <sub>3</sub> - <b>1a</b>	rt	4	0.13	5 min
<b>C</b> : SiCl <sub>4</sub> - <b>1a</b>	rt	7	0.17	≤5 min
<b>A'</b> : Me <sub>2</sub> SiCl <sub>2</sub> - <b>1b</b>	rt	4	0.13	—
<b>D</b> : MeSiCl <sub>3</sub> - <b>1b</b>	rt	4	0.13	~2 weeks
<b>D'</b> : MeSiCl <sub>3</sub> - <b>1b</b>	45 °C	4	0.13	~1 day
<b>E</b> : SiCl <sub>4</sub> - <b>1b</b>	rt	4	0.25	6 days

(Table 1). Depending on the specific starting material a sudden solidification occurred after a gelation time of less than five minutes in case of cyameluric acid ester **1a** and SiCl<sub>4</sub> or MeSiCl<sub>3</sub> (gels **B** and **C**) to 1–14 days in case of cyanuric acid derivative **1b** (gels **D**, **D'** and **E**), respectively. This phenomenology is characteristic for sol–gel processes. A typical example, showing images of the sol and the gel state are depicted in Fig. 1. After gelation the gels were stored at room temperature for four weeks. Only minor linear shrinkage in the range of 10% and little syneresis was observed during this ageing period. The aged gels were dried carefully at <50 °C under vacuum for ~24 h in order to obtain xerogels as white powders.

The xerogels were analysed with respect to their structure and morphology. XRD measurements gave no indication for the presence of any crystalline phases. This result was confirmed by HR-TEM (Fig. 2) images and electron diffraction patterns. FTIR spectra of all the prepared xerogels clearly indicate the presence of Si–O units showing characteristic absorption bands between 1000 and 1100 cm<sup>-1</sup>. Furthermore, those xerogels prepared from precursor **1a**, *i.e.* obtained by drying gels **B** and **C**, show characteristic signals at 1650–1680(vs, br), 1450–1460(m) and 790–800(vs) cm<sup>-1</sup> which are due to the C<sub>6</sub>N<sub>7</sub> heptazine nucleus.<sup>16</sup>



**Fig. 1** Sol-gel phenomenology: left: as prepared reaction mixture consisting of tris(trimethylsilyl)cyamelurate, chlorosilane and the solvent (THF); right: reaction mixture after gelation.

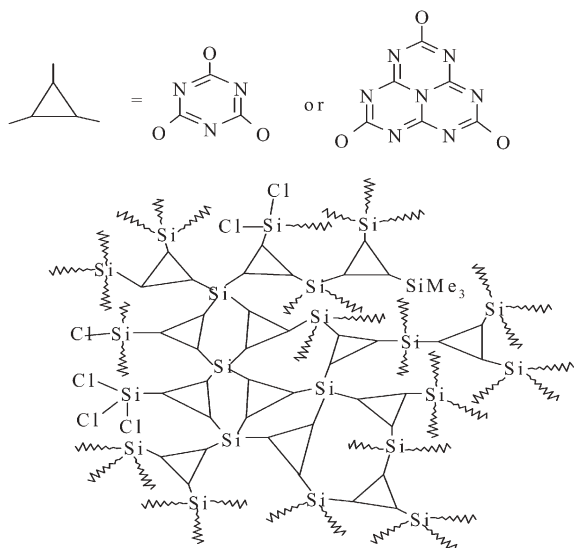


**Fig. 2** Typical HR-TEM (left) and SEM images of the xerogels. The scale bars correspond to 20 nm (left) and 20 μm (right).

The xerogels **D**, **D'** and **E** are characterised by the following set of signals at 1780(s, sh) 1700(vs), 1462(s), 1412–1420(s), 1398–1400(s) and 794–799(vs) cm<sup>-1</sup>, which are caused by the triazine C<sub>3</sub>N<sub>3</sub> heterocycle. Further bands at 1262(vs) cm<sup>-1</sup> and around 2830 to 3000(w) cm<sup>-1</sup> are attributed to Si–CH<sub>3</sub> units. Xerogels **B** and **C** show weak absorption bands around 604 cm<sup>-1</sup> while xerogels **D**, **D'** and **E** are characterised by a slightly stronger band at 530–534(m) cm<sup>-1</sup> which was attributed to Si–Cl vibrations indicating the presence of chlorine in the products. This observation was confirmed by the solid state NMR investigations discussed below. Combustion chemical analyses of the xerogels have not been performed so far. However, EDX examinations show that relatively low chlorine concentrations are present in the xerogels. About 2.5 and 3.5 mass% were found in **B** and **D** derived from **1a**, while ~1.5 and 2.5 mass% chlorine were detected in **D** and **E**.

Solid state <sup>29</sup>Si NMR was used to get more detailed information about the degree of condensation and the presence of end-groups in the polymers. For comparison the starting materials **1a** and **1b** were measured showing sharp singlets at 29.6 and 27.5 ppm, respectively, due to the ΔSi(OMe<sub>3</sub>)<sub>3</sub> groups. Xerogel **B** shows only one broad signal at –102 ppm, which was attributed to the Si(OC<sub>6</sub>N<sub>7</sub>)<sub>4</sub> units. The other **1a** derived xerogel **C** again shows one strong signal at –44.4 ppm, which should be due to MeSi(OC<sub>6</sub>N<sub>7</sub>)<sub>3</sub> units. A second weaker but sharper signal at 30.2 ppm was assigned to remaining COSiMe<sub>3</sub> endgroups. The <sup>29</sup>Si NMR spectra of the xerogels derived from **1b** on the other hand, indicate less condensed structures: xerogel **D** obtained from SiCl<sub>4</sub> shows a strong broad resonance at –90 to –100 ppm and three weaker signals centered at –75.8, –54.6 and –34.9 ppm, which were attributed to Si(OC<sub>3</sub>N<sub>3</sub>)<sub>4</sub>, SiCl(OC<sub>3</sub>N<sub>3</sub>)<sub>3</sub>, SiCl<sub>2</sub>(OC<sub>3</sub>N<sub>3</sub>)<sub>2</sub> and SiCl<sub>3</sub>(OC<sub>3</sub>N<sub>3</sub>) units, respectively. A further signal at 30.8 ppm is most likely due to OSiMe<sub>3</sub> end groups. Similarly, xerogel **E** derived from MeSiCl<sub>3</sub> shows a strong <sup>29</sup>Si NMR signal at –42.6 ppm for MeSi(OC<sub>3</sub>N<sub>3</sub>)<sub>3</sub> groups, and weaker resonances at –22 ppm for MeSiCl(OC<sub>3</sub>N<sub>3</sub>)<sub>2</sub>, and at –2 ppm for MeSiCl<sub>2</sub>(OC<sub>3</sub>N<sub>3</sub>) groups. These results correspond well with a much higher reactivity of SiMe<sub>3</sub>-groups on the C<sub>6</sub>N<sub>7</sub> nucleus as compared to the same substituents bound to the C<sub>3</sub>N<sub>3</sub> ring,<sup>10,16</sup> which is also supported by the much shorter gelation times found for the reactions with **1a**.

None of the sol–gel transitions was found to be reversible. The gels cannot be liquified mechanically, by solvent addition or by increasing the temperature. Polymers **A** and **A'**, which precipitate during the synthesis, as well as all of the xerogels **B** to **E** are neither soluble nor meltable. Thus, it is unlikely that the products are comprised of small oligomeric structures such as dendritic molecules. Our preliminary conclusion with respect to the chemical structure of the novel hybrids as derived from the above discussed analytical techniques (XRD, HR-TEM, EA & EDX, FTIR and NMR) can be summarised as follows: the gels are based on three-dimensionally cross-linked networks, comprised of linear and ring-like features as well as branched units, while the number of Si–Cl and OSiMe<sub>3</sub> end groups and therefore the degree of cross-linking varies depending on the trimethylsilyloxy-precursor, the chlorosilane and the reaction conditions (*T*, *c* *etc.*). A basic feature of the products is an alternating arrangement of the heterocyclic unit Δ and the inorganic or organometallic SiO-motives. An illustration for this model of the chemical structure is provided in Scheme 2.



**Scheme 2** A sketch of the chemical structure of the hybrid gels C and E.

Due to the presence of Si–O–C units it was expected that the products are sensitive to hydrolysis. Indeed, hydrolytic degradation was observed by FTIR spectroscopy after the samples were stored in air. This property of the hybrid materials is not necessarily a disadvantage, since it may be utilized for the design of biodegradable materials, for example.

Nitrogen adsorption measurements of the gels dried under vacuum at 200 °C did show small surface areas of <10 m<sup>2</sup>g. This is most likely due to a collapse of the porous network during drying. Similar results were reported for oxide and non-oxide gels.<sup>4</sup> Correspondingly, SEM images show relatively smooth surfaces and a glass-like morphology (Fig. 2).

Currently, we modify the novel gel synthesis presented here by replacing the three-fold functional units **III** and **IV** by two-fold functionalized bridges. The results of these experiments, which will be published elsewhere, clearly indicate that again sol–gel transitions based on exchange reactions take place. Thus, the novel approach to obtain hybrid gels by chlorosilane exchange reactions presented here is applicable also for other precursors, which are not based on the C<sub>3</sub>N<sub>3</sub> or C<sub>6</sub>N<sub>7</sub> groups. Nevertheless, the new inorganic–organic hybrid materials might show potentially useful, ceramic forming, metal coordination, or ion exchange properties.

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## Notes and references

‡ All manipulations were performed under inert (Ar or N<sub>2</sub>) atmosphere using standard Schlenk techniques or in a glovebox. The solvent,

tetrahydrofuran (THF), was distilled from a sodium–benzophenone mixture. Tris(trimethylsilyl)cyanurate<sup>9</sup> **1a** and tris(trimethylsilyl)cyanurate<sup>10</sup> **1b** were synthesized according the literature. Both precursors **1a** and **1b** were obtained in pure form and characterised comprehensively including single crystal X-ray structures (which will be published elsewhere).

Synthesis of polymer **A** (with Δ = C<sub>6</sub>N<sub>7</sub>) was performed by mixing 2 ml of THF with 31 mg of (CH<sub>3</sub>)<sub>2</sub>SiCl<sub>2</sub> and 70 mg of **1a** at room temperature. A milky suspension had formed after 1 h, *i.e.* precipitation occurred but no gelation was observed after eight weeks. The solvent was removed in vacuum and the residue characterised as described in the main text above.

Syntheses of polymer **A'** as well as gels **B** to **E** were conducted analogously. Further details are summarized in Table 1.

FT-IR spectra were measured on a Perkin Elmer 2000 spectrometer (KBr pellets). The X-ray diffraction (XRD) patterns of the products were recorded on a Siemens D-5000 diffractometer with Cu Kα radiation. The <sup>29</sup>Si-NMR measurements of the dried gels were obtained on a Bruker Avance<sup>®</sup> WB 400 MHz spectrometer with a resonance frequency of 79.51 MHz using magic-angle spinning (MAS) at 5 kHz and cross polarization (CP). The chemical shift is referenced to tetramethylsilane (TMS). Specific surface areas were determined with a Nova 3000 Quantachrome Instrument and calculated using the BET model. High resolution scanning electron microscopy (HR-SEM) was performed with LEO1530 microscope equipped with an energy dispersive X-ray (EDX) system. High resolution transmission electron microscopy (HR-TEM) images were obtained on a JEM 2010FEF, JEOL. Elemental analyses were performed by Analytisches Labor Pascher (Remagen-Bandorf, Germany).

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