Synthesis of Oriented Inorganic−Organic Nanocomposite Films from Alkyltrialkoxysilane−Tetraalkoxysilane Mixtures

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We report the successful formation of transparent films of ordered inorganic−organic hybrid materials derived via cohydrolysis and polycondensation of alkyltrimethoxysilane−tetramethoxysilane mixtures. This opens the possibility of structural and morphological variations of hybrids by utilizing both the molecular-assembling property of long-chain alkyltrialkoxysilanes and the network-forming ability of tetraalkoxysilanes. Highly organized inorganic−organic hybrid systems have emerged from expectations for novel functional materials and have attracted increasing attention because of their structural and functional varieties.[1,2] The sol−gel process using metal alkoxides is an effective way to produce inorganic−organic hybrid materials.[3,4] The reactions normally proceed via hydrolysis and random polycondensation of metal alkoxides to form amorphous materials, implying that control of the microstructures of final products remains to be addressed.

Research on materials design utilizing self-organization of amphiphilic molecules is growing, and polymerization of metal alkoxides in the presence of molecular assemblies of surfactants or related substances as structure directors has been reported.[5−9] Long-chain alkyltrialkoxysilanes and long-chain alkyltrichlorosilanes have been known to form spontaneously organized assemblies based on the amphiphilic nature of hydrolyzed species containing both hydrophilic silanol groups and hydrophobic alkyl groups. The interfacial deposition of Langmuir−Blodgett films[10,11] and self-assembled monolayers[12−14] of these silanes have been investigated. Recently, we reported that the hydrolysis and polycondensation of alkyltrialkoxysilanes with alkyl groups of C12−C18 yields inorganic−organic interstratified materials composed of lamellar alkylsiloxane polymers.[15] The vital aspect of this system is that the reactions can proceed via homogeneous solutions, and the products can be regarded as a new class of organic derivatives of inorganic layered materials. Although structurally similar products can be obtained from alkyltrichlorosilane−water systems,[16] it would be more desirable to utilize homogeneous media using alkoxysilanes to extend this materials system by introducing other components and to control morphologies.

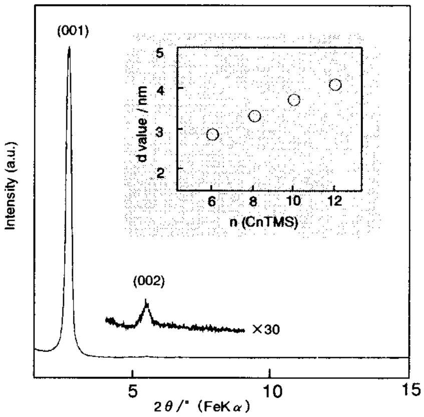

Figure 1. XRD pattern of the nanocomposite film from C_{12}TMS and TMOS mixture (at a molar composition of C_{12}TMS/TMOS/THF/H_2O/HCl = 1:4:20:15:0.01). Inset: The variation in the *d* value as a function of the number of carbon atoms (*n*) in the alkyl chain.

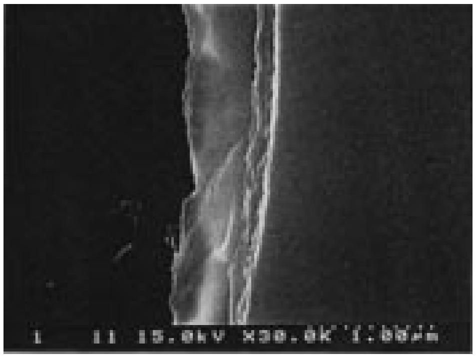

Figure 2. SEM image of the edge of the cracked nanocomposite film (TMOS/C_{12}TMS = 4).

Alkyltrimethoxysilanes with various alkyl chain lengths (C_nH_{2n+1}-$Si(OMe)_3$; C_nTMS, n = 6, 8, 10, 12, 14, and 18) and tetramethoxysilane (TMOS) were cohydrolyzed and polycondensed to form thin films.[17] A typical XRD pattern of the product in C_{12}TMS−TMOS system is shown in Figure 1. A sharp diffraction peak with a second order reflection due to an ordered structure of 4.0 nm periodicity was observed. The SEM image of the edge of the film (Figure 2) shows the stacked multilayers, and the TEM image (Figure 3) of the product clearly shows the layers indicating the presence of an inorganic−organic interstratified structure. A ^{29}Si MAS NMR spectrum of the powdered product (not shown) displays broad signals in the T^1−T^3 and Q^2−Q^4 regions[18] due to the formation of siloxane networks with various Si sites.[19] Our

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(17) Sample preparation was performed at room temperature. The composition of the starting solution was alkoxysilanes (C_nTMS + TMOS)/THF/H_2O/HCl = 1:4:x:0.002, where TMOS/C_nTMS molar ratio was varied. The ratio of water (x) was also varied in the range of 3−8, depending on the alkyl chain lengths. After the mixtures were stirred for 12 h (2 h for n = 6), the homogeneous sol solutions were spin-coated (3000 rpm, 10 s) on glass substrates to form thin films which were dried for 1 d. The gel films have a thickness of ca. 0.8 μm and high transparency in the visible region. The hydrolysis and polycondensation of C_nTMS alone did not produce homogeneously gelled films. The products were peeled off from the glass substrates and powdered for TEM observation, ^{29}Si MAS NMR, and FT-IR measurement.

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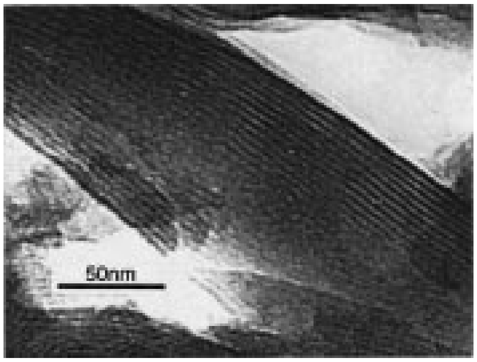

Figure 3. TEM image of the nanocomposite film (TMOS/C_{12}TMS = 4).

previous report shows that layered inorganic−organic nanocomposites derived from alkyltriethoxysilanes transform to an amorphous state upon heating at 110 °C.[15] In contrast, the present nanocomposite film was thermally stable even at 170 °C, which strongly indicates copolymerization between C_{12}TMS units and TMOS units.

All these data suggest that the film has a layered structure consisting of a siloxane network and organic layers containing ordered arrangements of alkyl chains, linked by Si−C bonds. Although the structure of the present nanocomposite films is somewhat similar to that of the products reported recently using alkyltrimethylammonium salts and partially hydrolyzed TMOS,[7a] they are different in the nature of the inorganic−organic interface.

Similar ordered transparent films were obtained from C_nTMS ($n = 6-10$)−TMOS systems, while the products derived from C_nTMS ($n \geq 14$)−TMOS systems were neither well-ordered nor transparent. This difference may arise from a segregating tendency based on strong associations of longer alkyl chains in C_nTMS during the deposition. There apparently are optimum reaction stoichiometries and reaction temperatures depending on the alkyl chain lengths for the preparation of these well-ordered nanocomposites. In the case of TMOS/C_nTMS = 4, the XRD patterns of the films exhibited most intense peaks when the molar ratios of water (x) were 8, 6, and 4, for alkyl chain lengths (n) of 6, 8, and 10, respectively. This trend corresponds to the lowering of hydrophobic character of shorter alkyl chains, indicating the important role of water in the formation of organized assembled structures.

As shown in Figure 1 (inset), the basal spacing (d) of the nanocomposite films depended on the alkyl chain lengths (n) of C_nTMS ($n = 6-12$), which showed a linear relationship. When the line is extrapolated into $n = 0$, the d-spacing becomes 1.6 nm, which corresponds to the thickness of the siloxane layer in the products prepared from the ratio of TMOS/C_nTMS = 4. To study the structural changes of the nanocomposite films, TMOS/C_{12}TMS ratio was varied. As shown in Figure 4, the basal spacing increased with the increase in the ratio, which corresponds to the formation of thicker siloxane layers, although the intensity of the diffraction peaks decreased gradually and became very broad when TMOS/C_{12}TMS = 12.

The arrangements of alkyl chains in the interlayers can be examined by IR spectroscopy. Products derived from the single precurser of long-chain alkyltriethoxysilanes exhibit bimolecular arrangements of *all-trans* alkyl chains almost perpendicular to the siloxane layers.[15] The absorption bands due to methylene modes (ν_a and ν_s CH_2) appeared at 2918 and 2849 cm^{-1}, respectively, indicative of crystalline state of the aggregates.[20,21] These two bands in the C_nTMS−TMOS derived nanocomposite films appear at 2924 and 2853 cm^{-1}. These shifts toward higher frequencies have been found to be associated with an increasing number of gauche conformers and disorder,[21] which is generally observed with the solid phase to liquid-crystal phase transition of long-chain amphiphiles.[22,23]

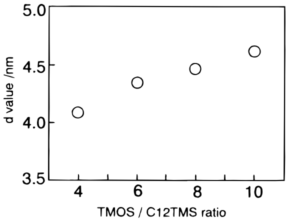

Figure 4. The variation in the *d* values of the nanocomposite films as a function of the TMOS/C_{12}TMS molar ratio.

In the cohydrolysis and condensation reactions containing more than two alkoxysilanes, the difference in the reaction rates of the alkoxysilanes should affect the structures of final products.[4] In the ^{29}Si NMR spectrum of the solution reacted for 12 h in the system of TMOS/C_{12}TMS = 4, the signal due to hydrolyzed monomeric species derived from C_{12}TMS was still observed, in contrast to that of oligomeric species derived from TMOS. This finding is explained by suppressed condensation of hydrolyzed C_{12}TMS species due to steric effects of long alkyl chains.[24] Further polymerization in the precurser solution leads to the formation of less-ordered composites.[25] When C_6TMS was used, products obtained from reaction times longer than 6 h were amorphous but an oriented film was obtained by reaction for 2 h. This result corresponds to the lower steric hindrance and higher condensation rates of this sample containing shorter alkyl chains.

The formation of molecular assemblies such as micelles and liquid crystals takes place mainly in aqueous systems and the presence of highly miscible organic solvents normally disturbs their formation.[26] In the presence of THF, which was used in this study, the formation of such molecular assemblies should not occur. The XRD patterns of the as-deposited film just after spin coating show very sharp diffraction peaks, indicating that the organization occurs during the evaporation of the organic solvent. On the other hand, products obtained by drying a hydrolyzed solution until gelation occurs in a reaction vessel show a substantial decrease in the ordering. Therefore, rapid evaporation of the organic solvent appears to be very effective for the formation of highly ordered products.[7a]

In conclusion, layered nanocomposite films comprised of bimolecular layers of alkyl chains covalently bonded to the silica layers were prepared via cohydrolysis and polycondensation of long-chain alkyltrimethoxysilanes and tetramethoxysilane. These results suggest a new methodology for constructing novel inorganic−organic interstratified materials derived from various compositions. Structual and morphological control of sol−gel derived inorganic−organic hybrid materials is also evident.

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(18) The environments of Si atoms formed in the hydrolysis and polycondensation processes are represented using the number of siloxane bonds. For TMOS-derived unit, an environment $Si(O_{0.5})_m(OR)_{4-m}$ (R = Me, H) is represented as Q^m. For C_nTMS-derived unit, an environment $C_nH_{2n+1}Si(O_{0.5})_m(OR)_{3-m}$ (R = Me, H) is represented as T^m.

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(25) When the reaction time is extended in these systems, the intensity of the XRD peaks decreases and even disappears in the products reacted for 12 d. The concentration of HCl in the reaction mixture also affected the ordering: the films became amorphous when the molar ratio of HCl to alkoxysilanes was increased to 0.02.

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