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Journal of Organometallic Chemistry 686 (2003) 223–227

Journal of Organo metallic Chemistry

www.elsevier.com/locate/jorganchem

Synthesis of multilayered silica-based hybrid films from difunctional organosilanes by co-hydrolysis and polycondensation with tetraalkoxysilane

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Received 7 April 2003; accepted 6 June 2003

Abstract

Decylethyldimethoxysilane (C10EtDMS) and didecyldimethoxysilane (2C10DMS) were used to prepare thin films of silica-based hybrids by co-hydrolysis and polycondensation with tetramethoxysilane (TMOS) followed by spin-coating. The length of the second alkyl chains (Et or *n*-decyl) had large effects on the formation of ordered hybrid films. In the case of C10EtDMS, transparent films of well-ordered lamellar hybrids were formed with various TMOS/C10EtDMS ratios by controlling the degree of polycondensation in the precursor solutions. In contrast, no ordered hybrids were obtained in the case of 2C10DMS under the same conditions, due to the larger steric hindrance of the longer second alkyl chain in the co-condensation. Increases of both TMOS/2C10DMS and HCl/Si ratios in the starting solutions promoted polycondensation and lead to the formation of ordered hybrid films.

Keywords: Organoalkoxysilane; Co-hydrolysis and polycondensation; Sol–gel process; Self-assembly; Hybrid material

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1. Introduction

Much attention has been focused on the silica-based hybrids derived from organoalkoxysilanes because of their potential for novel nanomaterials [1–4]. Recently, self-directed assembly of organoalkoxysilanes has attracted significant interests as a new approach to create nanostructured hybrids [5–13]. Molecular design of the precursors plays a key role in the self-assembly as well as in the modification of the structures and the properties of the resulting hybrids. In contrast to the growing number of studies based on trialkoxysilylated precursors with the general formula of $RSi(OR')_3$ or $(R'O)_3SiRSi(OR')_3$ (R, R′ = organic groups), there have been a few reports on the self-assembly of difunctional organosilanes having two organic substituents [8,11,13]. The use of organodialkoxysilanes contributes to the structural diversity of self-organized hybrids because two kinds of organic groups can be incorporated on a molecular scale.

We have recently reported the formation of multilayered alkylsiloxane films by hydrolysis and polycondensation of a series of alkylmethoxysilanes ($C_nH_{2n+1}Si(Me)_m(OMe)_{3-m}$, $n = 8$–12, $m = 0$–2) in the presence of tetramethoxysilane (TMOS) followed by spin-coating [13]. Although hydrolysis and polycondensation of organodialkoxysilanes generally result in the formation of linear or cyclic siloxanes, co-condensation of alkylmethyldimethoxysilane and TMOS in the precursor solutions enabled the self-assembly into lamellar structures upon evaporation of the solvents. The extension of this method to other alkoxysilanes will lead to the structural variation of the lamellar hybrids, which is of scientific interest.

In this paper, we employed two kinds of difunctional organosilanes, decylethyldimethoxysilane (C10EtDMS) and didecyldimethoxysilane (2C10DMS), to prepare

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doi:10.1016/S0022-328X(03)00619-3

hybrid films by co-hydrolysis and polycondensation with TMOS. The reaction processes were investigated and compared with those in the decylmethyldimethoxysilane (C10MeDMS)–TMOS systems, and the effects of the second alkyl chains, Me, Et or *n*-decyl, on the formation of ordered hybrids were studied.

2. Results and discussion

2.1. C10EtDMS–TMOS systems

X-ray diffraction (XRD) patterns of the hybrid films prepared from C10EtDMS–TMOS system (TMOS/C10EtDMS = 4, HCl/Si = 0.002) are shown in Fig. 1. The films obtained by spin-coating the precursor solutions after the reactions for 0.5 and 1 h have no ordered structure, whereas a sharp diffraction peak (*d* = ca. 3.8 nm) appeared in the low-angle region as the reaction time was extended to 6–12 h. The layered structure of the film (6 h) was confirmed by transmission electron microscopy (TEM) and also by the collapse of the nanostructure upon calcination at 450 °C for 6 h to remove organic moieties. Further reaction (24 h) caused the structural disordering and there appears to be an optimum reaction time for the preparation of well-ordered lamellar hybrid films. The reaction time also affects the macroscopic homogeneity of the films. The films were inhomogeneous at the early stages of the reaction (0.5–3 h), but became transparent after 6 h.

We also examined the effect of TMOS/C10EtDMS ratio on the formation of lamellar hybrid films. XRD patterns of the hybrid films prepared with various TMOS/C10EtDMS ratios are shown in Fig. 2. In the cases of TMOS/C10EtDMS = 4, 6, 8 and 10, transparent thin films of well-ordered lamellar hybrids were obtained after 6 h of the reaction. However, ordered hybrid films have never been formed with TMOS/C10EtDMS = 2. This result clearly shows that TMOS plays an essential role in the formation of ordered hybrid films. Interestingly, the *d* value of the films increases linearly with the increase in TMOS/C10EtDMS ratio (Fig. 3). This can be attributed to the formation of thicker siloxane layers, because there was no significant change in the conformation of the interlayer alkyl chains. IR spectra of the films showed the absorption peaks due to CH_2 stretching vibrations (ν_{as} (CH_2) and ν_s (CH_2)) at 2925 and 2855 cm^{-1}, respectively, indicative of *trans–gauche* conformations of the alkyl chains [14], which was unchanged by the variation of TMOS/C10EtDMS ratios.

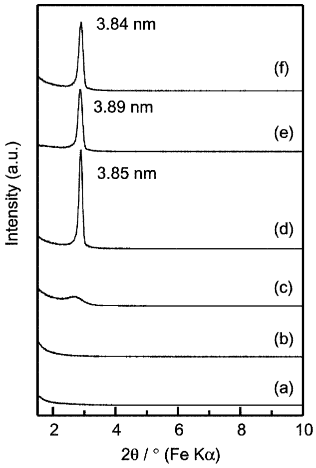

Fig. 1. XRD patterns of the hybrid films prepared from the precursor solutions after (a) 0.5 h, (b) 1 h, (c) 3 h, (d) 6 h, (e) 9 h and (f) 12 h of the reaction (TMOS/C10EtDMS = 4, HCl/Si = 0.002).

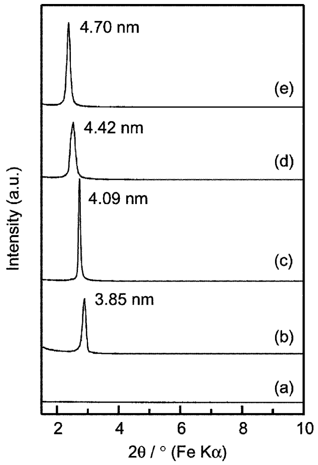

Fig. 2. XRD patterns of the hybrid films prepared with various TMOS/C10EtDMS ratios of (a) 2, (b) 4, (c) 6, (d) 8 and (e) 10 (6 h of the reaction with HCl/Si = 0.002).

We propose that such lamellar hybrid films are formed by the self-assembly of amphiphilic alkylsiloxane species, having both hydrophobic alkyl chains and hydrophilic silanol groups, into lamellar phases. The partitioning of the additional silicate species into hydrophilic layers may also occur during the self-assembly. The films are finally solidified by the polycondensation in the drying processes. The films prepared from C10EtDMS–TMOS systems are considered to have a layered structure similar to those derived from the previously reported C10MeDMS–TMOS systems

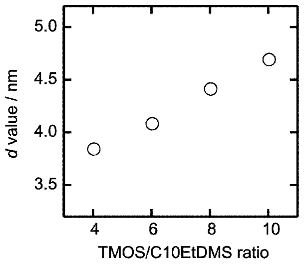

Fig. 3. The variation in the *d* values as a function of TMOS/C10EtDMS ratios.

which have a bilayer arrangement of alkyl chains covalently attached to siloxane layers [13]. However, the structures of the organic layers should be different because Et groups are incorporated instead of Me groups. In addition, it should be noted that phase (order–disorder) behaviors of the films with the reaction time are also different; C10MeDMS–TMOS system afforded highly ordered films even after the reactions for 0.5 and 1 h, although the films were inhomogeneous.

To elucidate the difference, co-hydrolysis and polycondensation processes in the precursor solutions were studied by ^{29}Si-NMR. Fig. 4 shows ^{29}Si-NMR spectra of the precursor solutions in C10EtDMS–TMOS system (TMOS/C10EtDMS = 4, HCl/Si = 0.002) after 0.5, 1, 3, 6, 9 and 12 h of the reaction. In the spectrum after 0.5 h, the signals due to TMOS-derived species appear in Q^1 and Q^2 regions (Q^x, $Si(OSi)_x(OH)_{4-x}$), and no signals due to the monomeric species are detectable in Q^0 region [15]. Also, the signal of C10EtDMS (−1.9 ppm) disappeared and two signals due to hydrolyzed monomeric species ($D^0_{(1OH)}$ and $D^0_{(2OH)}$ at −4.9 and −6.5 ppm, respectively) are observed, along with several small signals in the D^1 region (D^x, $R_2Si(OSi)_x(OH)_{2-x}$) [16]. Although the detailed assignments of the signals are unclear, the evidence for the co-condensation is provided by the appearance of the new signals in the Q^1 region (labeled with asterisks) that can never be detected when only TMOS was reacted. The D^0 signals gradually decrease as the reaction proceeds, but are still observed even after 12 h. This result is quite different from C10MeDMS–TMOS system where the D^0 species completely disappear within 3 h of the reaction [13]. Thus, the condensation rates of C10EtDMS and C10MeDMS are found to be different, which can be induced by larger steric hindrance of ethyl groups than methyl groups. As we reported previously, the self-assembly of alkyldialkoxysilanes–TMOS systems requires the formation of co-condensed oligomers in the precursor solutions; therefore, longer reaction was needed in the present systems to form ordered structures.

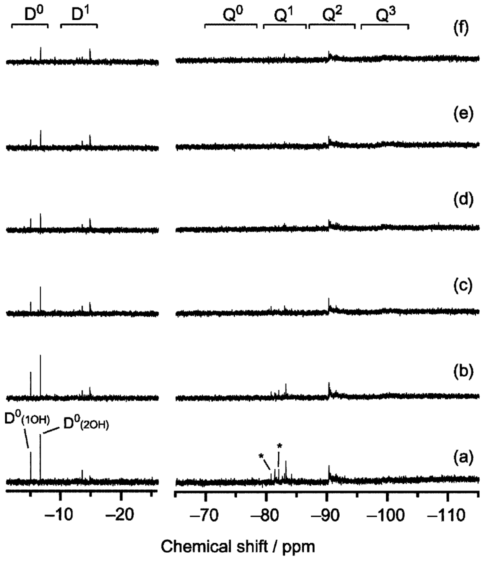

Fig. 4. Liquid-state ^{29}Si-NMR spectra of the precursor solutions after (a) 0.5 h, (b) 1 h, (c) 3 h, (d) 6 h, (e) 9 h and (f) 12 h of the reaction (TMOS/C10EtDMS = 4, HCl/Si = 0.002).

2.2. 2C10DMS–TMOS systems

The reaction in the 2C10DMS–TMOS system with TMOS/2C10DMS = 4 and HCl/Si = 0.002 did not afford well-ordered hybrid films independent of the reaction time (0.5–24 h) in the precursor solution. In addition, all of the films obtained were not transparent, and phase-separated morphologies were observed by optical microscopy. Similar results were also obtained for the system with TMOS/2C10DMS = 10 and HCl/Si = 0.002. In both of the systems, very small diffraction peaks at around $2\theta = 4.3°$ and $4.9°$ (d = ca. 2.6 and 2.3 nm, respectively) were typically observed in XRD patterns of the films, which may arise from the aggregates of hydrolyzed monomer or oligomers of 2C10DMS molecules due to the strong hydrophobic interactions.

The ^{29}Si-NMR spectra of the precursor solutions (TMOS/2C10DMS = 4, HCl/Si = 0.002) in the course of the reaction are shown in Fig. 5. Similar to C10EtDMS–TMOS system described above, TMOS

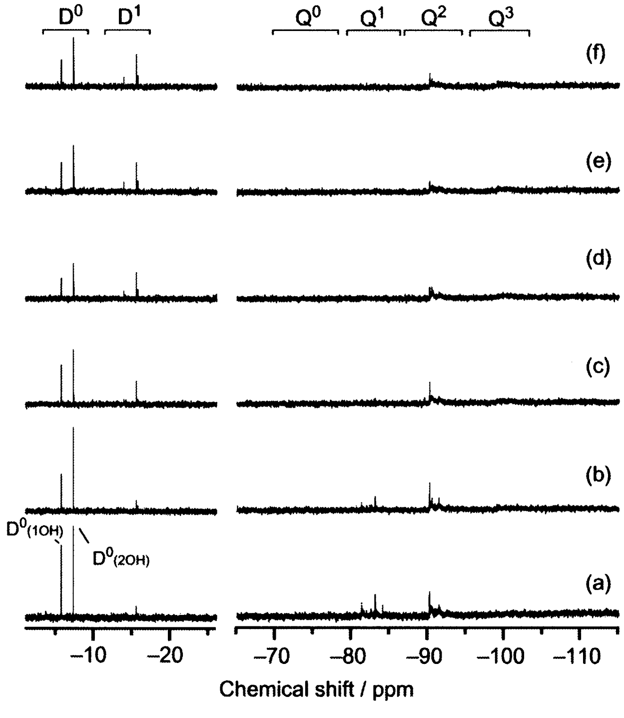

Fig. 5. Liquid-state ^{29}Si-NMR spectra of the precursor solutions after (a) 0.5 h, (b) 1 h, (c) 3 h, (d) 6 h, (e) 9 h and (f) 12 h of the reaction (TMOS/2C10DMS = 4, HCl/Si = 0.002).

molecules were hydrolyzed and polycondensed to form Q^1 and Q^2 units after 0.5 h of the reaction. However, the signals due to the co-condensed species are not clearly observed. On the other hand, the signals due to 2C10DMS (−2.4 ppm) disappeared and two signals assigned to the hydrolyzed monomeric species ($D^0_{(1OH)}$ and $D^0_{(2OH)}$ at −5.7 and −7.3 ppm, respectively) are mainly observed. Three signals at −13.8, −15.5 and −15.7 ppm, which appear as the reaction proceeds, can be assigned to the D^1 units formed by the self-condensation of 2C10DMS-derived units, because these signals can also be observed when only 2C10DMS was reacted under the same condition. Comparing the relative intensity ratios of the D^0 signals shown in Figs. 4 and 5, it is obvious that the polycondensation of the D^0 units is sterically more hindered in the case of 2C10DMS by the presence of two long alkyl chains. This can be a main reason for the formation of disordered and inhomogeneous films in this system.

We performed the reaction at the higher HCl/Si ratio of 0.01 with TMOS/2C10DMS = 10 to promote co-condensation reaction in the precursor solutions. As shown in Fig. 6, ^{29}Si-NMR revealed that the monomeric D^0 species disappeared until 6 h of the reaction under this condition. XRD patterns of the resulting films are shown in Fig. 7. The films obtained after 3 and 6 h exhibit low-angle diffraction peaks with the *d* values of 5.93 and 5.52 nm, respectively. The products are considered to have lamellar structures based on the general findings that the amphiphilic molecules having two long alkyl chains preferentially form lamellar phases in water [17] and in the presence of silicate species [18,19]. The *d* values are apparently larger than that derived from C10EtDMS with the same relative amount of TMOS (*d* = ca. 4.7 nm), suggesting that the dialkyl groups are arranged in a more extended state. However, it was still difficult to obtain well-ordered and transparent films in these systems, possibly due to the higher degree of polycondensation of TMOS-derived species as well as to the presence of self-condensed species of 2C10DMS. These results suggest that, in the case of organodialkoxysilanes with bulky organic groups, it is necessary to control the condensation rate between organodialkoxysilanes and TMOS to form well-ordered hybrid films.

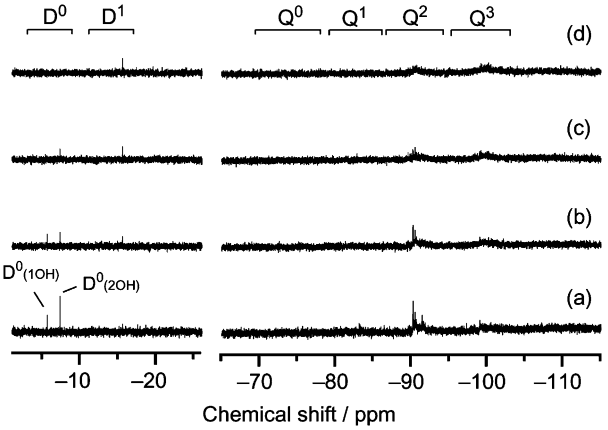

Fig. 6. Liquid-state ^{29}Si-NMR spectra of the precursor solutions after (a) 0.5 h, (b) 1 h, (c) 3 h and (d) 6 h of the reaction (TMOS/2C10DMS = 10, HCl/Si = 0.01).

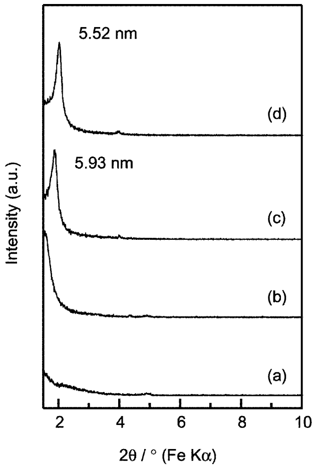

Fig. 7. XRD patterns of the hybrid films prepared from the precursor solutions after (a) 0.5 h, (b) 1 h, (c) 3 h and (d) 6 h of the reaction (TMOS/2C10DMS = 10, HCl/Si = 0.01).

3. Experimental

3.1. Precursor synthesis

C10EtDMS was synthesized by Pt-catalyzed hydrosilylation of 1-decene (Tokyo Kasei Co.) with dichloroethylsilane ($HSiCl_2Et$, Tokyo Kasei Co.), followed by methanolysis of Si–Cl groups. In a typical procedure, chloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$) dissolved in acetonitrile was added to a mixture of dichloroethylsilane and 1-decene, and the mixture was stirred at 70 °C for 2 h under N_2 atmosphere. Subsequently, methanolysis of Si–Cl groups was performed by the addition of methanol (dehydrated) in the presence of pyridine (dehydrated). Removal of pyridine hydrochloride followed by vacuum distillation afforded C10EtDMS as a clear liquid: ^{1}H-NMR (500 MHz, $CDCl_3$, δ ppm): 0.60–0.65 (m, 4H), 0.86–0.89 (t, 3H, CH_3), 0.96–1.00 (t, 3H, CH_3), 1.26 (m, 14H), 1.38 (m, 2H), 3.53 (s, 6H, OCH_3); ^{13}C-NMR (125.7 MHz, $CDCl_3$, δ ppm): 3.68, 6.40, 11.48, 14.14, 22.75, 22.76, 29.38, 29.42, 29.64, 29.73, 32.01, 33.49, 50.30; ^{29}Si-NMR (99.3 MHz, $CDCl_3$, δ ppm): −1.89.

2C10DMS was synthesized by the reaction of the Grignard reagent of 1-bromodecane (Tokyo Kasei Co.) with TMOS (Tokyo Kasei Co.). The solution of $C_{10}H_{21}MgBr$ was prepared by the reaction of 1-bromodecane with Mg powders in dry THF with a molar ratio of $Mg/C_{10}H_{21}Br = 1.2$. The Grignard reagent was added with stirring to a solution of TMOS ($C_{10}H_{21}Br/TMOS = 3$) and diethyl ether, and the mixture was stirred overnight at room temperature (r.t.). Filtration of the reaction mixture and vacuum distillation of the filtrate afforded 2C10DMS containing a small portion (~3%) of decyltrimethoxysilane as a clear liquid: ^{1}H-NMR (500 MHz, $CDCl_3$, δ ppm): 0.61–0.64 (m, 4H), 0.87–0.89 (t, 6H, CH_3), 1.26 (m, 28H), 1.38 (m, 4H), 3.54 (s, 6H, OCH_3); ^{13}C-NMR (125.7 MHz, $CDCl_3$, δ ppm): 11.91, 14.12, 22.72, 29.32, 29.38, 29.60, 29.70, 29.74, 31.96, 33.44, 50.28; ^{29}Si-NMR (99.3 MHz, $CDCl_3$, δ ppm): −2.36.

3.2. *Film preparation*

Precursor solutions were prepared by the co-hydrolysis and polycondensation of alkylmethoxysilanes (C10EtDMS or 2C10DMS) and TMOS in THF under acidic conditions. The molar compositions of the starting solutions were adjusted as follows: TMOS/alkylmethoxysilane = 2, 4, 6, 8 and 10; THF/Si = 4; $H_2O/OMe = 1$ and HCl/Si = 0.002 or 0.01. The solutions stirred for 0.5, 1, 3, 6, 9, 12 and 24 h were spin-coated (3000 rpm, 10 s) on glass (soda lime glass) substrates. Every coating procedure was performed at around 25 °C under the relative humidity of 30–45%. The resulting gel films were dried at r.t. for 1 day so that further polycondensation proceeded.

3.3. *Characterization*

XRD patterns of the films were taken on a Mac Science M03XHF^{22} diffractometer using Mn-filtered Fe–K_α radiation. Liquid-state ^{29}Si-NMR spectra of the precursor solutions were recorded on a JEOL Lambda-500 spectrometer with a resonance frequency of 99.05 MHz (64 scans were acquired with a recycle delay of 10 s). Sample solutions were put into 5-mm glass tubes, where THF-d_8 was mixed as a solvent (~10%) for obtaining lock signals and tetramethylsilane (TMS) was added for internal reference. A small amount of chromium(III) tris(acetylacetonato) was also added for the relaxation of ^{29}Si nuclei. TEM images of the films were taken with a JEOL 100CX microscope at an accelerating voltage of 100 kV. FTIR spectra were obtained by KBr method using a Perkin–Elmer Spectrum One spectrometer with a nominal resolution of 0.5 cm^{-1}. The films were scraped off from the substrates and powdered for IR and TEM measurements.

4. Conclusions

Multilayered silica-based hybrid films were prepared from two different alkyldimethoxysilanes ($R^1R^2Si(OMe)_2$, $R^1 = n$-decyl, $R^2 =$ Et or n-decyl) by co-hydrolysis and polycondensation with TMOS followed by spin-coating on glass substrates. It has been demonstrated that both C10EtDMS and 2C10DMS have the self-assembling ability to form lamellar structures where two organic groups per one Si atom are incorporated. The formation depends on the co-condensation between alkyldimethoxysilanes and TMOS; therefore, the reaction conditions should be controlled according to the length of the second organic groups. The present method can be applied to various types of organoalkoxysilanes to form lamellar hybrid films with varied interlayer structures.

Acknowledgements

We thank Prof. Y. Sugahara for discussion. The work was partially supported by a Grant-in-Aid for COE research, MEXT, Japan. A.S. thanks a financial support by Grant-in-Aid for JSPS Fellows from MEXT.

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