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Preparation of Silsesquioxane Particles via a Nonhydrolytic Sol−Gel Route

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A recently developed method of synthesizing organic−inorganic hybrid (nano)particles using a nonhydrolytic sol−gel route is reported. A range of silsesquioxane particles with diameters in the range ca. 0.1−2.0 μm has been prepared by reacting organotrichlorosilane precursors with dimethyl sulfoxide, used both as an oxygen donor and as a solvent, in the absence of a catalyst under nonaqueous conditions. Pure silica particles with diameters in the range ca. 100−400 nm have been produced by the same method using silicon tetrachloride as a precursor. Ethoxysilane, silanol, and, sometimes, paraformaldehyde groups are present in incompletely condensed species. The formation of silanol groups is insignificant in silsesquioxanes, but not in “unmodified” silicas. A major advantage of this approach is the absence of catalyst residues and, hence, color in the final product in comparison to the normal Lewis acid-catalyzed route.

1. Introduction

The sol−gel process has attracted considerable interest over the past four decades as a versatile low-temperature route to inorganic oxides and their hybrids. One of the major advantages of this method is the possibility to produce a wide range of product forms, such as fibers, coatings, porous monoliths, and nanoparticles. The nonhydrolytic sol−gel process has proved to be a useful route to both inorganic oxides and organically modified inorganic oxides, such as ormosils or organically modified silicas. Although the more widely used hydrolytic sol−gel approach still plays a dominant role by providing convenient methods for the production of ormosils,[1−5] the nonhydrolytic route has received a significant amount of attention over the past few years as an alternative method with a number of associated advantages, such as the potential to avoid the use of solvents, as well as the possibility to eliminate the presence of residual silanol groups in the product. A number of studies have focused on the nonhydrolytic sol−gel synthesis of inorganic oxides, such as titania,[6−9] alumina,[7,9] and silica,[7−11] which involves the reaction of a “metal” halide with an oxygen donor, such as an alkoxide, an alcohol, an ether, and so forth under nonaqueous conditions. More recently, this method has been extended to the production of ormosils, where the organic groups are normally alkyl chains, aryl groups, or vinyl groups.[12−14] Both ormosils containing one organic group every two silicon atoms and silsesquioxanes, where each silicon atom is covalently bonded to one organic group, can be obtained using the nonhydrolytic sol−gel route. According to the most common approach, the ormosils are synthesized by reacting silicon halides with alkoxysilanes or dialkyl ethers in the presence of a Lewis acid catalyst.[13−17] However, a plethora of work has been concerned with the synthesis of ormosil materials in the form of bulk or monolithic products, and the effort on ormosil particles, particularly nanoparticles, prepared by the nonhydrolytic sol−gel method has been very limited. The only relevant work in this area is previous work by our group,[17,18] in which methylsilsesquioxane particles were obtained by reacting methyltrichlorosilane with tetraethoxysilane in the presence of iron(III) chloride catalyst. In this way, very large aggregated, irregular particles with diameters in the range 1.0−9.0 μm were produced in the presence of surfactants under “pseudo-dispersion polymerization” conditions.

Here, we report a new nonhydrolytic sol−gel method for the synthesis of ormosil particles with diameters in the range ca. 0.1−2.0 μm. It has long been recognized that dimethyl sulfoxide is an effective donor, with oxygen, rather than

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sulfur, acting as a donor atom.[19] As early as 1961, Lappert and Smith[20] studied the reactions of certain sulfoxides with inorganic halides and noted that by reacting silicon tetrachloride with dimethyl sulfoxide a mixture was obtained, the distillation of which afforded a silica residue and a chlorosubstituted sulfide byproduct. Several groups have reported the formation of cyclic siloxanes by reactions of dimethyl-, diphenyl-, or methylphenyldichlorosilanes with dimethyl sulfoxide.[21−24] More recently, Bassindale et al.[25] have prepared hexasilsesquioxane cages by reacting organotrichlorosilanes with dimethyl sulfoxide in chloroform. Although no further analyses on the morphology of inorganic or organically modified silica materials produced in these studies were performed, we have adapted the use of dimethyl sulfoxide as an oxygen donor for the nonhydrolytic synthesis of organically modified silica particles. It is believed that the materials obtained here are of network silsesquioxane structure and not cyclic oligomers or cages. In this way, methyl-, ethyl-, and phenylsilsesquioxane particles have been prepared by reacting organotrichlorosilane precursors with dimethyl sulfoxide, used both as an oxygen donor and as a solvent, in the absence of a catalyst under nonaqueous conditions. The possibility of producing pure silica particles using this method has also been investigated. A major advantage of this approach is the absence of catalyst residues and, hence, color in the final product. It is believed that the procedure can be extended to a wide range of organically modified silicas.

One of the most promising potential applications of the ormosil materials that can be obtained using this approach is their use as nanofillers to modify the properties of selected polymer systems, such as acrylic, styrenic, and polyester polymers. The presence of organic groups and the possibility of reducing or eliminating the presence of hydroxy groups render the surface of the particles more hydrophobic than that of inorganic particles or ormosil particles produced via the hydrolytic route, thus offering the potential to improve compatibility between the filler and the host polymer, especially when the nanoparticles are encapsulated by polymerization of hydrophobic monomers, such as styrene.

2. Experimental Section

Materials. Dimethyl sulfoxide (DMSO) (99.7%, Acros Organics) was dried over calcium hydride and then distilled from calcium hydride at reduced pressure at ca. 100 °C. Phenyltrichlorosilane (97%, Aldrich), methyltrichlorosilane (97%, Aldrich), ethyltrichlorosilane (99%, Aldrich), and silicon tetrachloride (98%, Aldrich) were used as received. Absolute ethanol (99.86%, Hayman) was of analytical reagent quality.

Synthesis of Silsesquioxanes and Pure Silicas. The effects of reaction time, reaction temperature, and the nature of molecular precursors on the particle structure and morphology have been studied to develop a procedure that is best suited to the production of nanoparticles. A molecular precursor, methyl-, ethyl-, phenyltrichlorosilane, or silicon tetrachloride (20 mmol), was slowly added to DMSO (20 mL; 280 mmol) under vigorous stirring under nitrogen at room temperature. The temperature was gradually increased over a period of 30 min or 2.5 h to 40, 60, or 100 °C, and the reaction mixture was then stirred under nitrogen using an overhead stirrer for 3 h, so that the total reaction time was either 3.5 or 5.5 h. The resulting materials were isolated by centrifugation and washed several times with ethanol. The products were dried in air for 24 h and under vacuum for 48 h to yield fine white powders.

Characterization Techniques. Scanning electron microscopy (SEM) investigations were performed on a Hitachi S-3200N scanning electron microscope operating at 10 kV. The SEM samples were prepared by applying a layer of dry powder on a stub covered with a carbon film. The samples were coated with a layer of gold to avoid charging effects. Micrographs were taken at a number of random locations on the stub. About 50−100 particles were measured for each sample.

C and H elemental analyses were carried out on a Leeman Laboratories Inc. CE 440 elemental analyzer. S content was determined by combustion analysis using a Carlo-Erba elemental analyzer, and Cl was analyzed by means of Schöniger flask combustion and wet titration at Medac Ltd., Brunel Science Centre.

Transmission infrared (IR) spectra were obtained on a Perkin-Elmer 2000 FT-IR spectrophotometer. A finely ground sample was mixed with potassium bromide and pressed to form a disk, which was used to measure the IR spectrum.

Solid-state ^{13}C cross-polarized (CP) and ^{29}Si directly polarized (DP) nuclear magnetic resonance (NMR) spectroscopy was carried out at the University of Durham. The spectra were recorded on a Varian Unity Inova spectrometer equipped with a 7.5 mm magic angle spinning (MAS) probe. The ^{29}Si DP quantitative spectra were measured at ambient temperature using a 90° pulse angle, a 120.0 s recycle, an acquisition time of 15.0 or 20.0 ms, a spin-rate of ca. 5000 Hz, and a frequency of 59.58 MHz (ca. 500−700 repetitions). The ^{13}C CP spectra were obtained at ambient temperature using an acquisition time of 20.0 or 30.0 ms, a contact time of 1.0 ms, a pulse delay of 2.0 s, a spin-rate of ca. 4800 Hz, and a frequency of 75.43 MHz (ca. 200−2000 repetitions). The conventional Q^n notation was used to denote tetrafunctional silica species, whereas the conventional T^n notation was used to label trifunctional silica species, where n is the number of siloxane groups bonded to the silicon atom.

3. Results and Discussion

Over the past few years, several groups[12−14,25] have used the nonhydrolytic sol−gel method to synthesize organically modified silica materials, but little interest[17,18] has focused on the formation of silsesquioxane (nano)particles via this versatile route. Here, we report the synthesis of methyl-, ethyl-, and phenylsilsesquioxane particles with diameters in the range ca. 0.1−2.0 μm, and pure ("unmodified") silica particles with diameters in the range ca. 100−400 nm from molecular precursors with dimethyl sulfoxide used both as an oxygen donor and as a solvent. This approach has been studied over a wide range of experimental conditions, such as varying reaction time, temperature, and the type of molecular precursor. For methyl-modified materials, it is seen that polydisperse particles with diameters in the range ca.

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Table 1. Data on Products of Synthesis of Silsesquioxane and Silica Particles

		reaction temperature					
		40 °C		60 °C		100 °C	
material	reaction time/h	average diameters/nm	yield (%)	average diameters/nm	yield (%)	average diameters/nm	yield (%)
methyl-modified	3.5	280 ± 75	107	210 ± 60	109	330 ± 75	96
	5.5	280 ± 90	101	325 ± 60	100	270 ± 90	101
ethyl-modified	3.5	−	79	−	72	−	65
	5.5	470 ± 110	105	350 ± 45	96	45 ± 10 (∼150[a])	92
phenyl-modified	3.5	−	98	−	76	−	89
	5.5	810 ± 230 (∼2100[a])	92	100 ± 15 (1500[a])	46	940 ± 300	102
SiO_2	5.5	−	110	320 ± 150	76	105 ± 30	103

[a] The values in parentheses refer to the larger particles observed on the micrographs alongside the smaller particles.

150−400 nm are always produced (Table 1). In this case, well-defined quite regularly shaped particles are abundant, although some minor monolithic regions are also present, which are possibly formed by coalesced individual particles (Figure 1a). For ethyl- and phenylsilsesquioxanes, no particles, as in the case of ethylsilsesquioxanes, or very irregular aggregated particles with diameters in the range ca. 400−800 nm, as in the case of phenylsilsesquioxane materials, were observed for the reaction time of 3.5 h. By increasing the reaction time at room temperature from 30 min to 2.5 h, so that the total reaction time is increased from 3.5 to 5.5 h, micrographs similar to those recorded for methylsilsesquioxanes are obtained (Figure 1b). However, more monolithic regions, together with larger particles, which are apparently formed by coalesced smaller particles, are observed on the micrographs recorded for these materials. When the larger particles are taken into account, it is seen that for ethyl- and phenylsilsesquioxanes obtained at a reaction time of 5.5 h, the size of the particles decreases with increasing reaction temperature (Table 1). The same behavior is observed for pure silica particles (Figure 1c), which have been prepared at a reaction time of 5.5 h only.

Some of the silsesquioxanes produced in this study have been subjected to Soxhlet extraction with chloroform for 2 days. Only ca. 8−15% of each sample is dissolved in chloroform, and the IR spectra of the materials retained and dissolved in chloroform following Soxhlet extraction are almost identical. These observations, along with the analytical data discussed later, suggest that the materials obtained here are random or network silsesquioxane structures containing a small proportion of oligomeric species and not cage or cyclic structures.

It is believed that the mechanism behind this type of synthesis is the Pummerer rearrangement.[26] The simplified equations shown below describe the chemistry of this nonhydrolytic process:

$$2RSiCl_3 + 3(CH_3)_2SO \rightarrow [R_2Si_2O_3]_n + 3ClCH_2SCH_3 + 3HCl \quad (1)$$

$$SiCl_4 + 2(CH_3)_2SO \rightarrow SiO_2 + 2ClCH_2SCH_3 + 2HCl \quad (2)$$

In the case of organotrichlorosilane precursors, the products are formally silsesquioxanes, where each silicon atom is covalently bonded to one organic group, with the empirical

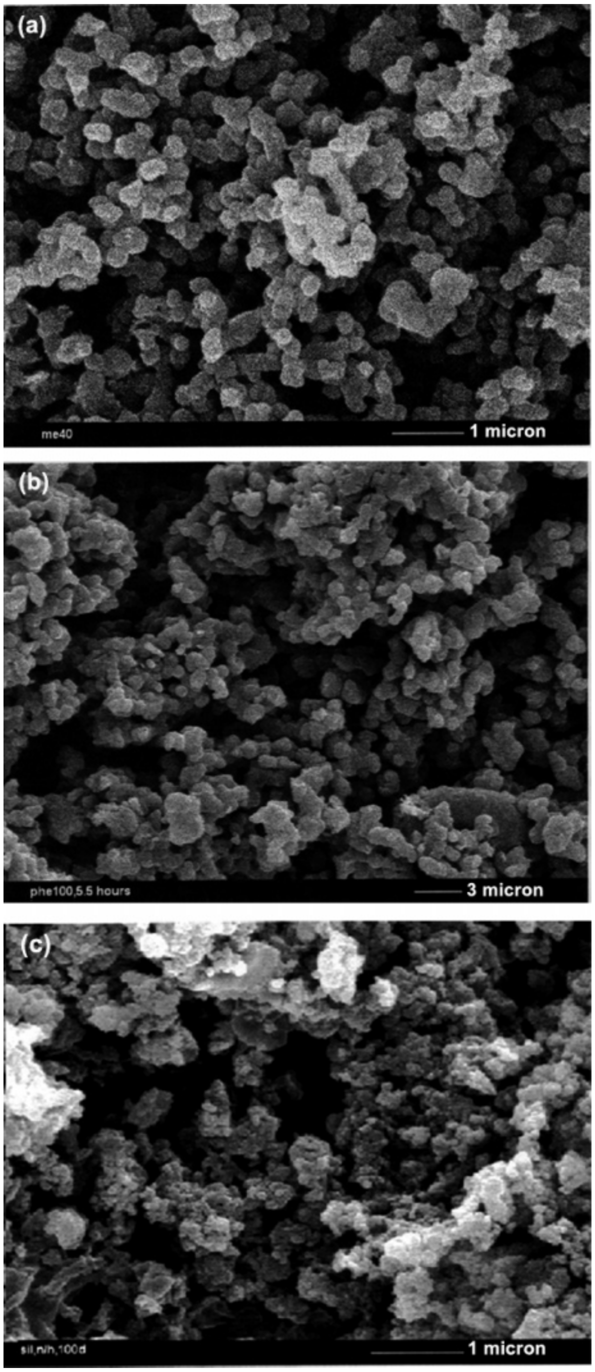

Figure 1. Scanning electron micrographs of (a) methylsilsesquioxane particles obtained at 40 °C, reaction time 3.5 h, (b) phenylsilsesquioxane particles obtained at 100 °C, reaction time 5.5 h, and (c) pure silica particles obtained at 100 °C, reaction time 5.5 h.

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Table 2. Elemental Analyses of Silsesquioxanes and Pure Silicas

		reaction temperature							
		theoretical		40 °C		60 °C		100 °C	
material	reaction time/h	C (wt %)	H (wt %)	C (wt %)	H (wt %)	C (wt %)	H (wt %)	C (wt %)	H (wt %)
methyl-modified	3.5	17.9	4.5	19.6	5.4	24.1	5.3	16.2	5.1
	5.5			19.8	5.4	17.4	5.0	16.7	5.1
ethyl-modified	3.5	29.6	6.2	29.5	6.8	24.2	6.6	23.3	6.6
	5.5			25.8	6.7	30.2	6.8	28.3	6.6
phenyl-modified	3.5	56.0	4.0	52.6	4.6	53.3	4.2	52.4	4.4
	5.5			53.3	4.3	52.8	4.1	51.9	4.2
SiO_2	5.5	0.0	0.0	11.2	3.2	4.9	2.7	4.3	2.3

formula $[R_2Si_2O_3]_n$, where R = methyl, ethyl, or phenyl. Although the nature of the byproduct has not been elucidated, the formation of chloromethyl methyl sulfide is supported by the results reported by Lappert and Smith.[20] It is anticipated that chloromethyl methyl sulfide or dichloromethyl sulfide, $(ClCH_2)_2S$, byproducts are removed in the nitrogen flow during the reaction or by washing with ethanol. However, in some cases, these highly reactive compounds, as well as the residual intermediate complexes containing chloromethyl sulfide fragments attached to the siloxane matrix, may be hydrolytically converted to paraformaldehyde species. Because no specific care has been taken to avoid the presence of moisture during the washing and drying stages of the process, the existence of paraformaldehyde groups bonded to or entrapped within the siloxane matrix is possible. Likewise, the possibility of the presence of some silanol species produced by Si−Cl hydrolysis cannot be ruled out. Any residual Si−Cl groups may also be converted to ethoxysilanes with ethanol used as a washing solvent.

The presence of residual S and Cl is insignificant, as confirmed by S and Cl elemental analyses performed for methylsilsesquioxanes, thus suggesting that almost no residual Si−Cl groups or chloromethyl sulfide compounds are present. It is seen that both S and Cl contents are more or less independent of the reaction temperature and decrease marginally with increasing reaction time from ca. 0.07% to <0.05% for S, and from ca. 0.9% to 0.3% for Cl. This observation suggests that either the condensations are more complete or the species containing these atoms are more easily removed or converted to other species with increasing reaction time.

High yields were obtained for most of the materials produced in this study, as calculated using the empirical formulas of the products (Table 1). The values above 100% are probably due to incomplete condensations and the presence of ethoxysilane groups and, possibly, silanol and paraformaldehyde species in the products. The results obtained from the elemental analyses agree moderately well with the theoretical values (Table 2). Likewise, the discrepancies between the predicted and experimental values can be explained by the presence of alkoxysilane and paraformaldehyde species, as discussed above. This consideration is supported by the presence of C and H in “unmodified” silica samples. It is seen that, for this material, both C and H contents decrease marginally with increasing reaction temperature, thus suggesting that the number of these atoms present in ethoxysilane and paraformaldehyde groups diminishes with increasing reaction temperature.

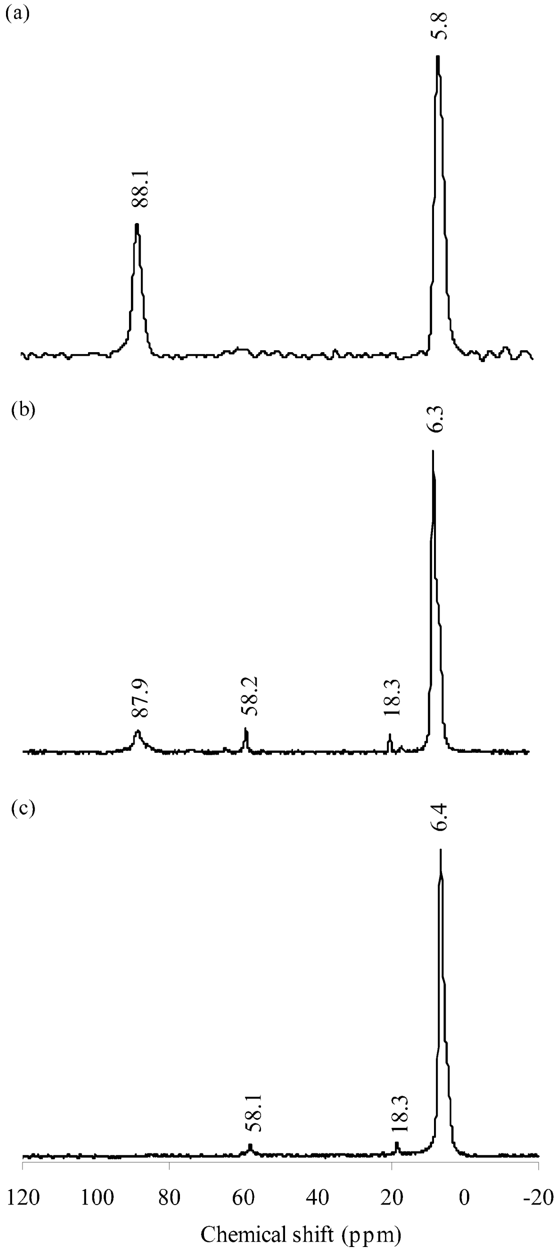

Figure 2. ^{13}C CP-MAS NMR spectra of ethylsilsesquioxanes obtained at (a) 60 °C, reaction time 3.5 h, (b) 40 °C, reaction time 5.5 h, and (c) 60 °C, reaction time 5.5 h.

The ^{13}C CP-MAS NMR spectra (Figure 2) show intense carbon resonances characteristic of methyl, ethyl, or phenyl groups. The retention of Si−R bonds is also confirmed by IR absorptions (Figure 3a) at 1275, 1260−1240, and 1430 cm^{-1}, characteristic of methyl, ethyl, and phenyl deforma-

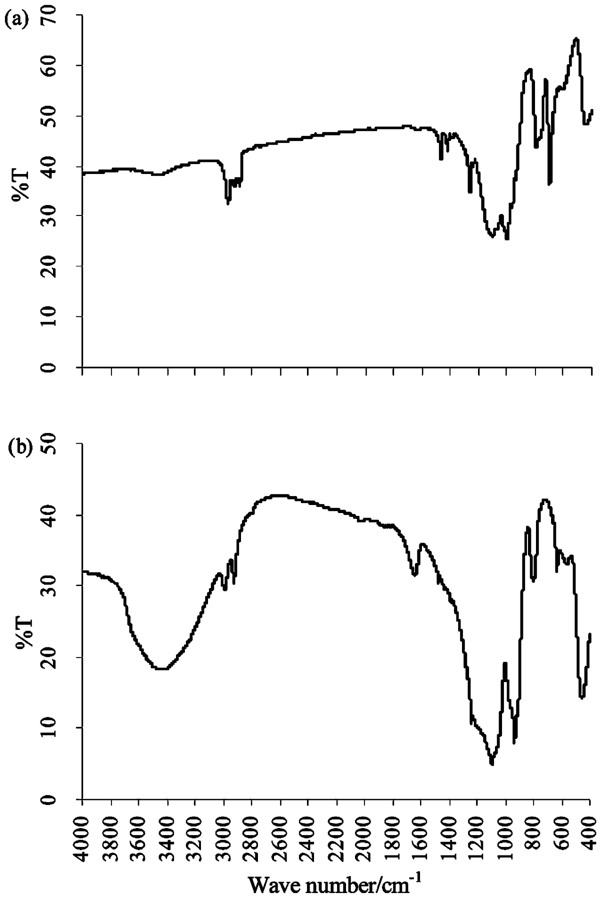

Figure 3. IR spectra of (a) ethylsilsesquioxane and (b) pure silica obtained at 40 °C, reaction time 5.5 h.

tions, respectively, Si−C stretching bands at ca. 700−790 cm^{-1}, C−H stretching vibrations at ca. 2880−3070 cm^{-1}, and an absorption at 1595 cm^{-1} characteristic of the benzene ring in phenylsilsesquioxanes.[27,28]

Most of the ^{13}C spectra recorded for the silsesquioxane materials exhibit relatively weak resonances at 18 and 58 ppm (Figure 2), characteristic of CH_3 and CH_2O carbon atoms, respectively, confirming the existence of ethoxysilane groups formed by reaction of ethanol with the residual Si−Cl groups. The presence of these species is more or less independent of the reaction conditions used in this study. Some of the ^{13}C NMR spectra obtained for the silsesquioxane and pure silica materials show quite intense carbon resonances at 88 ppm (Figure 2). This peak can be assigned to OCH_2O carbon atoms of paraformaldehyde species. The ^{13}C spectra suggest that the presence of residual species containing chloromethyl sulfide fragments, which are hydrolytically converted to paraformaldehyde species, is almost unaffected by the reaction temperature and diminishes with increasing reaction time. Thus, it can be inferred that the condensation reactions are more complete in the case of the longer reaction time. The formation of paraformaldehyde groups is also supported by well-defined IR absorptions at 2922 and 2980 cm^{-1}, although the absorptions at ca. 940 and 1100 cm^{-1} are masked by the strong Si−O−Si absorption[27] (Figure 3).

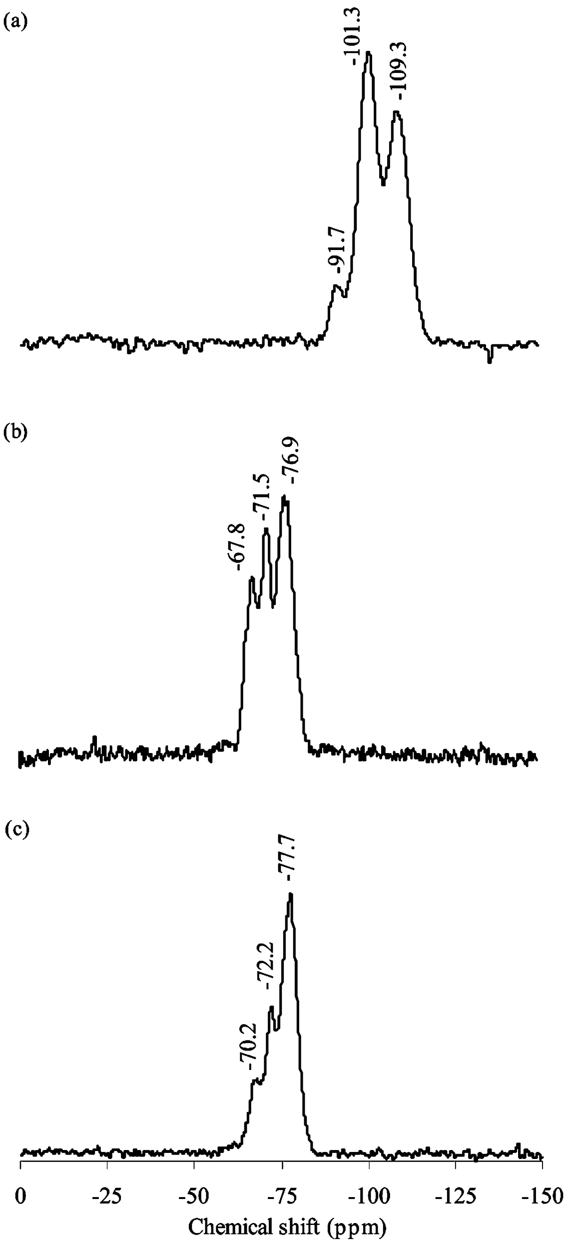

Figure 4. ^{29}Si DP-MAS NMR spectra of (a) pure silica obtained at 100 °C, reaction time 5.5 h, (b) phenylsilsesquioxane obtained at 100 °C, reaction time 5.5 h, and (c) phenylsilsesquioxane obtained at 100 °C, reaction time 3.5 h.

For silsesquioxanes, relatively weak absorptions between ca. 3100 and 3600 cm^{-1} can be assigned to the presence of some hydroxy groups (Figure 3a). For “unmodified” silicas, this absorption is significantly stronger and broader (Figure 3b), thus confirming that the residual Si−Cl species are more easily hydrolyzed in the case of the more hydrophilic silica system. Although Si−Cl hydrolysis is possible, the presence of hydrophobic organic groups in the silsesquioxanes appreciably retards this process as compared to the “unmodified” silica materials. For pure silicas, during the washing and drying stages of the process, the hydrolysis reactions prevail and no ethoxysilane groups are retained, as confirmed by the ^{13}C spectra obtained for these materials.

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Table 3. Quantification of the ^{29}Si NMR Spectra of Silsesquioxanes and Pure Silicas[a]

		reaction temperature								
		40 °C			60 °C			100 °C		
material	reaction time/h	T^3 or Q^4 (%)	T^2 or Q^3 (%)	T^1 or Q^2 (%)	T^3 or Q^4 (%)	T^2 or Q^3 (%)	T^1 or Q^2 (%)	T^3 or Q^4 (%)	T^2 or Q^3 (%)	T^1 or Q^2 (%)
methyl-modified	3.5	49.7	27.1	23.2	41.9	35.1	23.0	40.3	34.3	25.4
	5.5	51.8	24.9	23.3	52.3	24.5	23.2	56.1	25.5	18.4
ethyl-modified	3.5	37.2	39.6	28.2	52.5	25.5	22.0	53.1	25.5	21.4
	5.5	39.4	29.0	31.6	43.1	32.6	24.3	42.3	30.4	27.3
phenyl-modified	3.5	59.2	19.2	21.5	68.1	16.5	15.4	66.6	17.1	16.4
	5.5	43.9	19.7	36.4	73.6	16.0	10.4	54.5	17.6	27.9
SiO_2	5.5	44.3	48.5	7.2	44.7	47.4	7.9	45.0	46.5	8.5

[a] Q species only in the case of SiO_2.

The IR spectra show Si−O−Si absorptions at 1100 cm^{-1} (stretching), 1030 cm^{-1} (flexion), and 420−490 cm^{-1} (bending)[28,29] (Figure 3). The results of solid-state ^{29}Si DP NMR spectroscopy confirm the presence of T (monosubstituted) silica species and the absence of Q (unmodified) silica species in silsesquioxanes, thus suggesting that no Si−C linkages are broken during the nonhydrolytic reactions. For both silsesquioxanes and pure silicas, fully condensed T^3 or Q^4 species and partly condensed T^2 and T^1 or Q^3 and Q^2 species are abundant, whereas no T^0 or Q^0 species are observed in any of the spectra (Figure 4), indicating that, although the condensations are not fully completed, no unreacted organotrichlorosilane or tetrachlorosilane precursors are present. Unfortunately, the predictions made above concerning the degree of condensation cannot be confirmed by the results of deconvolutions of the ^{29}Si spectra, as there is no strong evidence to suggest that the amounts of T^3 or Q^4, T^2 or Q^3, and T^1 or Q^2 silica species are affected in a consistent manner by the reaction parameters used in this study (Table 3). It can only be inferred that the condensation is more complete in the case of phenylsilsesquioxanes. The degree of condensation achieved using this approach is less than that found for equivalent silsesquioxanes synthesized by a Stöber route, where the proportion of T^1 species is generally zero or negligible.[5]

The only silsesquioxane obtained here that is formally chemically identical to that prepared by Bassindale et al.[25] is phenylsilsesquioxane. However, whereas the ^{29}Si NMR chemical shift of phenyl hexasilsesquioxane cage structures obtained by Bassindale is ca. −67 ppm, the fully condensed phenylsilsesquioxane species produced here have a chemical shift of ca. −77 ppm, thus suggesting that the materials obtained using this nonhydrolytic method are of random or network silsesquioxane structure.

4. Conclusions

The nonhydrolytic sol−gel method has been extended to the formation of silsesquioxane and silica particles by reacting methyl-, ethyl-, phenyltrichlorosilane, and tetrachlorosilane precursors with dimethyl sulfoxide under nonaqueous conditions. For methylsilsesquioxanes, well-defined quite regularly shaped particles with diameters in the range of ca. 150−400 nm have been produced irrespective of the reaction conditions used in this study. The particles obtained in the case of ethylsilsesquioxanes, phenylsilsesquioxanes, and pure silicas are less regularly shaped and exhibit a greater degree of aggregation.

The formation of Si−O−Si bonds and the retention of Si−C bonds have been confirmed by solid-state ^{13}C and ^{29}Si NMR spectroscopy, together with IR analysis. Although condensations are not fully completed, no unreacted precursors are present in the products. The condensation is more complete in phenylsilsesquioxanes than in methyl- and ethylsilsesquioxanes and pure silicas. In incompletely condensed silica species, ethoxysilane, silanol, and, sometimes, paraformaldehyde species are present. The formation of silanol groups is insignificant in the case of silsesquioxanes, but not in the case of the more hydrophilic “unmodified” silica system. On the other hand, almost no ethoxysilane groups are present in pure silicas.

Further work is required to establish a method that provides a greater degree of condensation and a better separation of the byproducts. However, because one of the potential uses of such materials is as modifiers of the properties of polymers and polymer composites, a study of the effect of paraformaldehyde groups present in the product on compatibility between the filler and the host polymer would be useful. A much more detailed study would be needed to develop a procedure to produce more regularly shaped monodisperse silsesquioxane nanoparticles, and this will be the subject of future work.

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