

Novel polysiloxane and polycarbosilane aerogels *via* hydrosilylation of preceramic polymers†Gian Domenico Soraru,^{*a} Federico Dalcanale,^a Renzo Camprostrini,^a Amélie Gaston,^{‡a} Yigal Blum,^b Sara Carturan^c and Parakkulam Ramaswamy Aravind^{§a}

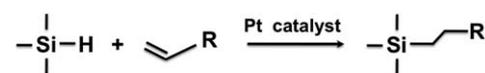
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We report new polysiloxane and polycarbosilane aerogels, which have been obtained by crosslinking Si–H-containing polymers with a C=C-containing crosslinker *via* hydrosilylation reactions. The crosslinking reaction has been carried out in a highly diluted solution using up to 97 vol% of solvent. The obtained aerogels have a colloidal structure with meso- and macropores. Density as low as 0.17 g cm⁻³ has been reached, which implies a porosity of *ca.* 84 vol%.

There has been considerable interest in aerogels ever since Kistler reported them in 1931.¹ These wonder materials have many fascinating properties such as high surface area (500–1000 m² g⁻¹),² high porosity (80–99.8%),³ low bulk density (0.003–0.8 g cm⁻³)⁴ and low thermal conductivity (~0.02 W m⁻¹ K⁻¹).⁵ These features have led to the use of aerogels for various scientific and industrial applications.⁶ Kistler synthesized first silica aerogels and subsequently aerogels of various single oxides, composite/mixed oxides, inorganic–organic hybrids, chalcogenides, organic aerogels like resorcinol–formaldehyde (RF), melamine–formaldehyde (MF) and polyurethane, carbon, cellulose, cobalt polysulfide and polyimide have been reported in the literature.⁷

Aerogels are normally synthesized by supercritical extraction of the solvent from the wet gels.⁷ Under supercritical conditions, there will be no distinction between the liquid and the vapour phases and hence the capillary stress could be almost eliminated resulting in a highly porous network. However active research is also being carried out to dry wet gels under ambient conditions by which the equipment limited supercritical drying could be avoided.^{8,9}



Reaction scheme of the hydrosilylation reaction

Scheme 1 Reaction scheme of the hydrosilylation reaction.

Hydrosilylation¹⁰ is a very efficient catalytic addition of Si–H bonds to carbon–carbon or carbon–heteroatom double bonds (Scheme 1). It is often used in the field of Polymer Derived Ceramics (PDC) to crosslink siloxanes and form the pre-ceramic network.^{11,12} It has not been reported yet in conjunction with aerogel formation. In the present work we report novel aerogels obtained by reacting two silicon-based polymers, containing Si–H groups with two different C=C-containing crosslinkers. In particular, polyhydridomethylsiloxane (PHMS) is cured with 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane (TMTV) and a polycarbosilane (PCS) is crosslinked with divinylbenzene (DVB) (Scheme 2). Both reactions are conducted in highly diluted solution conditions and in the presence of a Pt catalyst. The resulting wet gels are supercritically dried in CO₂ to obtain aerogels. The schemes for the two investigated reactions are reported below.

PHMS ($M_w = 1900$), TMTV ($M_w = 240$) and DVB (technical 80%, mixed isomers) were purchased from Alfa Aesar (Alfa Aesar, Ward Hill, MA, USA). Polycarbosilane (X9-6348, $M_w = 1400$) with a molecular structure formed by SiC₄ and SiC₃H Si units in a 1 : 1 ratio¹³ was supplied by Dow Corning (Dow Corning, Midland, MI, USA). Different compositions were prepared by altering the molar ratio of Si–H and vinyl (Vy) moieties of reactants and also the amount of solvent in order to study solutions with a vol% of solvent in the range 70–97 vol%. The catalyst concentration (platinum–divinyltetramethyldisiloxane complex, ~Pt 2% in xylene, Sigma-Aldrich, Saint Louis, MO, USA) for the siloxane-based system was maintained at 300 ppm (by weight) relative to PHMS while for the PCS-derived materials a constant Pt concentration of 10⁻⁴ mol L⁻¹ in the overall solution was selected.

The samples are labeled as follows: first we indicate the Si–H/Vy molar ratio, then the two types of reactants in each experimental set and finally the vol% of solvent, which was acetone for the PHMS-based system and cyclohexane for the PCS-based materials. For example, the sample 2 : 1 PHTV-90 refers to the material obtained from PHMS cured with TMTV using a Si–H/Vy molar ratio of 2 and 90 vol% of solvent (acetone).

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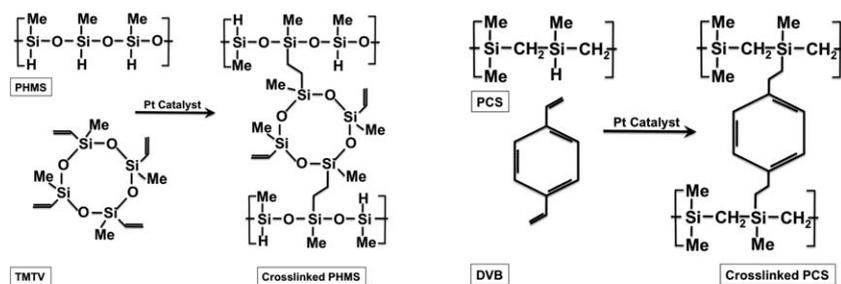
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The hydrosilylation reactions performed for generating the reported preceramic aerogels

Scheme 2 The hydrosilylation reactions performed for generating the reported preceramic aerogels.

In a typical reaction to prepare the 1 : 1 PHTV-90 sample, 1.00 g PHMS (0.99 cm³) was reacted (in the presence of Pt catalyst) with 1.32 g TMTV (1.38 cm³) in 16.86 g (21.27 cm³) of acetone. The total volume of the solution, neglecting as a first approximation the volume change of mixing, is 23.64 and the vol% of solvent becomes 90. The reaction mixture was stirred for 1 to 2 min and then 3 mL of the reaction mixture was transferred into a pressure reactor (Digestion Vessel, mod. 4749, Parr, IL, USA). The hydrosilylation reaction under these highly diluted conditions occurs only at temperatures higher than the boiling temperature of the solvent. Accordingly, the pressure reactor was transferred to an oven and the temperature was increased from room temperature to 120 °C in 1 h and then held at that temperature for 2 h. The wet gels were obtained after cooling the oven to room temperature.

For the PCS-based aerogels, in a typical reaction to prepare the 1 : 2 PCDV-90 sample, 0.30 g PCS (0.29 cm³) was mixed with 0.27 g DVB (0.30 cm³) in 4.15 g cyclohexane (5.35 cm³). The total volume of the resulting solution has been estimated following the same methodology used for the PHTV system. Since in this case the preceramic polymer, PCS, is a solid whose density was not available from the producer, the same has been measured by He pycnometer (PCS density = 1.04 ± 0.01 g cm⁻³). The reaction mixture was stirred for 5 to 10 min, loaded into the pressure reactor, which was transferred to an oven. The temperature of the oven was increased from RT to 200 °C in 1 h, then held at that temperature for 1 h and finally cooled to room temperature.

Accordingly, monolithic wet gel samples were obtained for the PHMS-based system while for the PCS-based samples usually large gel fragments were produced. For both systems the wet gels were then supercritically dried with liquid CO₂ using an in-house made equipment with two glass windows, for visual monitoring of the entire process. Before the supercritical drying the samples have been exchanged with liquid CO₂ twice a day for at least 5 days. The supercritical conditions were obtained by increasing the temperature from RT up to 55 °C and the pressure up to 100–110 bar. Finally the drying was performed at 55 °C by decreasing the pressure down to 1 bar over a period of 4–5 h.

Photographs of the wet gels and corresponding aerogels are provided in Fig. 1. The bulk density of the dried PHMS-based gels was calculated from their mass and volume. The specific surface area (SSA) of aerogels was determined by N₂ adsorption at 77 K (using a Micromeritics equipment, ASAP Model 2010, Norcross, GA, USA). The specific surface area was determined using the BET equation.¹⁴ The total pore volume (TPV) was calculated as TPV = $V_a D$, where V_a is the volume adsorbed at p/p_0 0.99 and D is the

density conversion factor (0.0015468 for nitrogen as adsorbate gas). The pore size distribution (PSD) was obtained using the Barrett–Joyner–Halenda (BJH) method.¹⁵ Assuming that the pores are cylindrical and open at both ends, the average pore size, expressed in nanometres, of a given sample is calculated using the equation 4000 TPV/SSA. Skeletal density of selected samples and starting PCS was measured with a helium pycnometer (Micromeritics, model 1035, Norcross, GA, USA).

The properties of the obtained aerogels are provided in Table 1.

The density and linear shrinkage of the PCDV aerogels could not be measured because of the high fragmentation of the gel during the process. Average pore diameter is calculated according to the equation, 4000 TPV/SSA, as reported in the text. Uncertainties of density

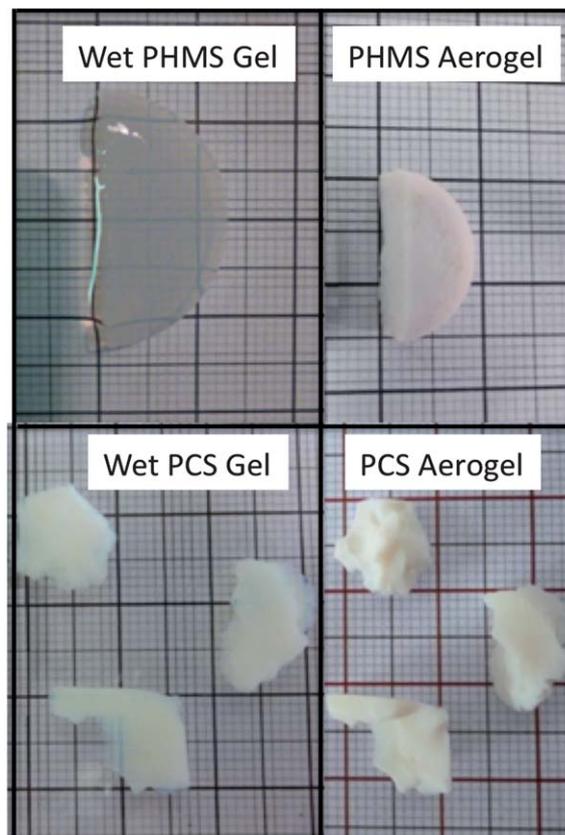


Fig. 1 Digital camera images of wet and corresponding aerogels: (top) 1 : 1 PHTV-90 and (bottom) 1 : 2 PCDV-80 samples.

Table 1 Properties of aerogel samples

| Sample | Density/g cm ⁻³ ±0.05 | Linear shrinkage (%) ±2 | SSA/m ² g ⁻¹ | TPV/cm ³ g ⁻¹ | Average pore diameter/nm |
|---------------|----------------------------------|-------------------------|------------------------------------|-------------------------------------|--------------------------|
| 1 : 1 PHTV-70 | 0.84 | 30 | 26 ± 3 | 0.04 | 6 |
| 2 : 1 PHTV-70 | 0.60 | 21 | 409 ± 4 | 0.65 | 6 |
| 1 : 1 PHTV-90 | 0.41 | 44 | 276 ± 4 | 0.76 | 11 |
| 2 : 1 PHTV-90 | 0.33 | 34 | 497 ± 6 | 1.85 | 15 |
| 2 : 1 PHTV-97 | 0.17 | 44 | 229 ± 3 | 0.72 | 13 |
| 1 : 2 PCDV-80 | — | — | 597 ± 6 | 1.90 | 13 |
| 1 : 2 PCDV-90 | — | — | 589 ± 6 | 1.81 | 12 |
| 1 : 4 PCDV-80 | — | — | 404 ± 4 | 2.12 | 21 |

and linear shrinkage are standard deviations of at least ten measurements. Error bars for the SSA values are derived from the application of BET multiple linear regression.

PHTV system: the density of aerogels decreases by increasing the vol% of solvent in the starting solution. For the 97 vol% sample, the density reaches a value of 0.17 g cm⁻³, which implies a porosity of around 84 vol%, considering that the skeletal density, measured with the He pycnometer, gives 1.09 g cm⁻³. The lower density of the 2 : 1 PHTV samples compared to the 1 : 1 is associated with a lower shrinkage during drying. The increase in the Si–H/C=C moieties ratio is expected to accelerate the hydrosilylation reaction and the crosslinking degree leading to a more rigid polymer network. It is worth mentioning here that the majority of shrinkage occurred during the exchange of acetone with liquid CO₂ prior to the supercritical drying step, suggesting that acetone swells the polymer network during synthesis resulting in the shrinkage upon its exchange with liquid CO₂. In spite of its lower density the 97 vol% sample has a lower TPV (0.72 cm³ g⁻¹) compared to the 90 vol% aerogel (1.85 cm³ g⁻¹). This apparent discrepancy can be attributed to the macroporosity present in the 97 vol% sample, which cannot be completely detected with the N₂ adsorption technique.

The adsorption–desorption isotherms are provided in Fig. 2. According to IUPAC classification,¹⁶ the isotherms are of Type IV, which is characteristic of mesoporous materials. The hysteresis loop is clearly visible in the regime of mesopore filling of the isotherms and corresponds to type H2. This type of hysteresis loop is typically attributed to the ink-bottle-shaped pore model,¹⁶ though more recently this behavior was observed also for materials with uniform

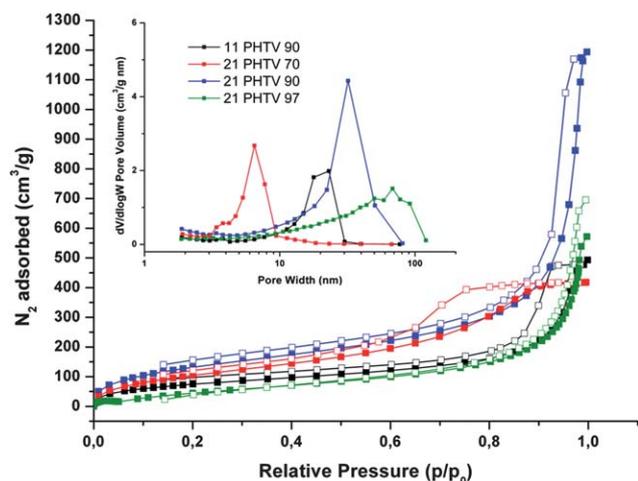


Fig. 2 N₂ adsorption/desorption isotherms for the PHMS-based aerogels. Inset shows the pore size distribution curves.

channel-shaped pores.¹⁷ As the vol% of solvent increases, the hysteresis loop shifts towards higher pressure regimes, as a result of mesopores widening and pore sizes broadening, as also observed in the BJH derived pore size distribution (PSD) plots reported in the inset of Fig. 2. The isotherms of 2 : 1 PHTV-90 and 2 : 1 PHTV-97 do not show a limiting adsorption at high p/p_0 , indicating the presence of a consistent fraction of macropores. Analysis of the N₂ adsorption experiments shows that TPV and average pore size increase with the Si–H/C=C molar ratio and with the dilution of the starting solution, when the vol% of solvent is increased from 70 to 90 vol%.

The FE-SEM images of the 2 : 1 PHTV samples obtained with different vol% of solvent (Fig. 3) show the formation of a typical colloidal gel. The SEM images clearly suggest an increase of porosity and pore size when the vol% of solvent increases from 70 to 97 vol%. The particle size increases when the solvent is increased from 70 to 90 vol% while does not clearly change from 90 to 97 vol%. Macropores ($d > 50$ nm) are visible in both the 90 and 97 vol% aerogels in agreement with the N₂ adsorption analysis.

The experimental results suggest that crosslinked polymer particles are initially formed *via* a precipitation–polymerization mechanism, which is similar to the process reported in the literature for the formation of spherical polymeric particles¹⁸ with a subsequent growth stage leading to the final gel formation. By increasing the dilution of the starting solution the nucleation rate is reduced resulting in the formation of larger particles and larger pore size.

These results agree well with the reaction mechanism proposed in the literature for Pt-catalyzed hydrosilylation reaction.^{19–21} Indeed, the reaction of the active Pt species with the Si–H moieties is the slow step in the catalytic cycle (rate determining step) and is dependent on

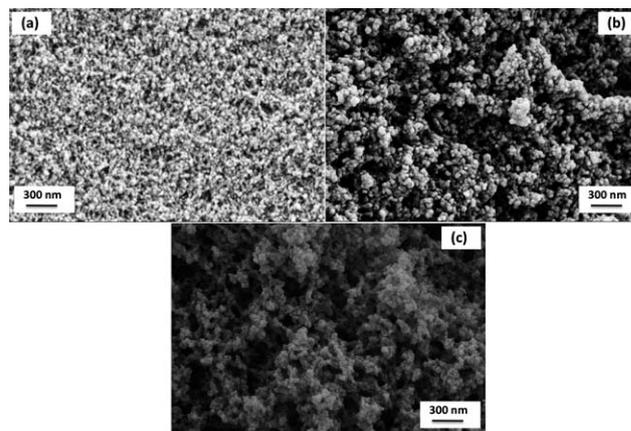


Fig. 3 FE-SEM images of the 2 : 1 PHTV aerogels at different vol% of solvent: (a) 70 vol%, (b) 90 vol%, and (c) 97 vol%.

the molar concentrations of the Si–H and the Pt species. Since the amount of Pt catalyst was maintained constant at 300 ppm (by weight) relative to PHMS, increasing the dilution of the solution at constant Si–H/C=C ratio induces a decrease of both the Pt and the Si–H functional groups molar concentration, with an overall decrease of crosslinking reactivity. Similarly, increasing the Si–H/C=C molar ratio—at constant vol% of solvent—leads to an increase of molar concentration of the Si–H groups with a corresponding increase of reactivity.

PCDV system: for this system only irregularly shaped fragments are obtained (see Fig. 1). The shrinkage of the PCS-derived aerogels seems to be lower compared to the shrinkage of the PHMS-based samples based on visual observations (Fig. 1). The N₂ adsorption–desorption isotherms, provided in Fig. 4, are close in shape to those observed for the system PHTV at high vol% of solvent (90 and 97 vol %). Accordingly, they are assigned to Type IV isotherms with narrow hysteresis in the high pressure range. Hence, the aerogels are mesoporous in nature, with large mesopores with maxima in the range 80–100 nm and a wide PSD, as revealed by the pore size distribution curves (Fig. 4). Moreover, the lack of limiting adsorption at saturation pressure indicates the presence of macropores, as clearly visible in the FE-SEM images (Fig. 5).

The SEM images also show the formation of a colloidal aerogel, similarly to the PHTV system. The SSA values range between 400 and 600 m² g⁻¹. TPV values in the range 1.81 up to 2.12 cm³ g⁻¹ have been obtained. The TPV is probably underestimated even for the PCDV samples due to the large amount of macropores. For these samples the underestimation of the TPV—due to the large fraction of macropores—associated with the asymmetry of the PSD curves in the region of small pore sizes could also explain why the average pore diameters calculated with the relation 4 000 TPV/SSA and reported in Table 1 are smaller than those observed from the maxima of the PSD curves. Indeed, average pore size ranges between 13 and 21 nm while the maxima of the PSD curves fell in the range 80–100 nm. The FE-SEM study reveals the presence, in all the studied samples, of macropores.

The N₂ adsorption study combined with the FE-SEM investigation suggests that the dependence of the aerogel microstructural features such as particle size and TPV on the Si–H/vinyl molar ratio and dilution of the starting solution is less significant for the

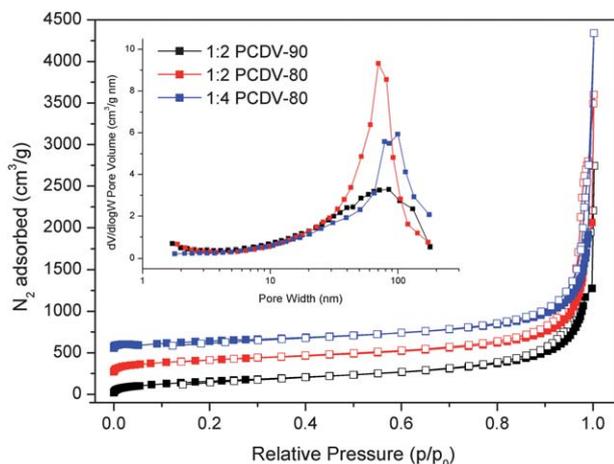


Fig. 4 N₂ adsorption/desorption isotherms for the PCS-based aerogels. Inset shows the pore size distribution curves.

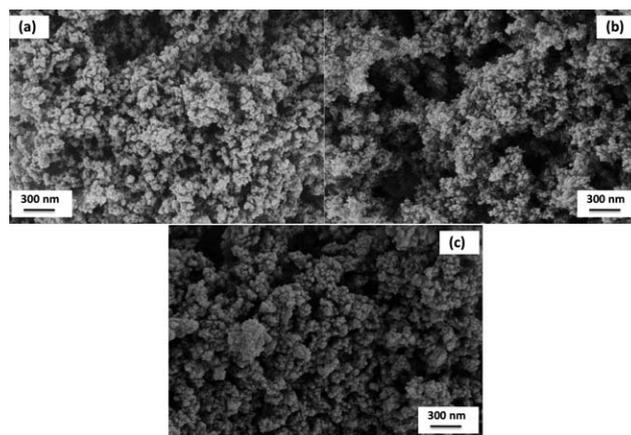


Fig. 5 FE-SEM images of the PCS-based aerogels: (a) 1 : 2 PCDV-80; (b) 1 : 4 PCDV-80 and (c) 1 : 2 PCDV-90.

PCS-based system, compared to the PHMS-based materials. Indeed, for the PCS-based aerogels, increasing the amount of solvent from 80 to 90 vol% while keeping the same Si–H/C=C molar ratio does not significantly change the aerogel microstructure and particle size. On the other hand, at constant dilution of the reagents (80 vol% of solvent) increasing the C=C/Si–H molar ratio from 2 up to 4 seems only to slightly decrease the particle size with a negligible effect on the pore size and porosity.

Conclusions

Novel polysiloxane and polycarbosilane aerogels have been prepared using the hydrosilylation reaction between Si–H and C=C moieties to crosslink the system in a highly diluted solution. To our knowledge, the use of hydrosilylation as the crosslinking mode in aerogel systems has not been reported before. Polyhydridomethylsiloxane has been crosslinked with tetramethyltetravinylcyclorosiloxane, in acetone using up to 97 vol% of solvent. At the same time, a Si–H-containing polycarbosilane has been crosslinked with divinylbenzene in cyclohexane using up to 90 vol% of solvent. The wet gels have been dried under supercritical conditions to obtain the corresponding aerogels upon exchanging the solvents with liquid CO₂. The FE-SEM and N₂ adsorption investigations showed the formation of colloidal aerogels with meso- and macropores. The particle size, pore size and TPV of the PHTV aerogels increased with the vol% of solvent of the starting solution, while for the PCDV samples the microstructure did not change significantly when the amount of solvent was increased from 80 to 90 vol%. We observed that increasing the Si–H/C=C molar ratio from 2 to 4 leads to a slight increase of the pore size and pore volume of the PCS-based aerogels.

These novel aerogels can open the way to the preparation of novel polymer-derived ceramic aerogels (PDC-aerogels) of different systems such as Si–O–C, Si–C, Si–C–N, *etc.*, which we plan to report in the near future in detail. Indeed, preliminary experiments demonstrated that monolithic mesoporous Si–O–C and Si–C aerogels could be easily obtained by pyrolysis in inert atmosphere starting from both PMHS- and PCS-based aerogels (Fig. S1†).

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