Layered assembly of alkoxy-substituted bis(trichlorosilanes) containing various organic bridges *via* hydrolysis of Si–Cl groups[†]

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Monoalkoxy derivatives of bis(trichlorosilanes) containing methylene, ethylene, and phenylene bridges (Cl₃Si–R'–SiCl₂OC₁₆H₃₃, R' = -CH₂–, -C₂H₄–, -C₆H₄–) were synthesized and self-assembly of the amphiphilic hydrolyzed species ((HO)₃Si–R'–Si(OH)₂OC₁₆H₃₃) was investigated. Hydrolysis of all Si–Cl groups was confirmed by liquid-state ²⁹Si and ¹³C NMR while the alkoxy groups were retained. The self-assembly was induced either by casting the hydrolyzed solutions on glass substrates or by cooling. The structures of the products were characterized by X-ray diffraction (XRD), electron microscopies (TEM and SEM), and solid-state ²⁹Si and ¹³C NMR. The products obtained from methylene- and ethylene-bridged monomers have lamellar structures consisting of bridged polysilsesquioxane layers and all-*trans* hexadecanol layers, which means that alkoxy groups were cleaved during polycondensation. The large difference in the *d* values of these hybrids (5.84 nm and 3.40 nm) suggests the variation in the arrangement of hexadecanol molecules within the layers. In contrast, the phenylene-bridged monomer afforded a lamellar solid (*d* = 5.14 nm) consisting of monomeric species, where both silanol groups and alkoxy groups mostly remain intact. This is attributed to the relatively stronger interaction and hydrogen-bonding networks between hydrolyzed species.

Introduction

Silica-based inorganic–organic hybrid materials have been extensively studied because of their potential for a wide range of applications.¹ Organosilanes, containing Si–C and Si–OR (or Si–Cl) bonds, are often used as precursors, and their chemical design is very important for the creation of hybrids with controlled structures and desirable properties.^{1,2} Precursors containing two trichloro- or trialkoxy-silyl groups, $X_3Si-R'-SiX_3$ (X = Cl or alkoxy), form an interesting class of hybrids, called bridged polysilsesquioxanes, in which organic (R') groups are homogeneously integrated as a part of the frameworks.^{3,4}

Recently, much effort has been directed to the structural organization of bridged silsesquioxanes at the nanometer length scale. The use of surfactants as structure directing agents allows the formation of various hybrid mesostructures where organic groups are homogeneously distributed within the frameworks.^{5–8} As an alternative approach, the self-directed assembly based on weak interactions between organic bridges has been demonstrated. Corriu *et al.* reported structural anisotropy in xerogels derived from precursors with rigid organic bridges such as allyl groups.^{9,10} Furthermore,

Moreau *et al.* reported the synthesis of lamellar bridged silsesquioxanes by incorporating amido groups to make use of the hydrogen bonding between molecules.^{11–14} By combining the above two approaches, hybrid mesostructures with molecular-scale periodicities in the frameworks have been synthesized by Inagaki *et al.*^{15–18}

On the other hand, we have reported the formation of lamellar hybrids from alkyltrialkoxysilanes via self-assembly and polycondensation of amphiphilic hydrolyzed species.¹⁹ More recently, this approach has been extended to the use of alkoxytrichlorosilanes ($C_nH_{2n+1}OSiCl_3$, n = 12-20).²⁰ Selfassembly of partially hydrolyzed monomers (alkoxysilanetriols) followed by polycondensation and cleavage of alkoxy groups led to the formation of lamellar silica (or silicic acid)alcohol nanocomposites. The resulting thin siloxane sheets are useful as nanofillers for nanocomposites with organic polymers. Moreover, esterification of the surface silanol groups with alcohols affords organically modified hybrids which are expected to have unique adsorption properties²¹ and a greater affinity to organic solvents.²² Although Ying et al. developed a ligand-assisted approach based on covalent linking of surfactants to metal alkoxides, previous reports are limited to the synthesis of mesostructured transition metal (Nb, Ta, and Zr) oxides.^{23,24} Our method using alkoxylated chlorosilanes is important as a new single precursor pathway to a wide range of nanostructured silica-based materials by the molecular design of chlorosilane moieties.

In this paper, we examined the monoalkoxy derivatives of bis(trichlorosilanes) containing methylene, ethylene, and phenylene bridges (Cl₃Si-R'-SiCl₂(OC₁₆H₃₃), R' = $-CH_2-(1)$, $-C_2H_4-(2)$, $-C_6H_4-(3)$) for possible starting monomers for synthesizing self-organized bridged silsesquioxanes. The

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organically-bridged silsesquioxane layers should be utilized as a completely new nanofiller as well as an organized building block for well ordered nanomaterials. The structures of the resulting products as well as the hydrolyzed intermediate species were characterized in detail, and the effect of the kind of bridging organic groups on the self-assembly behavior was discussed.



Experimental

Materials

Bis(trichlorosilyl)methane (Sigma-Aldrich, >97%) and 1,2bis(trichlorosilyl)ethane (Sigma-Aldrich, >97%) were used for the synthesis of **1** and **2**, respectively. Tetrachlorosilane (Tokyo Kasei Co., >98%) and 1,4-dibromobenzene (Wako Pure Chemical Industries, >98%), and magnesium turnings (Sigma-Aldrich, >98%) were used for synthesizing 1,4-bis(trichlorosilyl)benzene. 1-Hexadecanol (>95%) was purchased from Wako Pure Chemical Industries. Other chemicals including aniline (Wako Pure Chemical Industries, >99%), tetrahydrofuran (THF, Wako Pure Chemical Industries, dehydrated, >99.5%), and hexane (Kanto Chemical Co., >96%) were used as received.

Synthesis of $Cl_3Si-CH_2-SiCl_2(OC_{16}H_{33})$ (1)

The monoalkoxy-substitution of 1,2-bis(trichlorosilyl)methane was performed by the dropwise addition of 1-hexadecanol (9.3 g) dissolved in 30 mL of THF to a solution of 1,2-bis(trichlorosilyl)methane (10.9 g) in THF (20 mL). The gaseous HCl formed by the reaction was allowed to go out of the vessel. After stirring at room temperature for 3 h, the solvent was removed under reduced pressure. The residue was vacuum distilled to yield **1** as a clear liquid. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 0.87–0.89 (t, 3H; CH₃), 1.26 (m, 24H), 1.37 (m, 2H), 1.52–1.54 (t, 2H; SiCH₂Si), 1.61–1.64 (m, 2H), 3.91–3.94 (t, 2H); ¹³C NMR (125.7 MHz, CDCl₃): δ (ppm) 14.1, 18.2, 22.7, 22.5, 29.2, 29.4, 29.6, 29.7, 29.8, 31.4, 32.0, 65.2; ²⁹Si NMR (99.3 MHz, CDCl₃): δ (ppm) 4.6, –20.0.

Synthesis of $Cl_3Si-C_2H_4-SiCl_2(OC_{16}H_{33})$ (2)

The ethylene-bridged monomer **2** was synthesized from 1,2-bis(trichlorosilyl)ethane and 1-hexadecanol in a similar manner as for **1**. The amounts of the reactants were as follows: 1-hexadecanol (19.4 g) in THF (150 mL); 1,2-bis(trichlorosilyl)ethane (23.8 g) in THF (70 mL). The precursor **2** was obtained as a clear liquid. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 0.87–0.89 (t, 3H; CH₃), 1.26 (m, 24H), 1.31 (m, 2H), 1.51 (m, 2H; Cl₃SiCH₂CH₂Si), 1.61–1.64 (m, 2H), 3.89–3.92 (t, 2H; SiOCH₂); ¹³C NMR (125.7 MHz, CDCl₃): δ (ppm) 11.5, 14.1, 16.3, 22.7, 25.5, 29.2, 29.4, 29.6, 29.7, 31.5, 32.0, 65.1; ²⁹Si NMR (99.3 MHz, CDCl₃): δ (ppm) 12.5, –12.2.

Synthesis of Cl₃Si-C₆H₄-SiCl₂(OC₁₆H₃₃) (3)

1,4-Bis(trichlorosilyl)benzene was synthesized by the reaction of the Grignard reagent of 1,4-dibromobenzene (Tokyo Kasei. Co.) with tetrachlorosilane (Tokyo Kasei Co.). The reaction with 1-hexadecanol was performed in a similar manner for **1**. The amounts of the reactants were as follows: 1-hexadecanol (4.2 g) in THF (35 mL); 1,4-bis(trichlorosilyl)benzene (8.99 g) in THF (35 mL). Although 1,4-bis(trichlorosilyl)benzene is a crystalline solid at room temperature, **3** was obtained as a clear liquid. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 0.86–0.89 (t, 3H; CH₃), 1.26 (m, 24H), 1.38 (m, 2H), 1.67–1.70 (m, 2H), 4.01–4.04 (t, 2H; SiOCH₂), 7.87 (br, Ph); ¹³C NMR (125.7 MHz, CDCl₃): δ (ppm) 14.1, 22.7, 25.6, 29.2, 29.4, 29.6, 29.7, 31.6, 32.0, 65.3, 132.6, 133.5, 135.4, 136.3; ²⁹Si NMR (99.3 MHz, CDCl₃): δ (ppm) – 1.4, –25.3.

Hydrolysis and self-assembly processes

Alkoxy derivatives of organo(bis-trichlorosilanes) (1, 2, or 3, ca. 1.0 g) in THF (10 mL) were added dropwise to the mixture of THF (20 mL), aniline, and H₂O under vigorous stirring in an ice bath. The molar ratio of 1 (or 2 or 3) : H_2O : aniline was 1.0 : 5.5 : 5.5. Aniline was added to neutralize evolved HCl, which accelerates the polycondensation reaction. After stirring the mixture for 1 h, the precipitates of aniline hydrochloride were removed by filtration to give a clear solution. To this solution, THF was then added so that the concentration of Si species became *ca*. 0.025 mol L^{-1} . The self-assembly procedure was performed either by casting or by cooling these hydrolyzed solutions. The casting of the solutions on glass substrates followed by air-drying at 10 °C for 2 days yielded slightly yellowish thick films, and they were peeled off from the substrates and gently pulverized before characterization. The products derived from 1, 2, and 3 are denoted as 1H, 2H, and **3H**, respectively. On the other hand, cooling the hydrolyzed solutions to about -20 °C formed precipitates when 1 and 3 were used, whereas no precipitation occurred in the case of 2. The precipitates were filtered, washed with THF, and air-dried for 2 days to afford white powders.

Characterization

Liquid-state ²⁹Si and ¹³C NMR spectra were obtained on a JEOL Lambda-500 spectrometer with resonance frequencies of 99.25 and 125.65 MHz, respectively. The sample solutions were put in 5 mm glass tubes, and tetramethylsilane (TMS) was added as an internal reference. CDCl₃ or THF- d_8 was used to obtain lock signals. A small amount of Cr(acac)₃ was also added as a relaxation agent for ²⁹Si nuclei. Solid-state ²⁹Si magic-angle spinning (MAS) NMR analysis was performed on a JEOL JNM-CMX-400 spectrometer at a resonance frequency of 79.42 MHz, with a pulse width of 45°, and a recycle delay of 100 s. Deconvolution of spectra was performed by using a Gaussian function on Spinsight software ver. 4.3.2. Solid-state ¹³C cross-polarization (CP)/MAS NMR spectra were obtained on the same spectrometer at a resonance frequency of 100.54 MHz with a contact time of 1.5 ms and a recycle delay of 5 s. Chemical shifts for both ²⁹Si and ¹³C NMR were referenced to tetramethylsilane at 0 ppm. Powder X-ray diffraction (XRD) patterns were recorded on a Mac Science M03XHF22 diffractometer with Mn-filtered Fe Ka radiation or on a Mac Science MXP3 diffractometer with monochromated Cu Ka radiation. Transmission electron microscopic (TEM) images were obtained by a JEOL JEM-2010 microscope at an accelerating voltage of 200 kV. Field-emission scanning electron microscopic (FE-SEM) observations were performed for the samples coated with Pt-Pd using a Hitachi S-4500S field-emission microscope at an accelerating voltage of 15 kV. Thermogravimetric (TG) analysis was performed on a RIGAKU TG8120 instrument under a dry air flow at a heating rate of 10 $^{\circ}$ C min⁻¹, and the amounts of SiO₂ fractions in the products were determined by the residual weight after heating to 900 °C. The amounts of organic constituents were determined by CHN analysis (Perkin Elmer PE-2400).

Results

Hydrolysis of Si-Cl groups

Fig. 1 shows the liquid-state ²⁹Si NMR spectra of the solutions of 1, 2, and 3 after partial hydrolysis. The signals of the unreacted monomers are not observed, and each solution clearly shows two new signals. The chemical shifts of the signals are -40.2 ppm and -41.1 ppm for the solution of 1, -38.6 ppm and -39.4 ppm for 2, and -53.0 ppm and -54.4 ppm for 3. It is known that the ²⁹Si signals of trihydroxysilyl $(-Si(OH)_3)$ groups attached to alkyl or alkylene groups usually appear at around -39 ppm, and shift upfield (~ 1 ppm) when one hydroxy group is replaced by an alkoxy group.^{19,25-27} From these facts, the two signals observed for both 1 and 2 can be assigned to (HO)₃SiC and CSi(OH)₂(OC₁₆H₃₃), generated by hydrolysis of Si-Cl groups without the cleavage of alkoxy groups. The signals observed for the system of 3 (Fig. 1c) can also be assigned to a similar hydrolyzed monomer, although the signals are shifted considerably upfield from those of 1 and 2. Actually, the signal at -53.0 ppm is close to the ²⁹Si signals of phenylsilanetriol in acetone $(-53.1 \text{ ppm})^{28}$ and bis(trihydroxysilyl)benzene in DMSO (-54.3 ppm).²⁹ The other signal at -54.4 ppm is assigned to the Si atom having an alkoxy group.



Fig. 1 Liquid-state ²⁹Si NMR spectra of the solutions obtained by hydrolysis of (a) methylene-bridged monomer 1, (b) ethylene-bridged monomer 2, and (c) phenylene-bridged monomer 3.



Fig. 2 Liquid-state 13 C NMR spectra of the solutions obtained by hydrolysis of (a) 1, (b) 2, and (c) 3.

The corresponding ¹³C NMR spectra (Fig. 2) display the signals due to the bridging organic groups and hexadecyl chains. It is important that the signals assigned to the a carbon of -OC16H33 are observed at 62.6 ppm, 62.9 ppm, and 62.8 ppm for the hydrolyzed solutions of 1, 2, and 3, respectively. These chemical shifts are closer to those of 1-hexadecanol (62.5 ppm) than those of the unreacted monomers (in CDCl₃; 65.2 ppm, 65.1 ppm, and 65.3 ppm for 1, 2, and 3). However, we confirmed that alkoxy groups are not hydrolyzed, because a new set of signals were observed when a small amount of C16OH was added to these hydrolyzed solutions. The difference in the chemical shifts for the α carbons before and after hydrolysis of Si-Cl groups should be due to the variation in the electron density of adjacent Si atoms and also to the difference in the solvent (CDCl₃ or THF). These results are consistent with the ²⁹Si NMR data. indicating that controlled hydrolysis of alkoxy derivatives of bis(trichlorosilanes) can be performed in a similar manner for alkoxytrichlorosilanes.²⁰

Structure of the self-assembled products

The powder XRD patterns of the hybrid solids (1H, 2H, and 3H) obtained by casting the hydrolyzed solutions of 1, 2, and 3 are shown in Fig. 3. All of the samples exhibit the patterns characteristic of lamellar structures. The hybrid 1H, containing a methylene group, shows a peak at d = 5.84 nm and its second and third order reflections. The ethylene-bridged hybrid 2H exhibits a much smaller *d*-spacing of 3.40 nm. Remarkably, 3H shows a relatively strong peak at d = 5.14 nm accompanying the higher order reflections up to the tenth order.

At higher 2θ angles, all of the samples exhibit a peak at d = 0.41 nm, which corresponds to the distance between closely packed alkyl chains, as reported for crystalline



Fig. 3 Powder XRD patterns of the hybrids obtained by casting: (a) 1H, (b) 2H, and (c) 3H. The insets show the XRD patterns of higher 2θ regions.

n-alkanes and long-chain amphiphiles. Importantly, the pattern for **3H** shows several additional peaks (*e.g.*, d = 0.50 nm, 0.45 nm, and 0.34 nm) that are not assigned to the higher order reflections. We consider that these peaks arise from the ordered arrangement of O₃Si–C₆H₄–SiO₃ units. It is noteworthy that the *d*-spacing of 0.34 nm is almost identical to the spacing between stacked phenylene rings reported for the lamellar crystals of bis(trihydroxysilyl)benzene.²⁹ Also, the structural modeling of phenylene-bridged hybrid mesoporous silica showed a distance of ~ 0.44 nm between adjacent Si atoms.¹⁵ However, the detailed structure of **3H** is not yet well understood because of the low quality of the XRD data and the difficulty in obtaining large crystals required for single-crystal X-ray analysis.

FE-SEM observation revealed that these products have flake-like morphologies (Fig. 4). In particular, the angular shape of **3H** appears to reflect its crystalline nature. The TEM images of these products (Fig. 5) show layered structures, and their periodicities roughly correspond to the *d*-spacings determined by XRD. Such striped patterns were typically observed at the curved edges of the flake-like samples. The presence of molecular periodicity in **3H** was evidenced by the several spots observed in the electron diffraction (ED) patterns (Fig. S1, ESI[†]).

Fig. 6 shows the ¹³C CP/MAS NMR spectra of 1H, 2H, and 3H. The signals of methylene and ethylene groups are observed at -1 ppm and 5 ppm, and that of a phenylene group is observed as split signals at around 132 ppm. In addition, all of the hybrids show the signals of hexadecyl chains. The internal methylene carbons are detected at 33.3 ppm, which suggests the all-trans conformation of the interlayer alkyl chains.³⁰ It has been reported that the α carbons of alkoxy groups (SiOCH₂C) appear at ~1.0-1.5 ppm downfield from those of alcohol molecules (HOCH₂C).^{20-22,31} In the case of layered silicic acid-hexadecanol nanocomposites, the α carbons of the interlayer hexadecanol molecules appear at 63.1 ppm and shift to 64.7 ppm after esterification to form alkoxy groups.²¹ The hybrids 1H and 2H exhibit the signals of the α carbons at 63.0 ppm and 63.1 ppm, respectively, suggesting that the cleavage of alkoxy groups occurred to form alcohol molecules. In contrast, 3H exhibits the signal due to the α carbon at 64.2 ppm, which strongly suggests that the alkoxy groups remain intact.

The ²⁹Si MAS NMR spectra of **1H**, **2H**, and **3H** are shown in Fig. 7. The signals due to the T units $(T^x; CSi(OH)_{3-x}(OSi)_x; x = 0-3)$ are observed. The absence of the signals due to Q units $(Q^y; Si(OH)_{4-y}(OSi)_y; y = 0-4)$ means that the cleavage of Si–C bonds did not occur during the reaction. The hybrid



Fig. 4 FE-SEM images of (a) 1H, (b) 2H, and (c) 3H.



Fig. 5 Typical TEM images of (a) 1H, (b) 2H, and (c) 3H.



Fig. 6 Solid-state ¹³C CP/MAS NMR spectra of (a) 1H, (b) 2H, and (c) 3H.



Fig. 7 Solid-state ²⁹Si MAS NMR spectra of (a) 1H, (b) 2H, and (c) 3H.

Table 1 Ratios of total organic moieties $(C_{16}H_{33} + R')$ per 2SiO₂ unit

	Mass% C	Mass% H	Mass% N	Mass% SiO ₂	$\begin{array}{c} C_{16}H_{33}+R^{\prime}/2SiO_{2}\\ ratio \end{array}$
1H	59.0	9.3	0.5	27.8	0.97
2H	53.0	9.8	0.6	31.2	0.92
3H	52.5	9.9	0.3	28.0	1.1

1H exhibits T¹, T², and T³ signals at -50 ppm, -59 ppm, and -67 ppm, respectively. Similarly, **2H** shows the corresponding three signals at -48 ppm (T¹), -56 ppm (T²), and -67 ppm (T³). Thus the formation of siloxane networks was confirmed. On the other hand, the spectrum of **3H** mainly shows the signal due to the T⁰ unit (-52 ppm) along with a small signal due to the T¹ unit (centered at -61 ppm),^{3,32} suggesting that the polycondensation between silanol groups hardly occurred. From this result, in combination with the ¹³C CP/MAS NMR data showing the retention of the alkoxy groups, it is clear that **3H** consists of hydrolyzed monomers ((HO)₃Si–C₆H₄–Si(OH)₂OC₁₆H₃₃). We confirmed that polycondensation proceeded when **3H** was heated to 80 °C for 1 day, however, the XRD peak due to the lamellar structure almost disappeared.

The composition analysis (Table 1) shows that the $(C_{16}H_{33} + R')/2SiO_2$ ratios of the products are about 1, confirming that the products were formed by the assembly of hydrolyzed monomers. The presence of nitrogen is explained by the contamination of a small amount of aniline hydrochloride formed as a nonvolatile by-product in the hydrolysis step.

As we reported previously,²⁰ the self-assembly (crystallization) of alkoxysilanetriols was induced by cooling $(-20 \degree C)$ the hydrolyzed solutions. In the present system, we found that cooling of the hydrolyzed solutions instead of casting on glass substrates formed precipitates when 1 and 3 were used. The absence of nitrogen in the precipitates was confirmed by CHN analysis. The XRD patterns of the precipitates revealed the formation of lamellar phases with *d*-spacings of 5.84 nm and 5.33 nm (Fig. S2, ESI†). In addition, solid-state NMR analyses (Fig. S3 and S4, ESI†) suggest that the products are essentially the same as those obtained by casting. However, no precipitation occurred in the system of **2**.

Furthermore, the hybrids 1H, 2H, and 3H are obtained as thin films by spin-coating the hydrolyzed solutions of 1, 2, and 3 on glass substrates. The XRD patterns of the films derived from 1, 2, and 3 (Fig. S5, ESI†) show the peaks at d = 5.66 nm, 3.34 nm, and 4.82 nm, respectively. However, all the films exhibit no peak at d = 0.41 nm (data not shown). This indicates that the layers are to some extent oriented parallel to the substrate surface (*i.e.*, alkyl chains are not oriented parallel to the surface). It should also be noted that the film derived from 3 exhibits no higher order reflections of the peak at d =4.82 nm. This is probably due to the smaller size of the crystals of **3H** in the thin films compared to those formed by casting.

Discussion

The liquid-state ¹³C and ²⁹Si NMR analyses of the hydrolyzed solutions of **1**, **2**, and **3** revealed the formation of amphiphilic

species containing a hexadecoxy group and five hydroxyl groups attached to Si atoms. Upon casting these hydrolyzed solutions on glass substrates, evaporation of the solvent (THF) induces the self-assembly of these hydrolyzed species. On the other hand, cooling the hydrolyzed solutions also induced the self-assembly of hydrolyzed monomers even in the presence of solvents because the solubility of the hydrolyzed monomers decreased. However, the hydrolyzed solutions of **2** did not afford precipitates on cooling, which implies the lower self-assembling ability of the ethylene bridge compared to methylene and phenylene bridges disturbs the self-assembly of hydrolyzed species into lamellar solids. Precipitation may occur if the nature of solvent is changed or the hydrolyzed solution is cooled far below -20 °C.

When alkylene-bridged monomers **1** and **2** were used, cleavage of alkoxy groups occurred accompanying polycondensation between silanol groups to form siloxane networks. Such a phenomenon was also observed when alkoxytrichlorosilanes were used as precursors.¹⁹ The cleavage of alkoxy groups proceeds by condensation between Si–OR groups and neighboring Si–OH groups, and/or by the hydrolysis of Si–OR groups with water formed by condensation of Si–OH groups.

The degree of polycondensation in the silsesquioxane layers was calculated by the following equation: $1/3 \times I(T^1) + 2/3 \times I(T^2) + I(T^3)$, where $I(T^x)$ denotes the relative intensity ratio (%) of the T^x signals in the ²⁹Si MAS NMR spectra (Fig. 7). The hybrids with alkylene bridges (**1H** and **2H**) have the similar values of about 65%. This is lower than that of layered silica–alcohol nanocomposites (79%), which should be due to the presence of bridging organics between two $-Si(OH)_3$ groups. Interestingly, the phenylene-bridged hybrid **3H** was a crystalline solid composed of hydrolyzed monomers, and neither polycondensation of silanol groups nor cleavage of alkoxy groups occurred. This stability of hydrolyzed monomers is attributed to the formation of a strongly hydrogenbonded network, as reported for the crystalline solids of bis(trihydroxysilyl)benzene.²⁹

The proposed structural models of the hybrids **1H**, **2H**, and **3H** are illustrated in Fig. 8. All of the products have lamellar structures where the alkyl chains adopt all-*trans* conformations, as evidenced by XRD and ¹³C CP/MAS NMR. The variation of the *d*-spacings (5.84 nm, 3.40 nm, and 5.14 nm for **1H**, **2H**, and **3H**, respectively) is due to the difference in the

arrangements and tilting angles of hexadecanol molecules (or hexadecoxy groups) and $O_3Si-R'-SiO_3$ units, as well as to the difference in the length of the bridging organic groups.

The *d*-spacing of **1H** is larger by 0.75 nm than that of the layered structure (d = 5.09 nm) consisting of silicic acid layers and bimolecular layers of perpendicularly oriented hexadecanols (approximate thicknesses of 0.7 nm and 4.4 nm, respectively).²⁰ This indicates that 1H has a similar bilayer structure where the silsesquioxane layer consists of bimolecular layers of $O_{3/2}Si-CH_2-SiO_{3/2}$ units (2 × ca. 0.7 nm) (Fig. 8a). In contrast, **2H** has a much smaller *d*-spacing than that of 1H, which implies that hexadecanols are arranged in an interdigitated monolayer (Fig. 8b). A bilayer arrangement of hexadecanols is unlikely because it requires the long axis of the alkyl chains to be highly tilted away from the plane normal. The difference in the interlayer structures of 1H and 2H is probably due to the difference in the surface areas occupied by $Si(OH)_2 - R' - Si(OH)_3$ (R' = CH₂ or C₂H₄) units. The slightly larger head group area of ethylene-bridged monomers increases the average distance between alkoxy groups. As a result, a monolayer arrangement rather than a bilayer arrangement was favored for the close packing of alkyl chains.

It is apparent that 3H consists of bimolecular layers of hexadecoxy groups because the d-spacing (5.14 nm) is much larger than the extended molecular length of hydrolyzed monomers (ca. 3 nm). We propose that the $Si(OH)_2-C_6H_4 Si(OH)_3$ units also form bilayers (*ca.* 2 nm in thickness), and hexadecoxy groups are tilted away from the plane normal by $ca. 42^{\circ}$ to satisfy the layer thickness of ca. 3.14 nm (Fig. 8c). In contrast, when assuming a monolayer arrangement of Si(OH)₂-C₆H₄-Si(OH)₃ units (ca. 1 nm in thickness), the thickness of the alkoxy layer is calculated to be 4.14 nm, meaning that hexadecoxy groups are oriented almost perpendicular to the layers. However, this model is inconsistent with the generally accepted relationship between packing and arrangement of interlayer organic species because the monolayer arrangement of Si(OH)₂-C₆H₄-Si(OH)₃ units leads to the increase of the average lateral distance between alkoxy groups, which should cause a substantial tilting of alkoxy groups.

Recently, bis(trialkoxysilanes) with various organic bridges have been found to form hybrid solids with short- or longrange ordered structures. However, their formation requires either rigid aromatic bridges or those containing hydrogenbonding units in the precursors. The present results



Fig. 8 Proposed structural models of the layered hybrids 1H, 2H, and 3H.

demonstrate that the incorporation of long chain alkoxy groups enables the formation of lamellar hybrids even from alkylene-bridged precursors which generally afford nonordered xerogels. It will be possible to design novel bridged silsesquioxane materials with hierarchical structures by the choice of bridging organic groups. Moreover, because the morphology of the amphiphilic self-assemblies strongly depends on their geometrical packing parameters, the variation of the mesostructures from lamellar to higher curvature mesophases such as 2D hexagonal³³ and cubic is also expected.

Conclusions

We have demonstrated the formation of novel layered materials from alkoxyderivatives of bis(trichlorosilanes) having methylene, ethylene, and phenylene bridges. Selfassembly and subsequent polycondensation behaviors of amphiphilic hydrolyzed species depended on the kind of bridging organic groups. The precursors containing methylene and ethylene groups (1 and 2) afforded lamellar hybrids composed of bridged polysilsesquioxane layers and alcohol layers stacked alternately on a nanometer length scale. However, the arrangement of interlayer alcohol molecules was different. On the other hand, the monomer with a phenylene group (3) formed crystalline solids consisting of hydrolyzed monomers, which is possibly due to the stronger interaction between molecules and the formation of hydrogenbonding networks between silanol groups. We believe that the present methodology can be extended to the use of various organochlorosilane-based precursors. The use of multiple interactions, *i.e.*, hydrophobic interaction between long alkoxy groups combined with hydrogen-bonding or π - π interactions between organic bridges, is especially important toward the construction of hierarchically ordered hybrid systems.

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References

- 1 Special issue on Functional Hybrid Materials, ed. C. Sanchez, J. Mater. Chem. 2005, 15.
- 2 R. J. P. Corriu, Angew. Chem., Int. Ed., 2000, 39, 1376.

- 3 D. A. Loy and K. J. Shea, *Chem. Rev.*, 1995, **95**, 1431 and references therein.
- 4 K. J. Shea and D. A. Loy, Chem. Mater., 2001, 13, 3306.
- 5 S. Inagaki, S. Guan, Y. Fukushima, T. Ohsuna and O. Terasaki, J. Am. Chem. Soc., 1999, **121**, 9611.
- 6 T. Asefa, M. J. MacLachlan, N. Coombs and G. A. Ozin, *Nature*, 1999, **402**, 867.
- 7 A. Sayari and S. Hamoudi, *Chem. Mater.*, 2001, **13**, 3151 and references therein.
- 8 Y. Lu, H. Fan, N. Doke, D. A. Loy, R. A. Assink, D. A. LaVan and C. J. Brinker, J. Am. Chem. Soc., 2000, 122, 5258.
- 9 B. Boury, F. Ben and R. J. P. Corriu, Angew. Chem., Int. Ed., 2001, 40, 2853.
- 10 B. Boury and R. J. P. Corriu, *Chem. Commun.*, 2002, 795 and references therein.
- 11 J. J. E. Moreau, L. Vellutini, M. W. C. Man, C. Bied, J.-L. Bantignies, P. Dieudonné and J.-L. Sauvajol, J. Am. Chem. Soc., 2001, 123, 7957.
- 12 J. J. E. Moreau, B. P. Pichon, M. W. C. Man, C. Bied, H. Pritzkow, J.-L. Bantignies, P. Dieudonné and J.-L. Sauvajol, *Angew. Chem.*, *Int. Ed.*, 2004, **43**, 203.
- 13 J. J. E. Moreau, B. P. Pichon, C. Bied and M. W. C. Man, J. Mater. Chem., 2005, 15, 3929.
- 14 J. J. E. Moreau, B. P. Pichon, G. Arrachart, M. W. C. Man and C. Bied, *New J. Chem.*, 2005, **29**, 653.
- 15 S. Inagaki, S. Guan, T. Ohsuna and O. Terasaki, *Nature*, 2002, 416, 304.
- 16 M. P. Kapoor, Q. Yang and S. Inagaki, J. Am. Chem. Soc., 2002, 124, 15176.
- 17 M. P. Kapoor, Q. Yang and S. Inagaki, Chem. Mater., 2004, 16, 1209.
- 18 K. Okamoto, M. P. Kapoor and S. Inagaki, Chem. Commun., 2005, 1423.
- 19 A. Shimojima, Y. Sugahara and K. Kuroda, Bull. Chem. Soc. Jpn., 1997, 70, 2847.
- 20 Y. Fujimoto, A. Shimojima and K. Kuroda, *Chem. Mater.*, 2003, 15, 4768.
- 21 Y. Fujimoto, A. Shimojima and K. Kuroda, *Langmuir*, 2005, **21**, 7513.
- 22 Y. Mitamura, Y. Komori, S. Hayashi, Y. Sugahara and K. Kuroda, *Chem. Mater.*, 2001, 13, 3747.
- 23 D. M. Antonelli and J. Y. Ying, Angew. Chem., Int. Ed. Engl., 1996, 35, 426.
- 24 D. M. Antonelli, A. Nakahira and J. Y. Ying, *Inorg. Chem.*, 1996, 35, 3126.
- 25 Y. Sugahara, S. Okada, K. Kuroda and C. Kato, J. Non-Cryst. Solids, 1994, 167, 21.
- 26 R. J. Hook, J. Non-Cryst. Solids, 1996, 195, 1.
- 27 D. A. Loy, B. Mather, A. R. Straumanis, C. Baugher, D. A. Schneider, A. Sanchez and K. J. Shea, *Chem. Mater.*, 2004, 16, 2041.
- 28 S. D. Korkin, M. I. Buzin, E. V. Matukhina, L. N. Zherlitsyna, N. Auner and O. I. Shchegolikhina, *J. Organomet. Chem.*, 2003, 686, 313.
- 29 G. Cerveau, R. J. P. Corriu, B. Dabiens and J. L. Bideau, Angew. Chem., Int. Ed., 2000, 39, 4533.
- 30 W. Gao, L. Dickinson, C. Grozinger, F. G. Morin and L. Reven, Langmuir, 1997, 13, 115.
- 31 G. C. Ossenkamp, T. Kemmitt and J. H. Johnston, *Chem. Mater.*, 2001, **13**, 3975.
- 32 R. J. P. Corriu, J. J. E. Moreau, P. Thepot and M. W. C. Man, *Chem. Mater.*, 1992, 4, 1217.
- 33 A. Shimojima and K. Kuroda, Angew. Chem., Int. Ed., 2003, 42, 4057.