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Synthesis of functionalised porous network silsesquioxane polymers†

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Porous polyhedral silsesquioxane (POSS)-based network polymers are prepared using hydrosilation copolymerisation reactions of a silyl-functionalised POSS molecule with a vinyl-functionalised moiety. Characterisation of these solids show them to possess pore structures in the mesoporous regime, and polymers with longer organic linking groups showing evidence of flexible wall structures. Functionalisation of the polymers is carried out by reaction with triflic acid or sodium hydroxide, followed by incorporation of $CpTiCl_3$. EXAFS spectroscopy results are consistent with the titanium being coordinated to the oxygen atoms that make up part of a POSS unit.

Introduction

Polyhedral oligomeric silsesquioxanes (POSS) with the formula $R_8Si_8O_{12}$ provide an excellent platform for the synthesis of new inorganic–organic hybrid materials. Their well-defined, almost cubic silica-like core surrounded by eight organic groups (R) makes them topologically ideal for the preparation of intimate nanocomposite materials,[1] with the size of the inorganic region precisely defined by the size of the core. This has led to proposed uses of these molecules as hard blocks or reinforcing particles in high performance polymer materials.[2] Such polymers show many improved properties over those that use more traditional fillers (such as silica), including higher usage temperatures and increased fire retardance. The shape of the silica core of the molecule also lends itself well to the preparation of dendritic materials, where the large number of external branching sites on the core leads to a high concentration of dendrimer branch ends after relatively few generations.[3,4] These types of dendrimers have been studied as potential catalysts, and, when functionalised on the exterior with ligands such as phosphines, some very interesting effects on the selectivity of reactions have been observed.[5,6]

One striking feature of POSS molecules is their similarity to the secondary building units of zeolites. For example, the $R_8Si_8O_{12}$ unit shown in Fig. 1 can be regarded as structurally equivalent to the 4,4′ (double four-ring) unit found in zeolites LTA and ACO. The cubic topology of the molecule leads to some interesting opportunities to prepare micro- or mesoporous materials, as it is geometrically difficult to link cubes through only their corners and still fill all available space, although the degree of porosity must depend on the efficiency of polymerisation and the flexibility of the organic polymerisable group. Harrison and Kannengisser, and, subsequently, Laine *et al.* have shown that porous polymers can be prepared by the hydrosilylation of octavinyl-POSS species with octahydrido-POSS species (Fig. 1).[7,8] They reported polymeric materials with high surface areas that showed adsorption isotherms consistent with pores in the mesoporous regime. This paper reports an extension of this work to show that other silsesquioxanes also produce porous network polymers when copolymerised. In addition, we also show that it is possible to derivatise these porous polymers to yield potentially functional materials. In particular, we will report the incorporation of titanium into the polymers using a similar method to that used for the preparation of metallo-POSS homogeneous catalysts[9–11] or titanium-functionalised mesoporous solids.[12]

Experimental

All manipulations were carried out using standard Schlenk line techniques. MAS NMR spectra were collected at the University of Durham on a Varian UNITY 300 MHz spectrometer. Adsorption measurements were carried out using the Catalyst Evaluation and Optimisation Service at the University of Edinburgh and at the University of St. Andrews Centre for Advanced Materials. X-Ray fluorescence measurements were carried out in the Department of Geosciences at the University of St. Andrews.

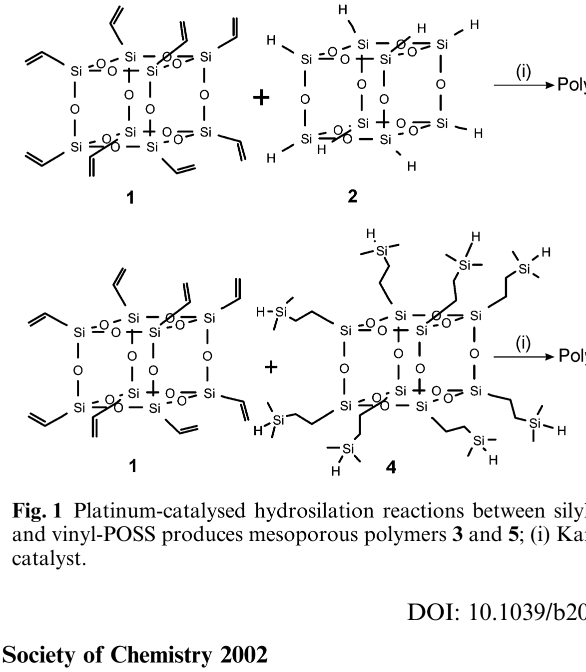

Fig. 1 Platinum-catalysed hydrosilation reactions between silyl-POSS and vinyl-POSS produces mesoporous polymers **3** and **5**; (i) Karstedt's catalyst.

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Synthesis of polymer 3

1 (0.3 g, 0.47 mmol) and **2** (0.2 g, 0.47 mmol) were stirred at room temperature in 20 cm^3 of dry toluene under argon for 4 h. After cooling to −78 °C, the solution was degassed and then maintained at 0 °C using an ice bath. Platinum divinyltetramethyldisiloxane complex in toluene (3.5 cm^3, 2 mM) was added to the solution, which was subsequently heated to 80 °C for 4 h. The product was recovered by filtration and dried for 48 h at atmospheric pressure (80 °C). The resultant polymer was dried under vacuum (80 °C, 0.02 mm Hg). Characterisation by N_2 and MAS NMR showed a similar polymer to that reported in ref. 8. Similar polymers can be prepared at room temperature.

Synthesis of polymer 5

Dry toluene (45 cm^3) was added to **1** (0.55 g, 0.876 mmol) and **4** (1 g, 0.876 mmol) under an argon atmosphere. The solution was degassed after cooling to −78 °C and then maintained at 0 °C using an ice bath. Platinum divinyltetramethyldisiloxane complex in toluene (3.5 cm^3, 2 mM) was added to the solution, which was subsequently heated to 80 °C for 4 h. The product was recovered by filtration, dried for 48 h at atmospheric pressure (80 °C) and dried *in vacuo* (100 °C, 0.02 mm Hg) to give a glassy solid (1.497 g). ^{29}Si CP MAS NMR (59.58 MHz, 25 °C): δ −80.9 ($O_3SiCH{=}CH_2$), −66.1 (O_3SiCH_2), −19.5 [CH_2SiMe_2H], 6.2 [$CH_2Si(CH_3)_2CH_2$]. $^{13}C\{^1H\}$ MAS NMR (75.43 MHz, 25 °C): δ −3.5 (CH_3), 5.5 (CH_2CH_2), 129.0, 135.9 ($SiCH{=}CH_2$).

Synthesis of polymer 6

Finely ground polymer **5** (0.502 g) was dried under vacuum for 2 h (100 °C, 0.2 mm Hg) and returned to atmospheric pressure under dry argon. Triflic acid (0.431 g, 2.87 mmol) was added to a suspension of the co-polymer in dry acetonitrile (10 cm^3). After stirring for 1 h at room temperature, additional dry acetonitrile (20 cm^3) was added to the reaction mixture and half of the liquid was decanted. This was repeated three times before the remainder of the liquid was removed under vacuum to leave a pale tan solid (0.475 g). ^{29}Si CP MAS NMR showed significant broadening of the resonance at −66 ppm (seen in the ^{29}Si CP MAS NMR of polymer **3**) and the appearance of a new peak at −60 ppm. There was also some evidence of a shoulder on the high-field side of the 6 ppm resonance.

Synthesis of polymer 7

A similar ring-opened polymer, **7**, can be prepared by treatment of polymer **3** with triflic acid or sodium hydroxide. Representative synthesis: 0.20 g POSS copolymer **3** was suspended in 10 ml methyl isobutyl ketone. To the mixture, 0.84 ml 1 M aqueous sodium hydroxide solution was added and the mixture was allowed to stir for 4 days. The solid was then removed by filtration, washed with acetone and dried under vacuum (80 °C, 0.05 mm Hg, 2 h).

Synthesis of polymer 8

Ring-opened POSS copolymer **7** (0.10 g) and trichloro(cyclopentadienyl)titanium(IV) (0.80 g, Aldrich) were purged three times with argon under standard Schlenk conditions. Anhydrous chloroform (10 ml, Aldrich) was added and the mixture allowed to stir for 24 h. After addition of 1.25 ml triethylamine (Acros; dried over 4 Å molecular sieves, Prolabo), the mixture was then stirred for a further 5 days. The suspended solid was then removed by filtration, and dried under vacuum (80 °C, 0.05 mm Hg, 2 h).

EXAFS spectroscopy

EXAFS data were collected on station 8.1 at Daresbury SRS (energy 2 GeV, current about 200 mA) by transmission. Wavelength selection was achieved using a double crystal Si(111) monochromator at 50% harmonic rejection. The Ti K-edge position was determined using titanium foil. The sample was mounted as a pellet with fused silica. The data were processed with EXCALIB (raw data processing), EXSPLINE (background subtraction) and EXCURV98 (comparing theoretical and experimental EXAFS).

Adsorption experiments

Nitrogen adsorption BET measurements[13] were conducted using a modified Hiden Analytical IGA-002. Samples were degassed for 2 h prior to analysis at a temperature of 125 °C whilst under vacuum to 10^{-7} mbar. Adsorption/desorption of nitrogen was conducted at 77 K. Adsorption measurements were collected firstly at a pressure of 10 mbar, and then in 30 mbar steps up to 870 mbar. Desorption measurement were then recorded, starting from 850 mbar, then decreasing in steps of 50 mbar to 50 mbar, with a final reading recorded at 30 mbar. The confidence level was 95% for both adsorption and desorption readings, with a time out set at 60 min. The pore size distribution was calculated using the cylindrical BJH method,[14] and the BET surface area calculated from the slope of the isotherm at P/P_0 values up to 0.20 (9 points).

Results

Synthesis and porosity of polymers

The reaction of octavinyl-POSS (**1**) with octahydrido-POSS (**2**) in the presence of a platinum-based hydrosilylation catalyst (Karstedt's catalyst) has been shown by Harrison and Laine to produce porous solids with N_2 adsorption isotherms indicative of porosity in the micro to meso range.[7,8] We have repeated these preparations using the reported conditions and obtained similar results. The N_2 isotherms show almost no hysteresis on desorption (Fig. 2). The pore size distribution, calculated using the BJH method, is similar to that reported by Laine.[8] Twelve samples of **3** were prepared and BET analysis of their N_2 adsorption yielded repeatable results showing surface areas between 450 and 550 $cm^3\ g^{-1}$. The porosity of polymer **3** was further assessed using cyclopentane adsorption, and the isotherm from this experiment is also shown in Fig. 2. As expected, the surface area accessible to this larger molecule is reduced, (*e.g.* from 475 to 323 $cm^3\ g^{-1}$), but still shows significant porosity, consistent with the presence of large pores.

To assess the thermal stability of the polymers and the effect of calcination on the porosity of the materials, samples of POSS copolymer **3** were calcined under a steady flow of oxygen. For each temperature studied, a sample was heated at 10 °C min^{-1} and allowed to remain at the set temperature for a period of 200 min. After being allowed to cool to room temperature, nitrogen absorption was used to determine the BET surface area. The results are reported in Table 1 and show a steady decrease in accessible surface area as the calcination temperature is increased. Thermogravimmetric analysis shows that, at 400 °C, the mass lost by the sample is almost sufficient to account for all the organic component of the polymer and that the residue is essentially a mesoporous (but not ordered) silica. Loss of organic material is complete at 600 °C.

To further investigate the effect of the flexibility of the linking organic group, a novel polymer based on reaction of octasilyl-POSS, **4** (which was prepared according to the previously reported method[3]), with **1** was synthesised. This produced a mesoporous material **5**. The N_2 adsorption isotherm is not of the classical type IV normally associated with mesoporous materials, as it contains a non-closing hysteresis of the H4 type

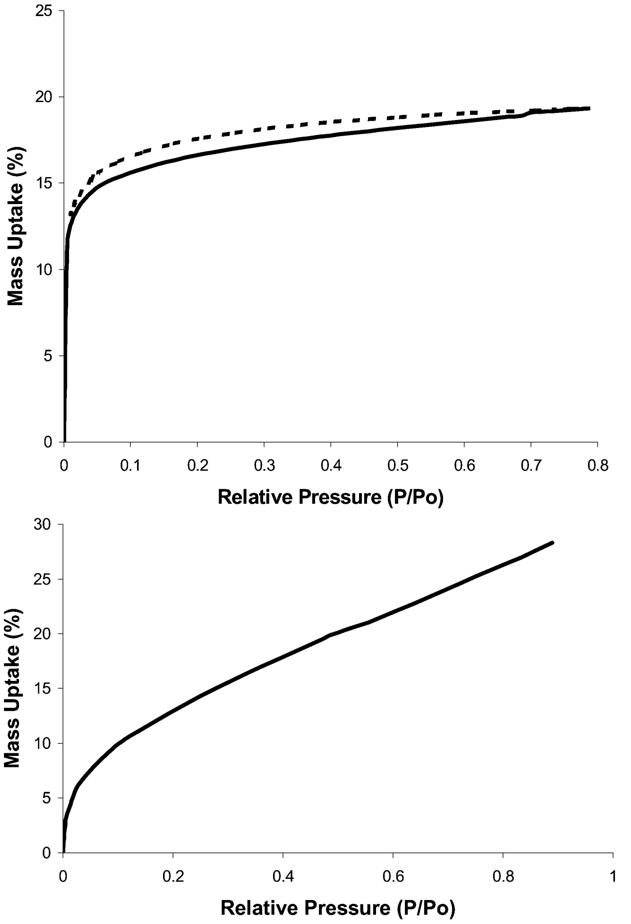


Fig. 2 Nitrogen (top) and cyclopentane adsorption isotherms for polymer **3**. The nitrogen isotherm shows both adsorption (solid line) and desorption (dashed line) steps.

Table 1 BET surface areas calculated from N_2 adsorption isotherms for calcined samples of polymer **3**.

Calcination temperature/°C	BET surface area/$m^2\ g^{-1}$
Not calcined	539
150	524
200	448
250	441
400	356

(Fig. 3) where the two branches remain nearly horizontal and parallel over a wide range of P/P_0.[15] The low pressure hysteresis extends to the lowest attainable pressures, indicating that some of the adsorption is irreversible under the experimental conditions. This phenomenon may be associated with the swelling of a non-rigid porous structure or with the irreversible uptake of molecules in pores (or through pore entrances) of about the same width as the adsorbate molecule.[16] This unusual behaviour is therefore probably due to the presence of micropores as well as mesopores in the polymer, and to the flexible nature of the organic linking groups. The materials were characterised by magic angle spinning (MAS) NMR (^{29}Si and ^{13}C), and from direct polarisation MAS NMR experiments the degree of cross-linking was estimated to be ~50 and ~80% for polymers **3** and **5**, respectively. This is as expected, as the longer more flexible organic group on the exterior of POSS molecule **4** will certainly lead to more linkages being possible for any given relative orientation of two POSS units in the polymer when compared to the more constrained molecule **2**.

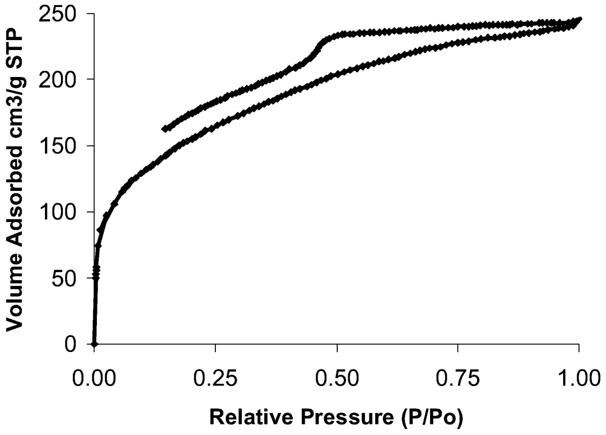


Fig. 3 N_2 adsorption isotherm for polymer **5**, clearly showing the H4-type hysteresis.

Functionalisation of the polymers

The similarity between the POSS species and the secondary building units found in zeolites such as Linde-A is obvious, and the preparation of these inorganic–organic hybrid materials which, while not crystalline, have very similar pore sizes to both the zeolite and mesoporous families of silicates, opens up the possibility of preparing network polymer 'mimics' of these very important materials. The presence of the organic group in the structure will undoubtedly lead to different properties (*e.g.* hydrophobicity) to those of zeolites, which may be advantageous in certain instances. However, in order to produce functional 'zeolite-like' materials, derivatisation of the POSS species must be accomplished. Feher has shown very elegantly how POSS species can, in solution, be 'ring opened' by reaction with organic acids and bases.[17–20] This remarkable reaction occurs in high yield to produce very specific products, and similar methods were used by us in an attempt to derivatise the POSS polymers we have prepared with silanol groups. Reaction of the polymer **5** with triflic acid under the conditions reported in ref. 17 yielded a new material, polymer **6** (Fig. 4), whose IR spectra showed considerable broadening in the Si–O–Si region compared to that from the parent polymer, consistent with a loss of local symmetry in the POSS species. ^{29}Si MAS NMR of the treated polymer revealed broadening of the resonance associated with the POSS silicon atoms at δ −66 ppm and a significant resonance at *ca.* −58 to −60 ppm (Fig. 5). These shifts are the same as those reported by Feher in ref. 17 for the disilanol-functionalised POSS species, and indicate that the reaction with the triflic acid has indeed ring opened a small proportion of the POSS species to produce silanol groups that can be further functionalised. Direct polarisation ^{29}Si NMR experiments indicate that the number of POSS species reacting is relatively small (<10%) and there is no evidence at the

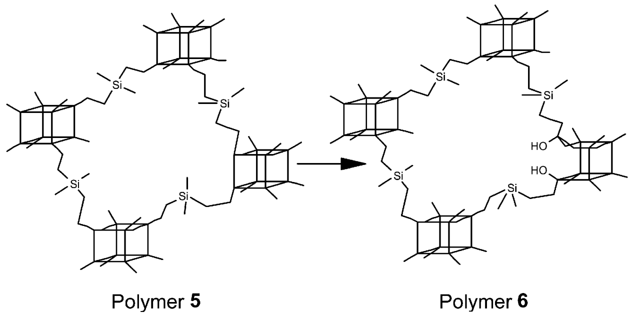


Fig. 4 Schematic diagram of polymer-opening experiments by reaction of polymer **5** with dilute triflic acid solution followed by hydrolysis. This diagram shows just two silanol groups on any POSS species. However, it is equally likely that there may be more than two per POSS unit.

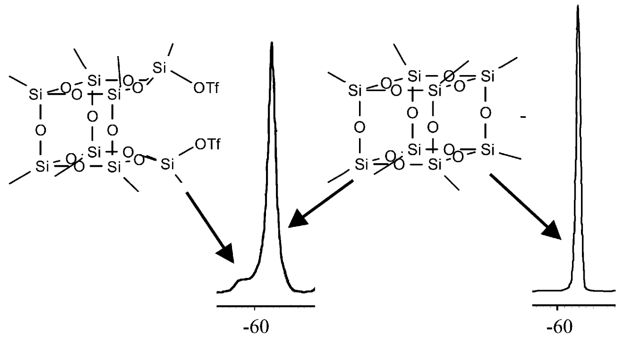
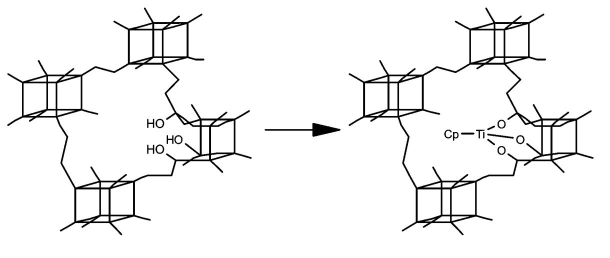


Fig. 5 The T3 regions of the ^{29}Si MAS NMR spectra of polymer **5** (right) and polymer **6** (left), showing a sharp resonance from silisesquioxane silicon atoms that is broadened after treatment with triflic acid. The small resonance at *ca.* −58 ppm is assigned to the T2 silicons from the 'ring-opened' silsesquioxane cube, in accordance with the solution-state ^{29}Si NMR data reported by Feher *et al.*[17–20]

present time as to the location of the reaction, although, because of the relatively large size of the pores, it would be expected that reaction would have taken place at both external and internal surface sites. Similar results are found on reaction of polymer **3** with triflic acid. Reaction of polymers **3** or **5** with bases, such as NaOH, leads to a greater proportion of ring-opened POSS species (from the ^{29}Si NMR spectra), but also further breakdown of the polymer structure and the appearance of resonances at *ca.* −100 ppm in the ^{29}Si MAS NMR, indicative of the production of $SiO_{4/2}$ (silica) species. Long reaction times or higher reaction temperatures leads to relatively more silica species being formed.

Functionalisation of polymers with titanium

Titanium-functionalised silica species have received much interest over recent years. Ti-POSS molecules have been shown by a number of groups to be excellent homogeneous catalysts,[9–11] and porous titanium-containing materials, such as the microporous TS-1 and mesoporous Ti-MCM-41, have been reported as excellent heterogeneous oxidation catalysts.[12] The silanol-containing polymers reported in the previous section should have POSS-species that are in essence identical to the incompletely condensed POSS species used to prepare the homogeneous Ti-POSS catalysts. Titanium has been incorporated into the polymers by reaction with $CpTiCl_3$ in the presence of a weak base such as triethylamine (Fig. 6). X-Ray fluorescence measurements on the resultant polymer showed that they contained between 4 and 5 wt% Ti, with almost no chloride left in the sample, indicating that the titanium has most likely become attached to the polymer framework. The porosity of this sample was studied using nitrogen adsorption, with the isotherm (Fig. 7) having a similar form to that of the isotherm for the unreacted polymer (Fig. 2), again with very little hysteresis on desorption. However, the BET surface area of the material has been reduced significantly, and a comparison of the pore size distribution with that of polymer **3** shows this clearly (Fig. 8).



Polymer **7** Polymer **8**

Fig. 6 Schematic representation of incorporation of titanium into silanol-containing polymers. The local structure around the titanium is consistent with the results from the EXAFS experiments. However, the exact arrangement and location of the silanol groups in **7** and the Ti–O–Si linkages in **8** is, at present, unknown, and this figure represents only one possibility.

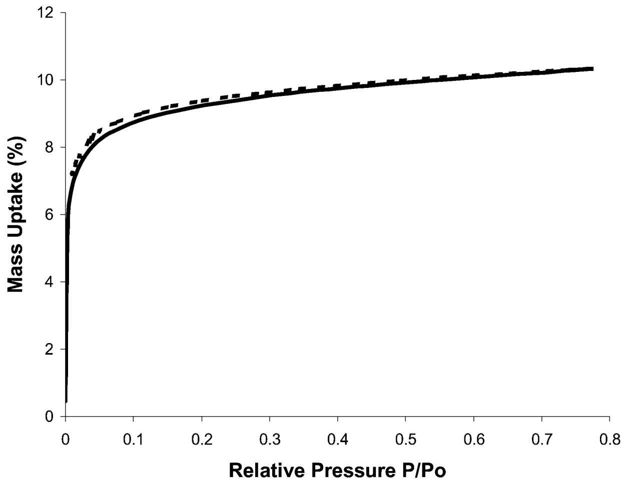


Fig. 7 Nitrogen adsorption (solid line) and desorption (dashed line) isotherms for the titanium-loaded ring-opened polymer **8**.

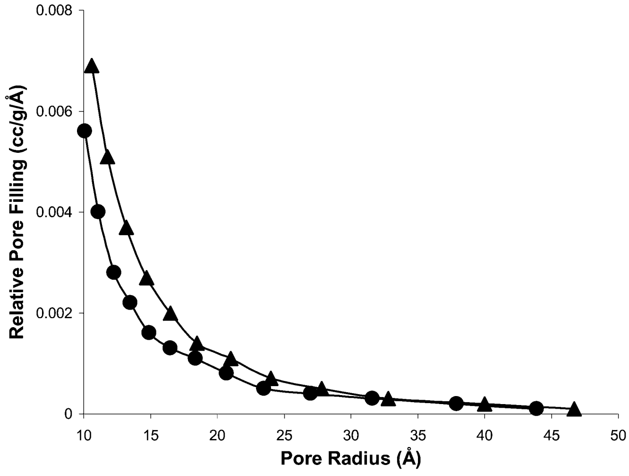


Fig. 8 Comparison of cylindrical BJH pore radii for silsesquioxane copolymer **3** (▲) and titanium-loaded ring-opened copolymer **8** (●).

The local structure around the titanium in polymer **8** was studied using EXAFS spectroscopy, and the results fitted reasonably well with the titanium being bound to one Cp group (5 carbons) and three oxygen atoms, with the next neighbour shell comprising three silicon atoms from a POSS unit. The results are therefore consistent with the titanium being bound through Ti–O–Si linkages to the POSS units in a similar manner to that seen in the single-crystal X-ray diffraction structures of Ti-POSS molecules. The fit to the EXAFS data is shown in Fig. 9, and the results are listed in Table 2.

Discussion

This work has shown that POSS-containing polymers can be prepared using hydrosilation reactions between Si–H and vinyl POSS species to produce materials with a mesoporous structure. We have extended the work previously published to produce a new polymer with longer organic linkages and shown that its N_2 adsorption isotherm is consistent with a 'flexible' structure.

Interestingly, the fascinating reactions of POSS molecules with triflic acid in solution also occur in the polymeric species,

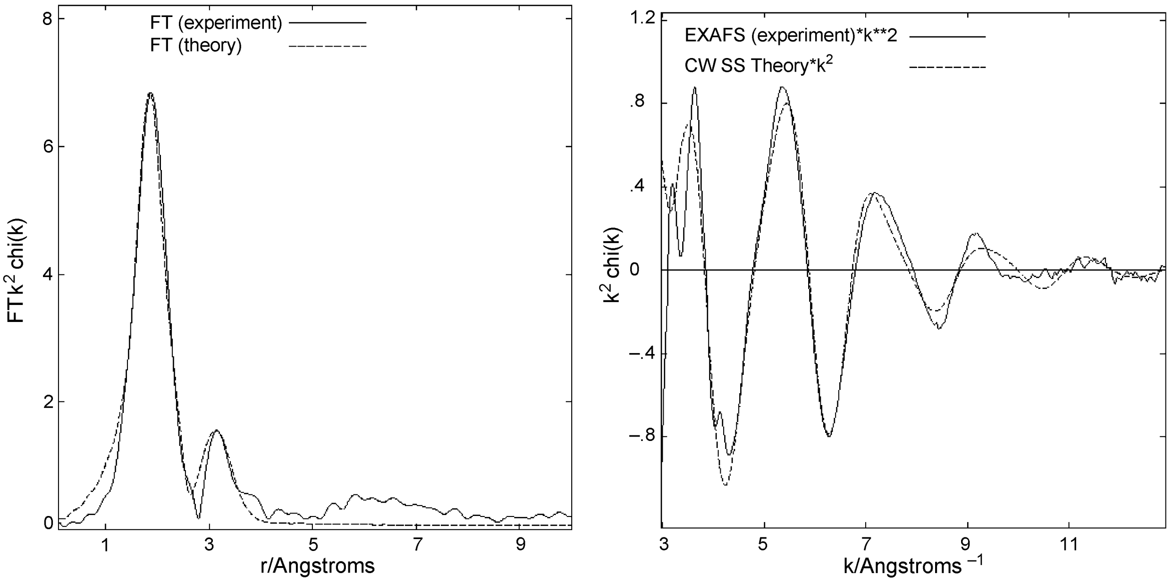


Fig. 9 Ti K-edge EXAFS spectra for polymer **8**, showing the experimental data (solid line) and the fitted curve (dashed line).

Table 2 Ti K-edge EXAFS data for polymer **8**[a]

	Ti–O/Å	Ti–C/Å	Ti–Si/Å
Refined EXAFS distances (*ca.* ±0.03 Å)	1.87	2.45	3.19
Occupation numbers (N)	3	5	3
Debye-Waller factors (σ^2)	0.009	0.015	0.017

[a]AFAC = 0.88; R = 29.81%.

with evidence that a number of the POSS units in the polymers are ring opened by having one or more of the Si–O–Si linkages broken. Similar reactions also occur with dilute sodium hydroxide. These reactions open up the exciting possibility of derivatising the polymers with metals. One obvious use of such metal-derivatised polymers is as catalysts, possibly used in a similar way to other porous solids like zeolites and mesoporous silica. In fact, there are potential advantages of using inorganic–organic hybrid polymers, including the fact that the presence of organic regions in the structure must surely affect the hydrophobicity of a catalyst, which can be important in a number of reactions. We have shown that it is possible to incorporate titanium into the polymer and so this scenario is a distinct possibility. Unfortunately, while the CpTiCl$_3$ species used as the titanium source is excellent for characterisation of the resulting polymers (the large number of equidistant carbon atoms from the titanium is an excellent marker in EXAFS spectroscopy), for this type of material to be useful for catalysis, the Cp units should be removed by calcination in oxygen. Unfortunately, the polymer network itself is not thermally stable enough to allow this activation procedure, and so catalytically active polymeric materials must be prepared that do not need this extra calcination step. Nevertheless, the characterisation of the polymers we have prepared does show that functional materials, such as catalysts, are achievable in this system.

Conclusion

We have prepared a number of porous inorganic–organic hybrid polymers and shown how it is possible to functionalise them with titanium. This provides a number of exciting possibilities for the production of inorganic–organic 'mimics' of zeolites and microporous materials, and work is continuing to prepare further examples of this type of polymer and to examine more closely their properties.

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