

Siloxane Network Formation from the $\text{Si}_8\text{O}_{20}^{8-}$ Silicate Species and Dimethyldichlorosilane

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Organic-silica hybrids were synthesized from the $\text{Si}_8\text{O}_{20}^{8-}$ silicate anion by the reaction with an excess of dimethyldichlorosilane. The structure of the hybrids has been found to comprise the $\text{Si}_8\text{O}_{20}^{8-}$ structure as a building block, linked by the $(\text{CH}_3)_2\text{Si}$ unit. ^{29}Si NMR signals from terminal groups in the hybrids have been assigned. When the amount of dimethyldichlorosilane present for the reaction is increased, the number of terminal groups decreases, indicating that cross-linking of $\text{Si}_8\text{O}_{20}^{8-}$ with dimethyldichlorosilane proceeds to form three-dimensional siloxane networks in the hybrids. Copyright © 1999 John Wiley & Sons, Ltd.

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INTRODUCTION

Polyhedral silsesquioxane¹ and siloxane^{2,3} compounds have been employed successfully as starting materials for organic-silica (SiO_2) hybrids.^{4–12} The salient feature of the hybrids is the regulated structure of the SiO_2 component involved. The polyhedral structure of the compounds becomes the building block of polymeric networks of the hybrids. Such a control over the SiO_2 component cannot be achieved by common hydrolysis and polymerization processes of alkoxysilane or chloro-

silane. Thus, this synthesis procedure for the hybrids is referred to as the building block approach.

Another feature of the hybrids is that the hybrids with three-dimensional networks often show high surface areas,^{6,7,9–12} which would be potential as membranes and catalyst supports. Accordingly, the polyhedral compounds are useful starting materials for high-surface-area organic- SiO_2 hybrids. However, some of them have not revealed a high surface area. Hoebbel *et al.* reported that the surface area of the hybrids varies drastically with bond length between polyhedral structural units.⁷ Agaskar reported that the hybrids he produced may have lamellar or columnar structures as one of possible reasons for the low surface area of the hybrids.⁵ These observations suggest that the polyhedral compounds would be competent for building units of a wide variety of nanostructures.

Synthesis of the hybrids has been carried out, in most cases, by hydrosilylation. In order to increase the types of the hybrids to be formed, however, it would be necessary to study on alternative reactions for linking the compounds without decomposition of their structures.

We have been studying the reaction of the $\text{Si}_8\text{O}_{20}^{8-}$ anion, formed selectively in methanolic tetramethylammonium $[\text{N}^+(\text{CH}_3)_4]$, TMA silicate solution, with dimethyldichlorosilane $[(\text{CH}_3)_2\text{SiCl}_2]$, DMDCS.^{10–12} It was demonstrated that the reaction gives organic- SiO_2 hybrids in which the $\text{Si}_8\text{O}_{20}^{8-}$ core is linked via the $(\text{CH}_3)_2\text{Si}$ unit. The specific surface area of the hybrids was low, but could be increased up to $339 \text{ m}^2 \text{ g}^{-1}$ by additional heat treatment at 350°C in air.

The synthesis of the hybrids was carried out by the reaction of $\text{Si}_8\text{O}_{20}^{8-}$ with DMDCS at a DMDCS/ SiO_2 molar ratio of 1.0, i.e. at a DMDCS/ $\text{Si}_8\text{O}_{20}^{8-}$ molar ratio of 8.0. In order to investigate the structural changes that take place

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in the products synthesized using larger amounts of DMDCS, the reaction has been conducted at DMDCS/SiO₂ ratios of 1.5 and 2.0 in this study. The products have been characterized with gel-permeation chromatography (GPC), differential thermal analysis–thermogravimetry (DTA–TG), and solid-state ¹³C and ²⁹Si NMR spectroscopy.

EXPERIMENTAL

Materials

A methanolic solution of TMA silicate with a SiO₂ concentration of 1.0 mol dm⁻³, a TMA hydroxide concentration of 1.0 mol dm⁻³, and an H₂O concentration of 10.0 mol dm⁻³, was used as the Si₈O₂₀⁸⁻ source. The procedure for the preparation is detailed in Ref. 13. The selective formation of the silicate anion in the solution was confirmed by a trimethylsilylation technique combined with gas chromatography¹⁴ and ²⁹Si NMR spectroscopy.¹⁵

Reaction of the Si₈O₂₀⁸⁻ species with DMDCS

The reactions at DMDCS/SiO₂ ratios of 1.5 and 2.0 were carried out at room temperature for 1 h using 2,2-dimethoxypropane as solvent, i.e. employing the same procedure as that for the reaction at the ratio of 1.0¹¹ THF was added to single-phase reaction mixtures to precipitate out TMA chloride formed as a by-product. Then, the filtrate was heated at 65 °C *in vacuo* to remove the solvent and low-boiling components, resulting in viscous products and residual TMA chloride. The products were recovered by dissolving in THF. (GPC measurements were conducted on these THF solutions.) By removing THF from the solutions at 160 °C *in vacuo* with an evaporator, the final products were obtained, which were not soluble in THF.

Hydrolysis treatment of the final product

The final product obtained by the reaction at a DMDCS/SiO₂ ratio of 1.5 (250 mg) was immersed in a mixture (10 cm³) of acetone, distilled water (2.5 cm³) and 0.5 mol dm⁻³ hydrochloric acid (2 cm³), then stirred at room temperature for 24 h in order to remove the methoxyl group in the product.

Analytical procedures

GPC curves of products soluble in THF were measured at 40 °C using a Shimadzu LC-6 liquid chromatograph equipped with a Shimadzu RID-6A differential refractive index detector and Tosoh G2000H8 and G4000H8 columns connected in series (i.d. 7.8 mm, length 60 cm each). The mobile phase was THF at a rate of 1.0 cm³ min⁻¹.

The solid-state ²⁹Si single-pulse/magic-angle spinning (SP/MAS) NMR spectra of the products shown in Fig. 2 (below) were obtained on a JEOL GSX-400 spectrometer. The analysis conditions were the same as those described in Ref. 11. The ¹³C and ²⁹Si NMR spectra, shown in Figs. 3 and 4, respectively, were obtained with a JEOL EX270WB spectrometer using spin-lock cross-polarization sequences in combination with MAS (CP/MAS). Samples were packed into the cylindrical zirconia rotor for the measurements. Line narrowing was achieved by high-power ¹H decoupling and MAS. The spinning rate was set at *ca* 6 kHz. The other conditions were as follows; for ¹³C, frequency 67.80 MHz, contact time 5 ms, repetition time 5 s, spectral width 27 kHz, 8000 data points; for ²⁹Si, frequency 53.54 MHz, contact time 9 ms, repetition time 5 s, spectral width 20 kHz, 8000 data points. Spectra were accumulated 200–400 times to achieve a reasonable signal-to-noise ratio. ¹³C and ²⁹Si chemical shifts were calibrated indirectly through the ¹³C and ²⁹Si signals due to polydimethylsilane and then converted to the values from tetramethylsilane.

The siloxane structural unit is denoted using the notations D and Q, which correspond to (CH₃)₂Si(O⁻)₂ and Si(O⁻)₄ siloxane units, respectively. Superscripts indicate the number of Si atoms adjacent to a siloxane structural unit.

DTA–TG analysis was conducted in air over the range of room temperature to 800 °C using a MAC Science TG–DTA 2000S analyzer.

RESULTS AND DISCUSSION

Figure 1 shows GPC curves of products formed upon reaction of Si₈O₂₀⁸⁻ with DMDCS at a DMDCS/SiO₂ ratio of (a) 1.5 and (b) 2.0. The molecular weight distribution of the product obtained by the reaction at the ratio of 1.0 was reported previously.¹⁰ Comparing these curves, the reaction at a higher DMDCS/SiO₂ ratio appears to give products with higher molecular weights.

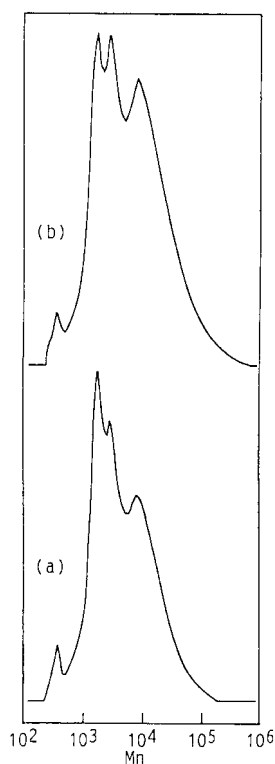


Figure 1 GPC curves of products obtained upon the reaction of $\text{Si}_8\text{O}_{20}^{8-}$ with DMDCS at a DMDCS/ SiO_2 ratio of (a) 1.5 and (b) 2.0 in 2,2-dimethoxypropane at room temperature for 1 h.

THF solutions of the products were then allowed to evaporate to remove the solvent and low-boiling components, resulting in the formation of final products which were insoluble in THF. The solid-state ^{29}Si NMR spectra of the final products at the ratio of 1.5 and 2.0 are shown in Figs. 2(b) and (c), respectively, whereas that of the product at the ratio of 1.0 is shown in Fig. 2(a) (adapted from Ref. 11).

The Q^4 unit in the products gives rise to a signal at -109.1 ppm. On the basis of the previous study,¹¹ the signal would be attributed to the unit involved in the $\text{Si}_8\text{O}_{20}^{8-}$ core. In addition, a signal at -17.7 ppm [labeled c in Fig. 2(b)] would be assigned to the D^2 unit adjacent to the Q unit, indicating the presence of $(\text{O}^-)(\text{CH}_3)_2\text{Si}-\text{O}-\text{Si}(\text{O}^-)_3$ bonds. These would indicate that the products at the ratios of 1.5 and 2.0 are also organic- SiO_2 hybrids consisting of the $\text{Si}_8\text{O}_{20}^{8-}$ structure as a building block, linked via the $(\text{CH}_3)_2\text{Si}$ unit.

Comparing these spectra, some differences can

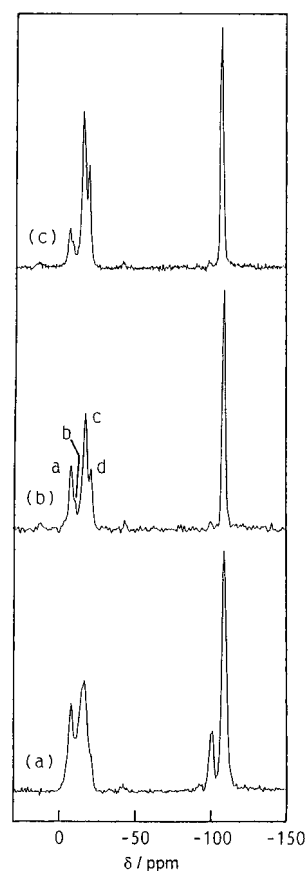


Figure 2 The ^{29}Si SP/MAS NMR spectra of organic- SiO_2 hybrids formed by the reaction of $\text{Si}_8\text{O}_{20}^{8-}$ with DMDCS at a DMDCS/ SiO_2 ratio of (a) 1.0, (b) 1.5 and (c) 2.0.

be observed which would be caused by the difference in the DMDCS/ SiO_2 ratio. The Q^3 signal at -100.1 ppm is seen clearly in Fig. 2(a), but its intensity is apparently low in the spectra of the hybrids obtained at the ratios of 1.5 and 2.0. This signal has been assigned to the Q^3 unit in the $\text{Si}_8\text{O}_{20}^{8-}$ building block of the hybrids which was left unreacted.¹¹ The disappearance of the signal would indicate that almost all the Q^3 units in the $\text{Si}_8\text{O}_{20}^{8-}$ species had undergone the reaction.

An alternative difference is seen in the D region from -8 to -21 ppm. Four distinct signals, labeled a–d in Fig. 2(b), appear in the region of spectra of the hybrids formed at the ratios of 1.5 and 2.0. Signal d at -21.3 ppm is ascribable to the D^2 unit connecting to D units, and signal c at -17.7 ppm to the D^2 unit connecting to Q units.^{10–12,16,17} These signals increase in intensity with an increase in the

Table 1. Ratio of the weight loss of organic-SiO₂ hybrids over the temperature range 345–536 °C to the weight of residual SiO₂ powders, measured by TG analysis in air

DMDCS/SiO ₂ ratio for the reaction	Ratio of weight loss (wt%)
1.0	4.7
1.5	5.9
2.0	10.7

DMDCS/SiO₂ ratio for the reaction, suggesting that a larger proportion of the organic moiety is incorporated into the hybrids.

This finding can be confirmed with DTA–TG. The DTA curves of the hybrids formed at the ratios of 1.5 and 2.0 show similar characteristics to those of the hybrids at the ratio of 1.0;¹² weight loss takes place together with exothermal reactions at 245–295 and 345–646 °C. We previously reported that the thermal decomposition of CH₃–Si≡ bonds in the hybrids takes place at 345–536 °C.¹² Therefore, the content of the organic moiety in the hybrids can be estimated roughly from the weight loss occurring in this temperature range (Table 1). It is seen that a larger proportion of the organic moiety is involved in the hybrids formed by the reaction at a higher DMDCS/SiO₂ ratio.

Signal a at –8.8 ppm has been assigned to the D¹ unit with the hydroxyl group, i.e. the (HO)(CH₃)₂Si(OSi) unit, in the previous work.¹¹ Therefore, signal b at –10.8 ppm, which remained unassigned, is expected to result from D¹ units in a different state.

For the assignment, the hybrids formed at the ratio of 1.5 were submitted to hydrolysis treatment. This is because the presence of the CH₃–O–Si≡ bond in the hybrids formed by the reaction at the ratio of 1.0 was demonstrated by FT-IR spectroscopy and solid-state ¹³C NMR spectroscopy,^{11,12} but no apparent signal for the linkage was found in their solid-state ²⁹Si NMR spectrum. The formation of the methoxyl group in the hybrids was considered to result from esterification taking place simultaneously with the reaction of Si₈O₂₀^{8–} with DMDCS,^{11,12} since a considerable amount of methanol was present in the reaction system, which was supplied from the methanolic solution of TMA silicate employed as the Si₈O₂₀^{8–} source and was additionally formed by the hydrolysis of the solvent, 2,2-dimethoxypropane. The reaction system was acidic owing to the presence of Cl[–] formed

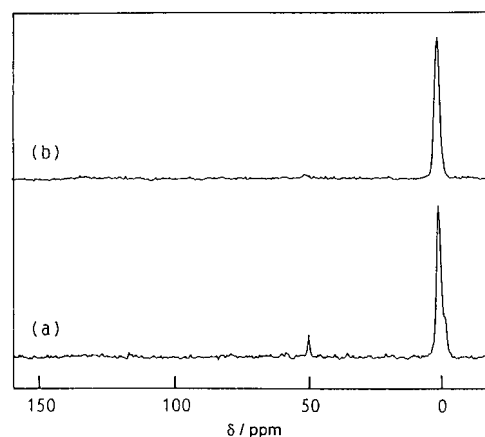


Figure 3 The ¹³C CP/MAS NMR spectra of organic-SiO₂ hybrids at a DMDCS/SiO₂ ratio of 1.5 (a) before and (b) after the hydrolysis treatment.

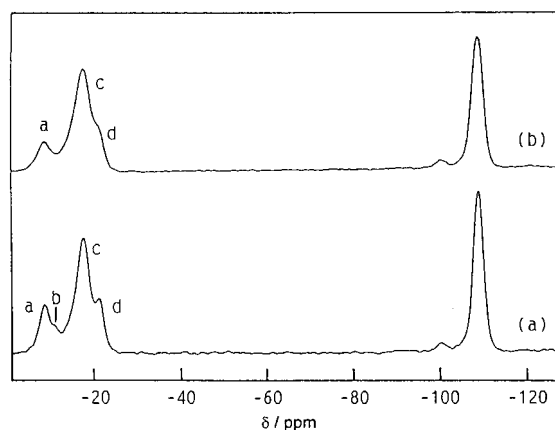


Figure 4 The ²⁹Si CP/MAS NMR spectra of organic-SiO₂ hybrids obtained at a DMDCS/SiO₂ ratio of 1.5 (a) before and (b) after the hydrolysis treatment.

from DMDCS, which was suitable for the esterification.

Figures 3 and 4 show solid-state ¹³C and ²⁹Si NMR spectra, respectively, of the hybrids (a) before and (b) after the hydrolysis treatment. The hybrids before hydrolysis give rise to a signal at 50.1 ppm in the ¹³C NMR spectrum [Fig. 3(a)], which has been assigned to the CH₃–O–Si≡ group in the hybrids.^{11,12} The signal disappears after hydrolysis [Fig. 3(b)], indicating removal of the methoxyl group by this treatment. The removal causes signal b to disappear in the solid-state ²⁹Si NMR spectrum, as is seen in Fig. 4(b). Thus, signal

b would be attributable to the D¹ unit with the methoxyl group, (CH₃O)(CH₃)₂Si(OSi).

It was reported, however, that D¹ units in compounds consisting of D units solely give rise to signals around -12 ppm in ²⁹Si NMR spectra,^{18,19} which is ca 4 ppm lower than the signals due to D¹ units in the hybrids. Considering that signals due to D² units connecting to Q units appear ca 4 ppm upfield of those due to D² units connecting to D units,^{16,17} replacement of D units adjacent to a D unit with Q units is likely to result in ca 4 ppm shift to the higher frequency. This fact would suggest that signals a and b are due to D¹ units neighboring the Q unit. In other words, all D¹ units in the hybrids would attach to the Si₈O₂₀⁸⁻ core.

With increasing DMDCS/SiO₂ ratio for the reaction, signals a and b and the signal due to the Q³ unit decrease in intensity, indicating a decrease in the number of terminal groups in the hybrids. Recalling that the GPC curve of THF-soluble products formed at a higher DMDCS/SiO₂ ratio moves toward the higher molecular weight, it appears that the reaction at the higher ratio promotes cross-linking, resulting in the formation of three-dimensional siloxane networks in the hybrids.

CONCLUSION

The reactions of the Si₈O₂₀⁸⁻ silicate species with DMDCS at DMDCS/SiO₂ ratios of 1.5 and 2.0 gave organic-SiO₂ hybrids with larger organic contents, which were also found to consist of the Si₈O₂₀⁸⁻ core as a building block linked via the (CH₃)₂Si unit. The reaction at a higher DMDCS/SiO₂ ratio increased the degree of cross-linking, leading to the development of three-dimensional siloxane networks of the hybrids. In addition, information on structures of terminal D¹ units could be obtained from solid-state ²⁹Si NMR spectra of the hybrids.

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