Bull. Chem. Soc. Jpn., 70, 2847—2853 (1997)

Inorganic–Organic Layered Materials Derived via the Hydrolysis and Polycondensation of Trialkoxy(alkyl)silanes

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(Received May 28, 1997)

Triethoxy(alkyl)silanes containing 12—18 carbon atoms in the alkyl groups were hydrolyzed and polycondensed to form ordered structured materials. The XRD pattern of each condensed product showed sharp diffraction peaks with higher orders. The basal spacings approximately corresponded to twice the extended molecular length of the alkyl groups, and increased linearly as a function of the alkyl chain length. The SEM images of the products exhibited a platy morphology, and the ^{29}Si CP/MAS NMR spectra revealed the formation of siloxane bonds with various silicon sites from T^1 to T^3 environments. All of these results indicated the formation of highly-organized inorganic–organic layered materials.

There have been many efforts to construct highly organized material systems. Among them, materials design utilizing the self-organization of amphiphilic molecules has attracted much attention as a unique method to prepare novel morphologies and structures. Alkoxysilanes have already been employed to prepare a variety of organized silica-based materials by using organic molecular assemblies, such as surfactant liquid-crystal phases[1—3] or synthetic bilayer membranes,[4] as templates. These studies are of importance from various aspects, including the structural control of inorganic materials as well as the biomimetic processing of inorganic–organic nanomaterials.

On the other hand, the sol–gel process[5] of alkoxy(organo)-silanes has widely been studied as an effective way to synthesize inorganic–organic hybrid materials.[6] Although hydrolysis and polycondensation processes of usual alkoxysilanes result in the formation of amorphous materials, a sort of structural control can be expected by incorporating organic groups in the inorganic framework. Fukushima et al. reported inorganic–organic interstratified layered polymers formed by the hydrolysis and polycondensation of 3-(methacryloxy)propyltrimethoxysilane in the presence of Mg^{2+} (or Ni^{2+}) ions.[7] Self-organization of organic groups by hydrophobic interactions has been pointed out to be a driving force in the formation of an ordered structure.

Organosilanes containing long-chain alkyl groups are practically useful as surface modifying agents of inorganic powders, such as silica gel to control hydrophilic/hydrophobic and polar/nonpolar properties.[8,9] Though these molecules are organophilic, they can be recognized to be amphiphilic as hydrolysis proceeds to form hydrophilic silanol groups. Many studies have been reported on the interfacial deposition of Langmuir–Blodgett films[10—12] and self-assembled monolayers,[13—16] in both of which a molecular-level control of the alkylsilyl groups arranged in two-dimensional array was attained. Consequently, it is quite reasonable to expect that these amphiphilic molecules can form an anisotropic molecular assembly, even by reaction in solution states. Therefore, we expected that inorganic–organic nanomaterials with a specifically assembled structure can be obtained by the hydrolysis and polycondensation of trialkoxy(alkyl)silanes in a homogeneous solution; preliminary results have already been reported by us.[17] This is a new approach to design novel inorganic–organic nanostructured materials, and is also of interest compared with previous systems containing alkoxysilane–surfactant systems. Although Parikh et al. have recently reported on the formation of layered polymers via hydrolytic polycondensation of trichloro(alkyl)silanes in water,[18] our system is focused on the formation of ordered structures derived from a homogeneous solution using trialkoxy(alkyl)silanes.

The polycondensation reactions of triethoxy(alkyl)silanes with carbon numbers of 6 and 9 ($RSi(OEt)_3$; $R = i\text{-}C_9H_{19}$, $n\text{-}C_6H_{13}$) have already been investigated by Andrianov et al., and the formation of low-molecular-weight oligomers with ethoxy and hydroxy groups under acid-catalyzed reactions in nonpolar solvents[19] has been reported. However, there had been no attempts to prepare nanomaterials with ordered structures until Stucky et al. recently mentioned that solids with lamellar structures were formed by the reaction of triethoxy(hexadecyl)silane ($C_{16}H_{33}Si(OEt)_3$) under acidic conditions.[20] However, no detailed analyses of the products have been presented.

In the present study, therefore, triethoxy(alkyl)silanes containing long-chain alkyl groups were utilized as the starting materials, and hydrolysis in a homogeneous solution and subsequent polycondensation were attempted; also, the formation of ordered structures based on molecular assembly was studied.

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Experimental

Materials. Triethoxy(octadecyl)silane ($C_{18}H_{37}Si(OC_2H_5)_3$), triethoxy(hexadecyl)silane ($C_{16}H_{33}Si(OC_2H_5)_3$), and triethoxy(dodecyl)silane ($C_{12}H_{25}Si(OC_2H_5)_3$) were purchased from Chisso Co. and used without further purification. Triethoxy(tetradecyl)silane ($C_{14}H_{29}Si(OC_2H_5)_3$) was prepared by the reaction of trichloro(tetradecyl)silane (Tokyo Kasei Co.) with ethanol, and the complete conversion to ethoxy groups in the products was confirmed by ^{29}Si NMR.

Reaction Procedure. Triethoxy(alkyl)silane ($C_nH_{2n+1}Si(OEt)_3$; C*n*TES, $n = 12$, 14, 16, and 18) was added to a mixture of ethanol, water, and hydrochloric acid, and the reaction mixture was stirred at room temperature or at a lower temperature of 5 °C. The composition of the starting mixture was C*n*TES : EtOH : H_2O : HCl = 1 : 100 : x : 0.001 (molar ratio), where $x = 30$, 40, 60, 80. The variation in the molar ratios of HCl (0.01, 0.1, and 1.0) in a mixture of C18TES was also conducted in the case of $x = 30$. Upon the addition of the alkoxysilanes the mixture was initially an emulsion state, but became a clear homogeneous solution, followed by the formation of white precipitates. The precipitates were filtered and dried at 60 °C for 1 d to yield white powders.

Analyses. X-Ray powder diffraction (XRD) patterns were recorded on a Rigaku RAD-1B diffractometer (Mn filtered Fe-$K\alpha$ radiation). Carbon-13 and Silicon-29 CP/MAS NMR spectra of solid samples were obtained on a JEOL GSX-400 spectrometer at frequencies of 100.40 and 79.30 MHz, respectively. (200 and 1000 scans were taken respectively, with a same delay time of 5 s) The liquid-state ^{29}Si NMR spectra were measured on a JEOL EX-270 spectrometer at 53.54 MHz. In this case, TMS was used as the internal reference and $CDCl_3$ was used for obtaining NMR lock signals. Scanning electron micrographs (SEM) were observed on a Hitachi S-2500 at an operating voltage of 25 kV.

Results and Discussion

Structure of Hydrolyzed and Polycondensed Products. The structures of the products strongly depended on the molar ratio of water in the system. Above a certain value of water, several diffraction peaks were observed in lower 2θ regions of the XRD patterns. The most intense peaks were observed when the molar ratio of water (x) was 30, 40, 60, and 80 when the carbon number of the alkyl chains (n) in the triethoxy(alkyl)silanes (C*n*TES) was 18, 16, 14, and 12, respectively (Fig. 1). Along with a decrease in the molar ratio of water, the intensities of the diffraction peaks decreased continuously and the products finally became an amorphous state. On the other hand, when the molar ratio of water was increased, inhomogeneous mixtures with separated organic phase were obtained, and desired reactions in homogeneous media could not be performed. In addition, when shorter-chain alkylsilanes (C12- and C14TES) were used, the products obtained at room temperature were either liquids or amorphous, while ordered-structured materials were obtained by reactions at 5 °C. This behavior corresponds to the general findings that the solvophobic property of alkyl chains is eminent in the presence of a large amount of water in their surroundings, and that the solubilities of solutes (i.e. trialkoxy(alkyl)silanes in this case) decrease at lower temperatures. Similar to amphiphilic molecules, the assembly of molecules based on hydrophobic interactions of alkyl groups may be a driving force in the formation of ordered structures.

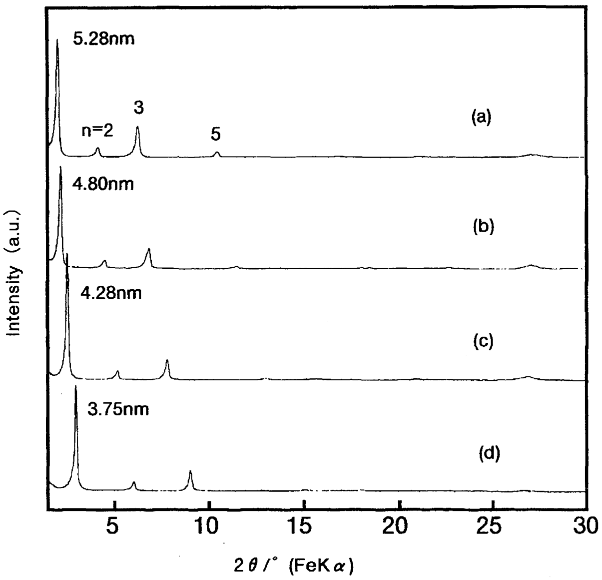

Fig. 1. XRD patterns of the products in $C_nH_{2n+1}Si(OEt)_3$: EtOH : H_2O : HCl=1 : 100 : x : 0.001 system: (a) n=18/x=30, (b) n=16/x=40, (c) n=14/x=60, (d) n=12/x=80.

The XRD patterns of the products with the variation of the alkyl chain lengths are shown in Fig. 1. The diffraction peaks at the lowest 2θ angles are due to basal spacings corresponding to the long-range orders of 5.28, 4.80, 4.28, and 3.75 nm, and the peaks at higher angles correspond to higher order diffractions. These patterns are ascribable to the formation of layered structures, and the basal spacings are interpreted as being the repeating distances of those layers. The broad peaks at around $2\theta = 27°$ ($d = 0.42$ nm) can be attributed to alkyl chain packing within the layers.

The basal spacings increased linearly along with an increase in the alkyl chain lengths, as shown in Fig. 2. The basal spacing increased by 0.253 nm per one carbon (i.e. the

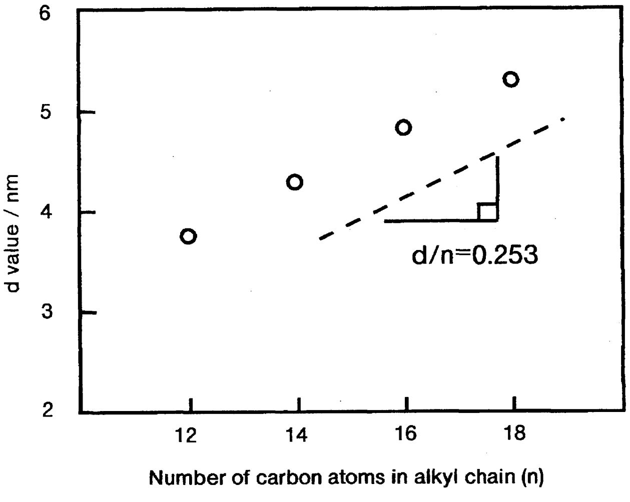

Fig. 2. The variation in the d value as a function of alkyl chain length.

slope of the line ($\Delta d/n$) is 0.253 nm/n), which corresponds to a value of twice the average C–C bond distance of *all-trans* alkyl chains. Therefore, all of the products are considered to have bimolecular layered structure with alkyl chains perpendicular to the layers. Because the structures of these products were the same, a detailed analysis was performed for the polycondensed product derived from C18TES.

The ^{13}C CP/MAS NMR spectrum of the product obtained from C18TES showed a signal due to *all-trans* interior methylene groups at 32.8 ppm. No signal at a higher field around 30.0 ppm due to *gauche* deficients was detected. From these results, alkyl chains in the interlayer regions are considered to be conformationally *all-trans* and highly ordered. The SEM image of the product (Fig. 3) also exhibited the platy morphologies, and all of these results confirmed the layered structure of the products obtained from a homogeneous solution containing long-chain alkoxy(alkyl)silanes.

In the ^{29}Si NMR spectrum, Si atoms normally show various signals with different chemical shifts, depending on the number of siloxane bonds formed by the hydrolysis and polycondensation reactions. When trifunctional alkoxysilanes are used, these signals are designated as T^m (m=0—3), where m denotes the number of siloxane bonds. As shown in Fig. 4a, the spectrum of the starting material (C18TES) shows the only signal in the T^0 region. Figure 4c shows the ^{29}Si CP/MAS NMR spectrum of the final product, which exhibits broad signals in the T^1, T^2, and T^3 regions, indicating the formation of siloxane networks. The IR spectrum of the product showed split absorption bands due to the siloxane framework at around 1000—1150 cm^{-1}, and the bands due to silanol groups at around 3300—3500 cm^{-1} and 890 cm^{-1}.

Based on the results described above, the resultant products are considered to comprise two-dimensional siloxane frameworks. Sjöblom et al. have pointed out that there should be some spatial restriction for the formation of two-dimensional siloxane frameworks because of the occupying volume of the alkyl groups.[11] Siloxane linkage in the present products should have linear polymers to some extent in order to take two-dimensional configurations. This point is nicely in accord with the ^{29}Si CP/MAS NMR results which clearly shows the substantial presence of T^2 units. However, it should be noted that the presence of T^1 and T^3 signals indicates a partial variation in the siloxane linkage.

Formation Process. Although the C18TES-derived product was insoluble in typical organic solvents, the precipitate before drying dissolved in THF very easily. In the liquid-state ^{29}Si NMR spectrum (as shown in Fig. 4b), the signal assigned to the completely hydrolyzed monomeric species ($C_{18}H_{37}Si(OH)_3$) was mainly observed. This finding means that the precipitate is a sort of aggregate of silanetriols, and that polycondensation proceeds by solid-state polymerization during the drying process.

Figure 5 shows the variation in the XRD patterns during the drying process. As shown in Fig. 5a, the aggregate

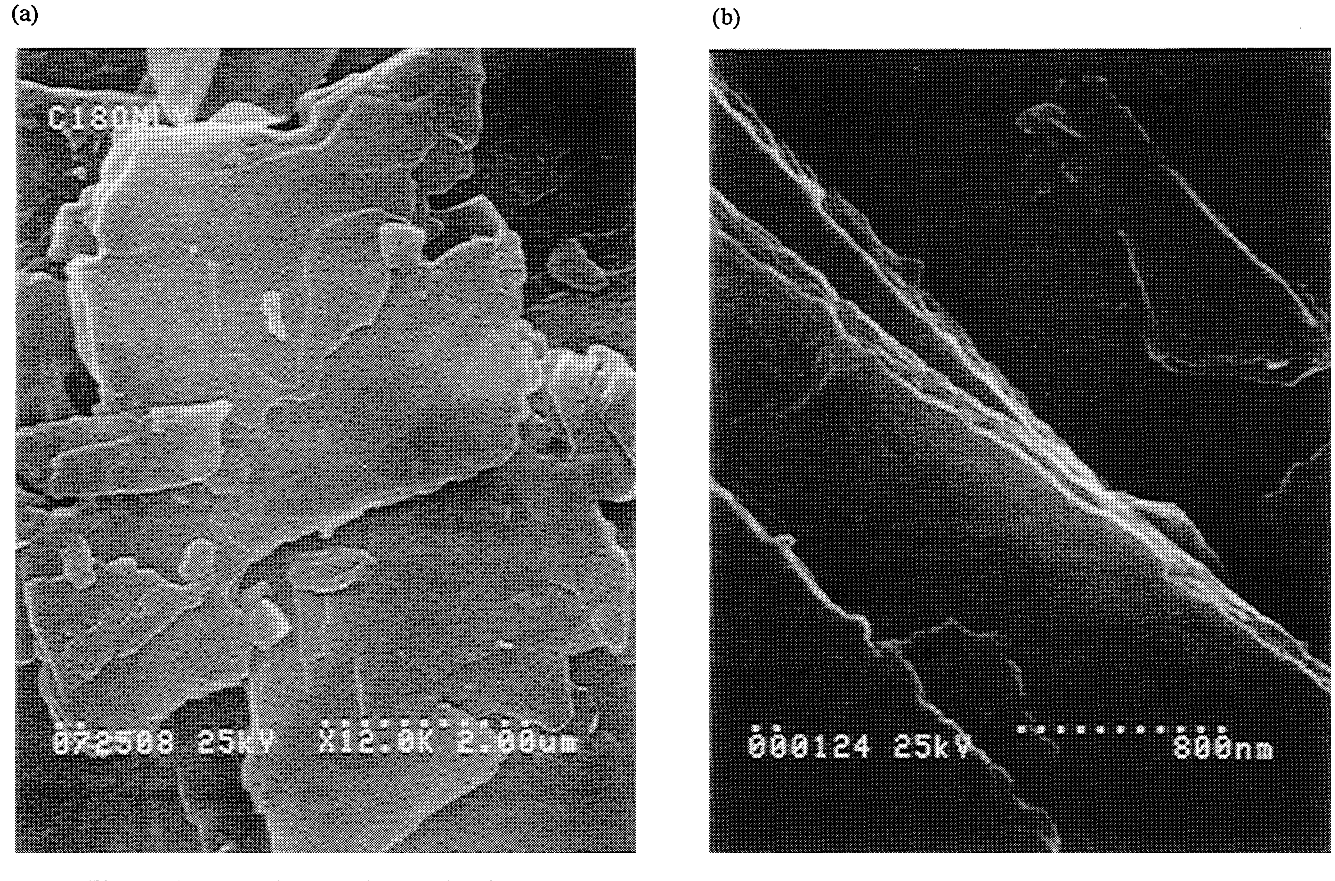

Fig. 3. Scanning electron micrographs of the product in $C_{18}H_{37}Si(OEt)_3$: EtOH : H_2O : HCl = 1 : 100 : 30 : 0.001 system.

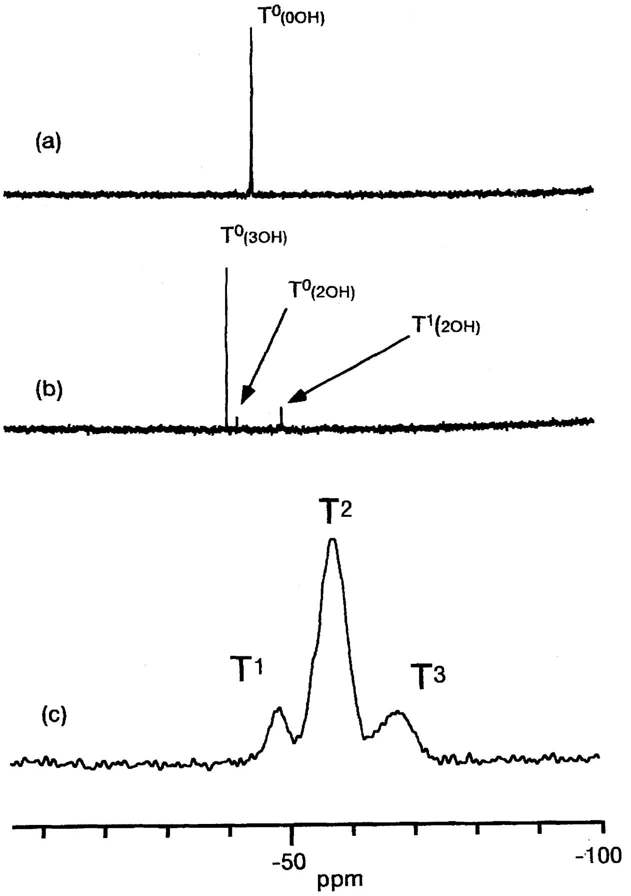

Fig. 4. Liquid state ^{29}Si NMR spectra of (a) $C_{18}H_{37}Si(OEt)_3$, (b) THF solution of the precipitate, and (c) ^{29}Si CP/MAS NMR spectrum of the final product.

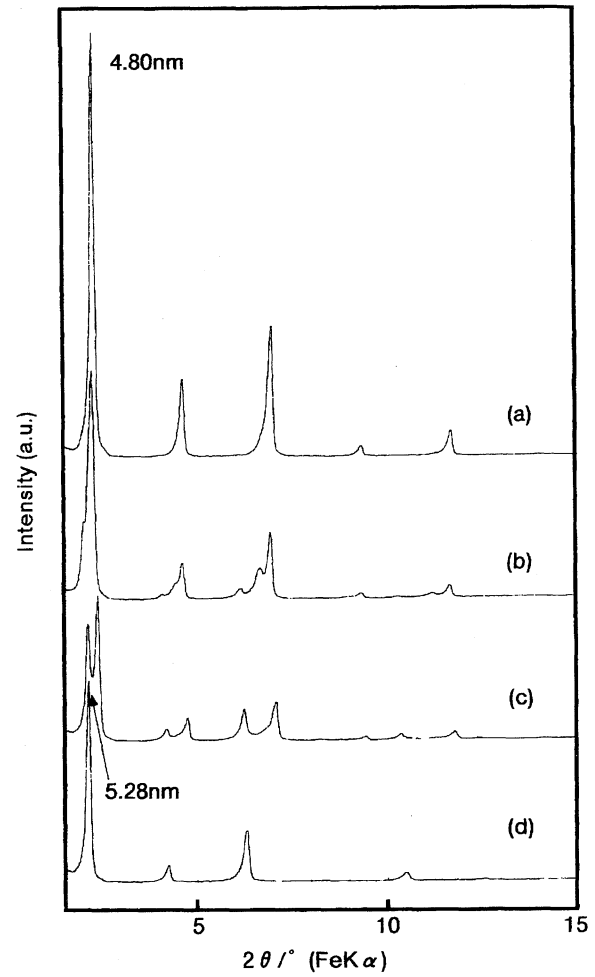

Fig. 5. The variation in XRD patterns of the precipitates in $C_{18}H_{37}Si(OEt)_3$: EtOH : H_2O : HCl=1 : 100 : 30 : 0.001 system dried for (a) 0 h, (b) 6 h, (c) 1 d at RT, and (d) 1 d at 60 °C.

of octadecylsilanetriol also takes a bilayer arrangement corresponding to a basal spacing of 4.8 nm. Along with an increase in the drying time at room temperature, the intensity of the diffraction peak decreased, indicating the proceeding of polycondensation. Simultaneously, a lower diffraction peak (basal spacing of 5.28 nm) appeared. Although it took several days for the 4.8 nm peak to disappear, only several hours was necessary to obtain a single phase with a basal spacing of 5.28 nm by increasing the drying temperature up to 60 °C. The increase in the basal spacing by ca. 0.5 nm may be ascribed to a variation in the oriented angles of the alkyl chains and/or a distortion of the inorganic framework.

In the system of C18TES, the variation in the XRD patterns of the products with the molar ratio of hydrochloric acid was also examined, as shown in Fig. 6. This figure clearly indicates that the structural ordering of the products decreased along with an increase in the hydrochloric acid as a catalyst. Furthermore, when trichloro(octadecyl)silane ($C_{18}H_{37}SiCl_3$) was added into the water, the mixture was not homogeneous, and the diffraction peaks of the products were relatively weak, and a highly ordered structure was not obtained. In the sol–gel processes of alkoxysilanes, the hydrolysis rate of the alkoxy groups increased along with the concentration of the catalyst.[5] Considering the higher hydrolysis rates of the chlorosilanes compared with those of the alkoxysilanes, the above results apparently indicate that, upon the formation of an ordered structure, mild reaction processes should be favorable for the alkylsilane molecules to arrange in particular regularities according to their hydrophobic and hydrophilic interactions.

In the ^{29}Si CP/MAS NMR spectra of the C18TES-derived material, as shown in Fig. 7, a new signal at −54 ppm appeared and the relative intensity gradually increased along with an increase of hydrochloric acid. In the systems of tetraethoxysilane (TEOS) and triethoxy(methyl)silane (MTES), the signals due to cyclic species normally appears at a lower field than the normal chemical shifts of linear polymers.[21,22] Therefore, a decrease in the ordering of the products with the amount of hydrochloric acid is related to the formation of some cyclic species, which can be explained by the proposed model, which claims that a linear siloxane linkage is necessary for a two-dimensional arrangement of long-chain alkylsilyl groups.[11]

Discussion on the Structure of Inorganic–Organic Layered Materials. With regard to the hydrolysis and poly-

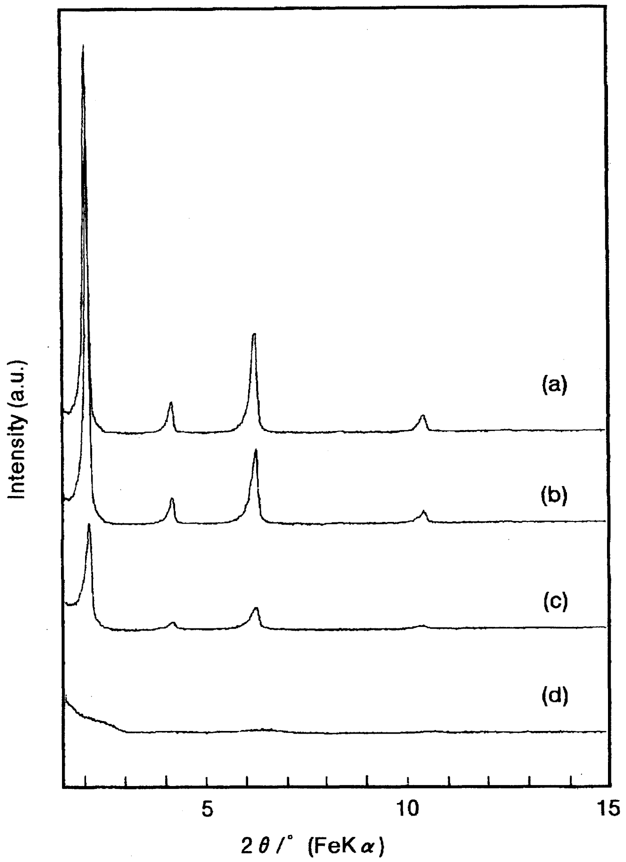

Fig. 6. XRD patterns of the products with different HCl molar ratios in $C_{18}H_{37}Si(OEt)_3$: EtOH : H_2O : HCl = 1 : 100 : 30 : y system: y = (a) 0.001, (b) 0.01, (c) 0.1, (d) 1.0.

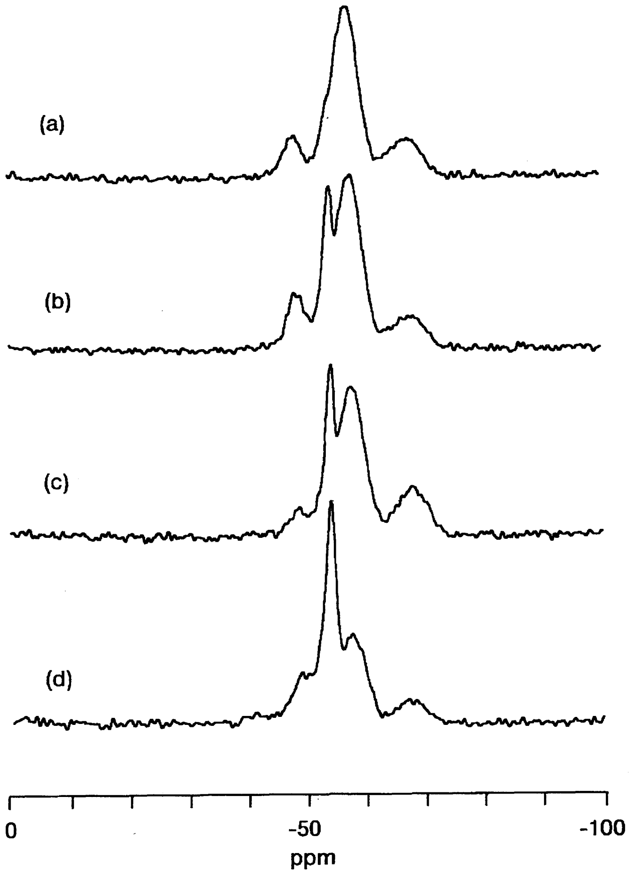

Fig. 7. ^{29}Si CP/MAS NMR spectra of the products with different HCl molar ratios in $C_{18}H_{37}Si(OEt)_3$: EtOH : H_2O : HCl = 1 : 100 : 30 : y system: y = (a) 0.001, (b) 0.01, (c) 0.1, (d) 1.0.

condensation of chloro(organo)silanes with bulky organic groups, it has been known that it is possible to separate silsesquioxane[23,24] or silanetrilos,[25] depending on the reaction conditions. Silanetriols can take several crystal structures by inter- and intra-hydrogen bondings of neighboring silanol groups. In particular, t-$BuSi(OH)_3$ and c-$C_6H_{11}Si(OH)_3$ have been reported to take double-sheets structures where organic groups are pointing toward each other as silanol groups are pointing toward each other in a similar way.[26,27] These findings correspond to the fact that the products (precipitates) before drying are mainly aggregates of silanetriols composed of bilayer structures. However, in the XRD pattern of the product derived from C18TES, the long-range ordering of layers are outstanding, whereas periodicity along with other axes was not clearly observed, suggesting a good relation to the common mesophases, that is the so-called lamellar phases in the usual surfactant–water systems.[28] The association states of amphiphilic molecules in water are proposed to be closely related to their molecular shapes, which is described in terms of the packing parameters.[29] Based on this proposal, alkylsilanetriols obtained by hydrolysis can be regarded as being amphiphilic molecules in which the occupied space of the hydrophilic part (head groups) is small; therefore, lamellar packing, rather than spherical or rod-like aggregates, is very favorable.

On the other hand, inorganic layered materials, such as layered silicates and clay minerals with alkylammonium salts, are one of the well-known systems where long-chain alkylammonium cations can be intercalated by ion exchange. Lagaly et al. and other researchers have reported various arrangements of alkyl chains present in the interlayer regions.[30] Organic derivatives of inorganic layered materials are also known, and several reports have shown a swelling behavior in organic solvents. However, the present layered products exhibit no swelling behavior. This result may be interpreted as meaning that the bilayer structures are retained by the close packing of *all-trans* alkyl chains, and that van der Waals interactions between adjacent layers are relatively high.

Thermal Behavior. The dried product derived from C18TES became liquid upon thermal treatment above 100 °C. The DTA curve of the product showed a sharp endothermic peak around this temperature. This behavior is ascribed to an incompleteness of the siloxane linkage for the formation of a rigid and thermally stable inorganic network, and the product cooled to room temperature was amorphous. As shown in Fig. 8, the ^{29}Si CP/MAS NMR spectra of the products before and after this thermal treatment indicated the disappearance of the T^1 signal and a relative increase in the T^3 signal, meaning progress of the condensation re-

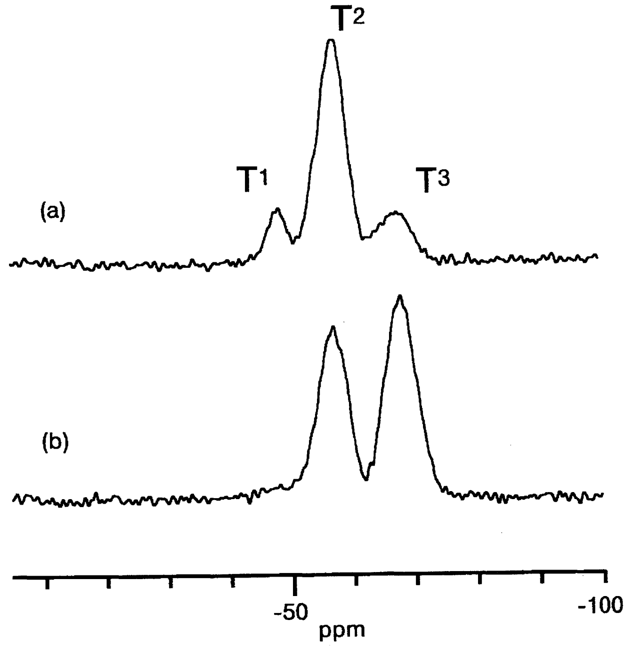

Fig. 8. ^{29}Si CP/MAS NMR spectra of the products in $C_{18}H_{37}Si(OEt)_3$: EtOH : H_2O : HCl = 1 : 100 : 30 : 0.001 system: (a) as-synthesized (layered structure), (b) after thermal treatment at 110 °C for 15 min (amorphous).

action between unreacted silanol groups. The IR spectrum of the product after the heat treatment showed a substantial decrease in the absorption bands due to the silanol groups, which is consistent with the NMR results. By a thermal treatment of the product, interlayer alkyl chains can take some random orientations, which can cause a further condensation of the residual silanol groups due to a relaxation of the steric hindrance which is accompanied by the formation of a layered structure. Also, this further condensation resulted in an irreversible skeletal change to cause disordering. The IR (CH stretching region) and the ^{13}C CP/MAS NMR spectra of the products before and after the heat treatment did not show any significant changes, indicating that no substantial changes occurred in the aggregate state of the alkyl chains.

Conclusions

Homogeneous solutions of the triethoxy(alkyl)silane (C*n*TES, $n = 12—18$)–ethanol–water–hydrochloric acid system were hydrolyzed and polycondensed to produce lamellar siloxane polymers when the molar ratio of water to alkoxysilane was over a certain value. The alkyl chains were thought to arrange double layers perpendicular to the siloxane layers. The ^{29}Si NMR spectra of the products indicated that the precipitates formed during the hydrolysis of the homogeneous solutions were aggregates of alkylsilanetriols, and that polycondensation proceeded in the drying processes. Along with an increase in the molar ratio of hydrochloric acid, the ordering of the product decreased, where some cyclic species were detected. The present findings strongly indicate that the self-organization of long-chain trialkoxy(alkyl)silanes is quite effective for the formation of ordered structures. This method is quite meaningful for the construction of inorganic–organic nanostructured materials by the polymerization of metal alkoxides or copolymerization of two or more metal alkoxides.

This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture.

References

1) Q. Huo, D. I. Margolese, U. Ciesla, D. G. Demuth, P. Feng, T. E. Gier, P. Sieger, A. Firouzi, B. F. Chmelka, F. Scguth, and G. D. Stucky, *Chem. Mater.*, **6**, 1176 (1994).

2) M. Ogawa, *J. Am. Chem. Soc.*, **116**, 7941 (1994).

3) M. Ogawa, *J. Chem. Soc., Chem. Commun.*, **1996**, 1149.

4) K. Sakata and T. Kunitake, *J. Chem. Soc., Chem. Commun.*, **1990**, 504.

5) C. J. Brinker and G. W. Scherer, "Sol–Gel Science," Academic Press, San Diego (1990).

6) H. K. Schmidt, "Sol–Gel Science and Technology," World Scientific, Brazil (1989), p. 432.

7) Y. Fukushima and M. Tani, *J. Chem. Soc., Chem. Commun.*, **1995**, 241.

8) K. Albert and E. Bayer, *J. Chromatogr.*, **554**, 345 (1991).

9) M. Pursch, A. Jager, T. Schneller, R. Brindle, K. Albert, and E. Lindner, *Chem. Mater.*, **8**, 1245 (1996).

10) J. Wood and R. Sharma, *Langmuir*, **10**, 2307 (1994).

11) J. Sjöblom, G. Stakkestad, H. Ebeltoft, S. E. Friberg, and P. Claesson, *Langmuir*, **11**, 2652 (1995).

12) M. Lindén, J. P. Slotte, and J. B. Rosenholm, *Langmuir*, **12**, 4449 (1996).

13) J. Sagiv, *J. Am. Chem. Soc.*, **102**, 92 (1980).

14) A. Ulman, "An Introduction to Ultrathin Organic Films from Langmuir–Blodgett to Self-Assembly," Academic Press, New York (1991), p. 256.

15) C. R. Kessel and S. Granick, *Langmuir*, **7**, 532 (1991).

16) X. Xiao, G. Liu, D. H. Charych, and M. Salmeron, *Langmuir*, **11**, 1600 (1995).

17) A. Shimojima, T. Inoue, Y. Sugahara, and K. Kuroda, "70th Spring Annual Meeting of the Chemical Society of Japan," Tokyo, April 1996, Abstr., No. 2C411.

18) A. N. Parikh, M. A. Schivley, E. Koo, K. Seshadri, D. Aurentz, K. Mueller, and D. L. Allara, *J. Am. Chem. Soc.*, **119**, 3135 (1997).

19) K. A. Andrianov and B. A. Izmailov, *Zh. Obshch. Khim.*, **46**, 114 (1976).

20) Q. Huo, D. I. Margolese, and G. D. Stucky, *Chem. Mater.*, **8**, 1147 (1996).

21) F. J. Feher, D. A. Newman, and J. F. Walzer, *J. Am. Chem. Soc.*, **111**, 1741 (1989).

22) Y. Sugahara, S. Okada, S. Sato, K. Kuroda, and C. Kato, *J. Non-Cryst. Solids*, **167**, 21 (1994).

23) R. H. Baney, M. Ito, A. Sakakibara, and T. Suzuki, *Chem. Rev.*, **95**, 1409 (1995).

24) R. Murugavel, A. Voigt, M. G. Walawalkar, and H. W. Roesky, *Chem. Rev.*, **96**, 2205 (1996).

25) N. Winkhofer, H. W. Roesky, M. Noltemeyer, and W. T. Robinson, *Angew. Chem.*, **104**, 670 (1992).

26) R. Murugavel, V. Chandrasekhar, and H. W. Roesky, *Acc. Chem. Res.*, **29**, 183 (1996).

27) H. Ishida, J. L. Koenig, and K. C. Gardner, *J. Chem. Phys.*,

77, 5748 (1982).
28) G. J. T. Tiddy, *Phys. Rep.*, **57**, 1 (1980).
29) D. J. Mitchell and B. W. Ninham, *J. Chem. Soc., Faraday Trans. 2*, **77**, 601 (1981).
30) G. Lagaly, K. Beneke, and A. Weiss, *Am. Mineral.*, **60**, 642 (1975).