

Highly defined pore size distribution in sol-gel silicate glasses induced by incorporation of an oligomeric siloxane

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Doping of sol-gel derived tetramethoxysilane (TMOS) glasses with small amounts of octaphenylcyclotetrasiloxane (OPCTS) induces a remarkably narrow pore size distribution.

The use of sol-gel techniques for the preparation of silicates employing surfactant aggregates as templates has opened the way to a range of possible applications of these well defined mesoporous materials.^{1,2} Using surfactant aggregates displaying hexagonal,¹ cubic,² and lamellar³ phases, highly ordered silicate materials with predefined pores could be obtained. Organically modified alkoxy silane precursors (ormosils) can also be used to modify the pores in sol-gel derived silica materials, but this does not lead to a better definition of the shape and size of the pores.^{4,5} However, by the incorporation of non-crosslinking oligosiloxane units of defined size into the inorganic polymer network, better definition of the pore size may be achieved without the use of relatively large quantities of organic materials, and without the need for their removal.

The hydrolytic ring-opening of octaphenylcyclotetrasiloxane (OPCTS) **1** provides well defined ormosil units which may be incorporated into a silicate network. The resulting octaphenyltetrasiloxanediol (OPTSD) units would then provide segments of defined length which could be used to tailor the pore size in these mesoporous materials.

The ring-opening hydrolysis reaction of OPCTS should be carried out preferably in the presence of an excess of prehydrolysed TMOS in order to ensure reaction of the terminal OH groups of OPTSD with the sol-gel network and prevent polysiloxane formation. However, it was not possible to perform this reaction under standard hydrolysis conditions due to precipitation of the apolar OPCTS in aqueous media. This problem was circumvented by adding a 1 : 1 (v/v) mixture of thf and concentrated hydrochloric acid to a stirred thf solution of TMOS and OPCTS at 50 °C.[†] Nevertheless, no more than 10 mol% (based on silicon) could be added to the mixture without immediate precipitation. Gelation of the mixture occurred within 2 h and the gel was kept at 50 °C in a sealed vessel for 16 h. After ageing for two weeks at room temperature, small needle-shaped crystals had formed inside the transparent material. The crystalline material was removed by dissolution in thf followed by recrystallisation. Powder diffraction experiments demonstrated that they consisted of OPTSD. The glassy gels were washed with ethanol to remove remaining acid and aged for two more weeks. The diffraction patterns of the powdered ormosil revealed that washing had removed all the

crystalline material and that the resulting glass was completely amorphous.

The glasses were transparent. However, drying in air or exposure to water turned them into opaque materials. Glasses prepared without the addition of OPCTS remained transparent upon exposure both to air and water.

The incorporation of ring-opened OPCTS units into the sol-gel network was examined using FTIR and solid-state ²⁹Si NMR spectroscopy.[‡] Comparison of both the FTIR and NMR spectra obtained for the ormosil with those obtained from a reference material prepared without OPCTS revealed that diphenylsiloxane units were incorporated into the new material. Both spectroscopic techniques showed furthermore that the presence of diphenylsiloxane units in the ormosil did not merely arise from entrapped OPTSD, but that it was chemically incorporated in the silica network.

Comparison of the FTIR spectra of the ormosil with those obtained from OPTSD revealed shifts to higher wavenumbers for two of the Si-Ph vibrations, from 741.7 to 744.5 and from 718.2 to 719.3 cm⁻¹, respectively,[§] indicating restricted conformational motions of the OPTSD units due to incorporation in the silicate network. More concrete evidence was obtained from the solid-state NMR experiments which revealed that condensation with the silicate network must have been complete since the resonance at δ -39.6, assigned to the terminal D₁ unit⁶ of OPTSD, was no longer present in the ²⁹Si NMR spectrum of the ormosil (Fig. 1).[¶]

The pore size distribution of the ormosil was determined using thermoporometry^{7,8} and compared to the pore size distribution found in the reference material. The results presented in Fig. 2 show that the addition of a small amount of OPCTS has a dramatic effect on the porosity of the material. The ormosil has small pores with diameters distributed over a range of 4–10 nm (*i.e.* a distinctly wider range than in the

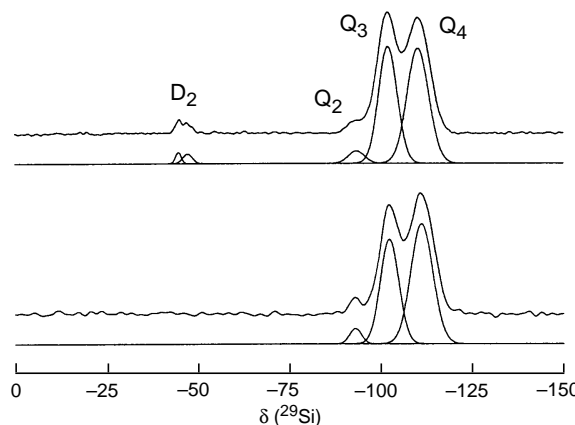
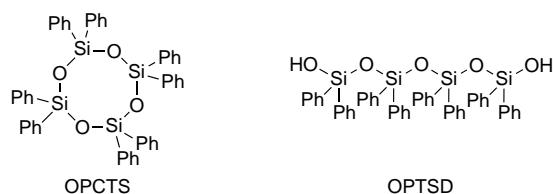


Fig. 1 ²⁹Si solid-state NMR spectra of sol-gel glasses prepared from 100% TMOS (lower trace) and from a 96 : 4 mixture (based on Si) of TMOS and OPCTS (upper trace). Gaussian fits are shown below each trace. The spectra were obtained at 59.665 MHz with single-pulse excitation at a MAS frequency of 5.0 kHz using high-power proton decoupling and a relaxation delay of 300 s.

reference compound) and also another type of pores with diameters of approximately 4.5 nm and a very narrow size distribution range. This result shows that incorporation of OPCTS modifies the overall network structure in the host material as well as generating new, sharply defined pore structures.

Remarkably, the ^{29}Si NMR spectra (Fig. 1) reveal that only 1 mol% of OPTSD is incorporated into the sol-gel network. It is also clear from Fig. 1 that incorporation of OPTSD units causes only a small decrease in the functionality of the Q atoms (the average number of Si-O-Si bonds per Q atom) from 3.503 ± 0.008 to 3.470 ± 0.007 . This change is due to an increase in the relative amount of Q_3 atoms (from 40 to 45%) and a decrease in Q_4 atoms (from 55 to 51%). The number of Si-O-Si links between OPTSD and the silicate network is not sufficient to explain this change in functionality or the dramatic changes in pore size distribution. However, the OPTSD modifies the overall network in other ways (*e.g. via* steric effects) as well as by changes in the type of linkages. Full understanding of these

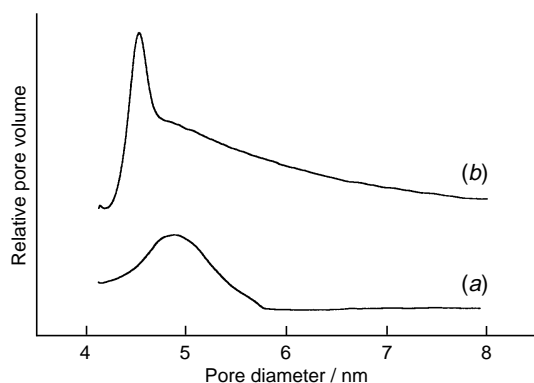


Fig. 2 Pore size distributions of sol-gel glasses prepared from 100% TMOS (a) and from a mixture of TMOS and OPCTS (4% based on Si) (b) determined from thermoporometry experiments^{7,8}

effects requires further experiments using similar modifiers with different substituents, which are in progress.

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Footnotes

† Comparison of powder diffraction patterns of OPCTS before and after hydrolysis indicated that ring opening was complete when the described procedure was applied.

‡ Solid-state ^{29}Si NMR experiments were performed using a Chemagnetics CMX 300 Infinity spectrometer, using magic angle spinning and proton decoupling.

§ Similar but reversed spectral changes are observed upon ring opening of OPCTS which leads to a shift of the same Si-Ph vibrations from 742.5 to 741.7 and from 720.3 to 718.2 cm^{-1} , respectively. These shifts to lower wavenumbers were interpreted as an increase in conformational motion due to a released ring strain.

¶ The notations D_n and Q_n are used to describe the chemical environment of silicon atoms which could form two and four possible Si-O-Si bonds, respectively. The number of bonds actually present is represented by n .

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