

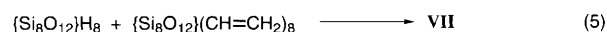
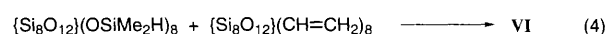
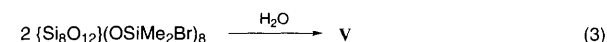
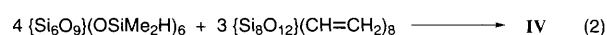
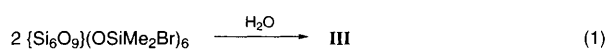
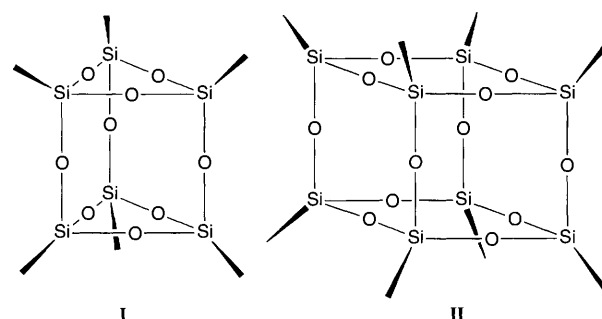
# Porous materials derived from trigonal-prismatic $\{\text{Si}_6\text{O}_9\}$ and cubane $\{\text{Si}_8\text{O}_{12}\}$ cage monomers

Philip G. Harrison\* and Rainer Kannengiesser

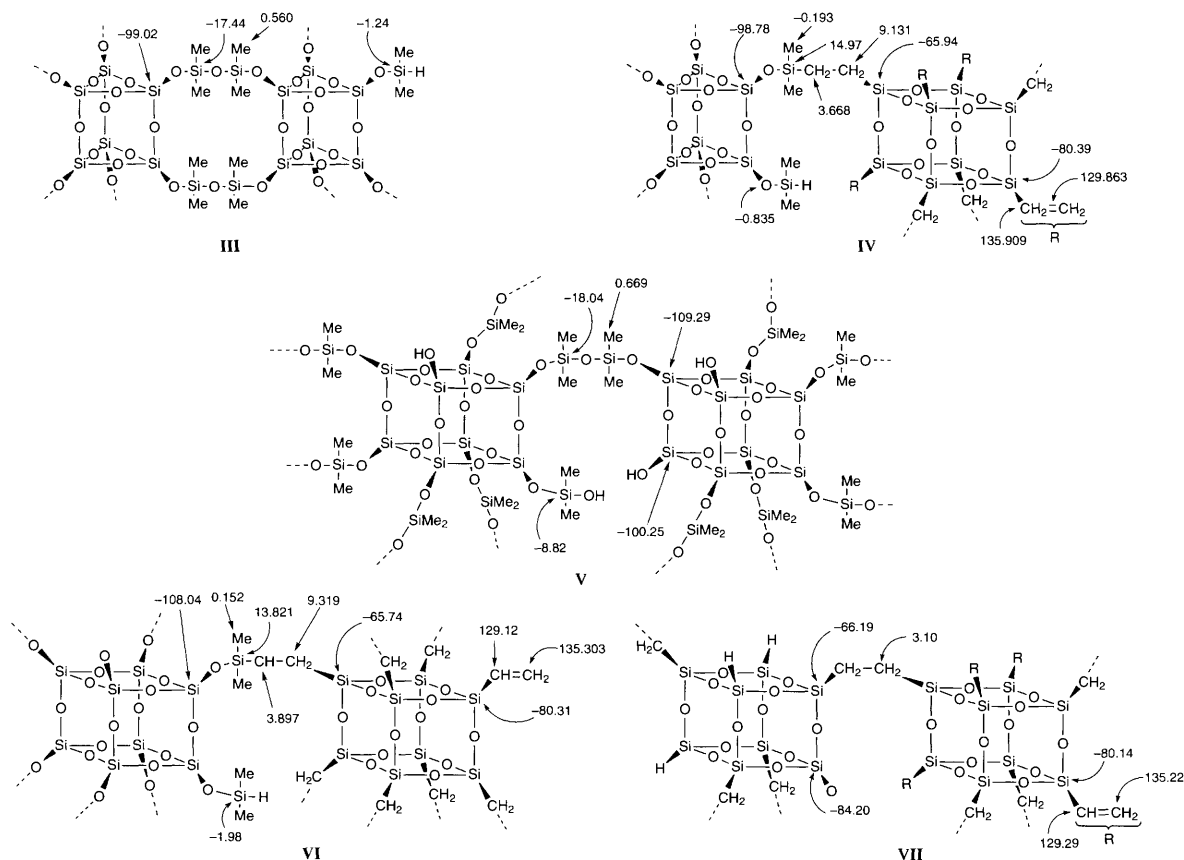
Department of Chemistry, University of Nottingham, University Park, Nottingham, UK NG7 2RD

New porous polymers are synthesized from  $\{\text{Si}_6\text{O}_9\}$  and  $\{\text{Si}_8\text{O}_{12}\}$  cage precursors and characterised by  $^{29}\text{Si}$  and  $^{13}\text{C}$  solid-state NMR spectroscopy; the specific surface areas of the polymers vary from 12.2 to 573  $\text{m}^2 \text{g}^{-1}$ .

Controlled pore inorganic solids play a key role in modern chemical technology as, *inter alia*, heterogeneous catalysts, adsorbents, and porous membranes. Although over the last several decades there has been enormous progress in the development of new porous materials, there exists an unsatisfied demand for still better materials. Zeolites are the epitome of porous materials. An examination of their structures shows that the smallest architectural unit is the cubane  $\{\text{Si}_8\text{O}_{12}\}$  although larger polyhedra are observed. Smaller cages, in particular the trigonal-prismatic  $\{\text{Si}_6\text{O}_9\}$  cage, are not found in zeolites. A rational synthetic approach to new porous materials which involves molecular precursors of the same polyhedra would therefore be potentially very fruitful. Spherosilicates of the general formula  $[\text{Si}_n\text{O}_{3n/2}]$  possessing a reactive *exo*-cage functionality are ideal candidates as precursors for three-dimensional structure formation. Here we describe routes to new porous materials based on preformed molecular cage



Scheme 1



Scheme 2

silicates in which both the cage structure and the inter-cage linkage unit may be varied, thereby enabling the possible tailoring of the porous characteristics of the resulting polymer.

Preparative routes to five new polymers **III–VII** derived from either the  $\{\text{Si}_6\text{O}_9\}$  **I** and/or the  $\{\text{Si}_8\text{O}_{12}\}$  **II** frameworks are shown in Scheme 1, eqns. (1)–(5). Two methods have been employed: (i)  $\text{H}_2\text{PtCl}_6$ -catalysed hydrosilylation of vinyl-substituted cages, and (ii) hydrolysis of bromosilane functions, and the general structures of the polymers formed are illustrated schematically in Scheme 2. The hydrosilylation reactions were carried out in refluxing toluene, gelation occurring after *ca.* 15 min. Hydrolysis of the bromosilanes was effected by ice–water. After separating off and drying *in vacuo*, the polymers were isolated as insoluble glassy powders.

Characterization of the structures of the polymer is most easily accomplished using  $^{29}\text{Si}$  and  $^{13}\text{C}$  solid-state NMR spectroscopy, and structures **III–VIII** are annotated with appropriate chemical shift data (ppm). Spectra for polymers **IV** and **V** exhibit only very small resonances due to unreacted cage functions, indicating that *ca.* 89 and 95%, respectively, of the available exocyclic functions (determined from integrated peak areas) participate in polymer linkage formation. In contrast, spectra for the other polymers show that the degree of polymerisation is much less, and only *ca.* 60–68% of linkage formation occurs under the conditions employed.

The two polymers derived from  $\{\text{Si}_6\text{O}_9\}$  cages, **III** and **IV**, as well as polymer **V** exhibit type II nitrogen adsorption isotherms with hysteresis on the desorption arm, behaviour characteristic of mesoporous materials. Specific surface areas of **III** and **IV**

are relatively low at  $12.2\text{ m}^2\text{ g}^{-1}$  (**III**) and  $63.4\text{ m}^2\text{ g}^{-1}$  (**IV**), but that of **V** is significantly higher ( $218.3\text{ m}^2\text{ g}^{-1}$ ). The adsorption isotherms of **VI** and **VII** are both type I but also exhibit hysteresis indicative of mixed microporous/mesoporous character. Specific surface area values for these polymers are  $147.0$  and  $573.7\text{ m}^2\text{ g}^{-1}$  respectively, the latter being comparable to values found in zeolites and much higher than the highest previously reported for polymers derived from molecular  $\{\text{Si}_8\text{O}_{12}\}$  cage precursors ( $206\text{ m}^2\text{ g}^{-1}$  and  $300\text{ m}^2\text{ g}^{-1}$ ).<sup>2,3</sup> Other similar polymers previously described exhibited either very small ( $4\text{--}7\text{ m}^2\text{ g}^{-1}$ )<sup>4,5</sup> or no significant surface area.<sup>1,6</sup> Powder XRD showed all the polymers to be amorphous.

We thank the SERC for an allocation of time on the solid-state NMR service at the University of Durham.

## References

- 1 D. Hoebbel, K. Endres, T. Reinert and H. Schmidt, *Mater. Res. Soc. Symp. Proc.*, 1994, **346**, 863.
- 2 D. Hoebbel, I. Pitsch, D. Heidemann, H. Jancke and W. Hiller, *Z. Anorg. Allg. Chem.*, 1990, **583**, 133.
- 3 D. Hoebbel, K. Endres, T. Reinert and I. Pitsch, *J. Non-Cryst. Solids*, 1994, **176**, 179.
- 4 D. Hoebbel, I. Pitsch and D. Heidemann, *Z. Anorg. Allg. Chem.*, 1991, **592**, 207.
- 5 D. Schultze, P. Kolsch, M. Noack, P. Toussaint, I. Pitsch and D. Hoebbel, *Z. Anorg. Allg. Chem.*, 1992, **612**, 137.
- 6 P. A. Agaskar, *J. Chem. Soc., Chem. Commun.*, 1992, 1024.

Received, 2nd November 1995; Com. 5/07241G