

Novel Layered Silica/Organic Polymer Hybrid Films with the Interface Linked by Si–C Bonds

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Inorganic–organic hybrids films composed of alternating layers of siloxane network and organic polymer assemblies linked by Si–C bonds have been prepared via co-hydrolysis and polycondensation of alkenyltriethoxysilane–tetraethoxysilane mixtures followed by organic polymerization, providing a new methodology for the design and construction of inorganic–organic nanostructured materials.

Inorganic–organic hybrid systems are of current interest for the production of new materials with controlled structures, morphologies, and unique properties.¹ The sol–gel processing using organoalkoxysilanes has been extensively studied as a versatile route to prepare a wide variety of hybrid materials.² Recent developments have focused on the nanostructural design utilizing the self-organization of amphiphilic molecules as structure directors.³ Various mesostructured materials have been produced by the sol–gel reactions under the presence of surfactants, and covalently attached organic moieties can be incorporated by co-condensation of organoalkoxysilanes.^{3–5} The nanostructures of the resulting hybrid materials are dominated by the silica-surfactant mesophase, and the incorporation of an increasing amount of an organoalkoxysilane component generally causes a structural disordering.⁵ On the other hands, Brinker et al. proposed an efficient self-assembly process for preparing organic polymer–silica layered nanocomposite systems.⁶ However, the structural ordering of the nanocomposites still depends largely on the surfactant assemblies, and decreased to some extent when the surfactants were removed. Therefore, materials design without surfactant assemblies is a promising approach for the fabrication of novel hybrid materials with precisely controlled architectures.

Several reports have shown that organoalkoxysilanes can act as a structure director to form lamellar inorganic–organic hybrids^{7–9} based on the self-organization property induced by the hydrolysis of alkoxy-silyl groups. As an extension of this material system, we have recently demonstrated a morphological control into transparent and oriented thin films by co-hydrolysis and polycondensation reactions of alkyltrialkoxysilane and tetraalkoxysilane mixtures, and by subsequent spin-coating procedure.¹⁰ As compared to the construction of alkylsiloxane multilayers by the repeated deposition of self-assembled monolayers derived from alkyltrichlorosilanes,¹¹ our synthetic approach offers many advantages of conventional sol–gel processing, and may be applicable for materials with various compositions by utilizing organoalkoxysilanes with desired functionalities.

In this paper, as a model for novel silica/organic polymer hybrid systems, alkenyltrialkoxysilane containing a reactive terminal double bond was employed to construct layered nanocomposite films by co-hydrolysis and polycondensation reactions with tetraalkoxysilane. Then, interlayer organic groups

were polymerized to form novel transparent thin films of layered silica/organic polymer hybrids with covalently linked inorganic–organic interface.

A typical procedure for the film formation is as follows. Co-hydrolysis and polycondensation of 7-octenyltriethoxysilane [CH₂=CH(CH₂)₆Si(OEt)₃; v-C8TES] and tetraethoxysilane [Si(OEt)₄; TEOS] were conducted at a molar composition of v-C8TES:TEOS:EtOH:H₂O:HCl=1:4:50:19:0.03.¹² The precursor solution reacted for 2 h was spin-coated (3000 rpm, 10 s) on glass substrates to form highly transparent thin films with a thickness of ca. 300 nm after drying at 60 °C for 24 h. Subsequently, vinyl polymerization in the hybrid films was performed by UV irradiation (20 W low-pressure Hg lamp) in nitrogen atmosphere for 12 h.

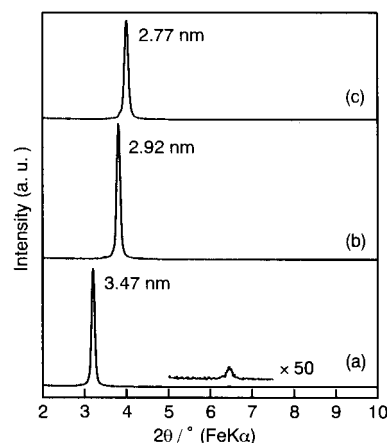


Figure 1. XRD patterns of the hybrid films. (a) as-deposited, (b) dried at 60 °C for 1 d, and (c) UV irradiated for 12 h.

The XRD patterns of the hybrid films are shown in Figure 1. The as-deposited film before drying showed a sharp diffraction peak with a second order reflection due to a multi-lamellar structure of ca. 3.5 nm periodicity. The *d* spacing of the film decreased to 2.92 nm after drying, mainly caused by the evaporation of the volatile components (Figure 1b). The IR spectrum of the film (Figure 2a) shows the absorption bands due to the siloxane framework (1000–1200 cm⁻¹, 450 cm⁻¹) and the terminal double bonds in the organic groups at 3079 cm⁻¹ (=CH stretching), 1642 cm⁻¹ (C=C stretching), and 910 cm⁻¹ (=CH₂ out-of-plane deformation). These results suggest that the films are composed of a lamellar structure of siloxane networks and organic assemblies containing vinyl functionalities without decomposition. Our previous investigation on the structure of hybrid films from alkyltrialkoxysilane–tetraalkoxysilane systems¹⁰ confirmed that the products were composed of an interstratified structure of siloxane layers and bimolecular assembly of interlayer alkyl chains. The films obtained in the present study were considered to have a similar structure containing bilayer arrangement of octenyl groups, since

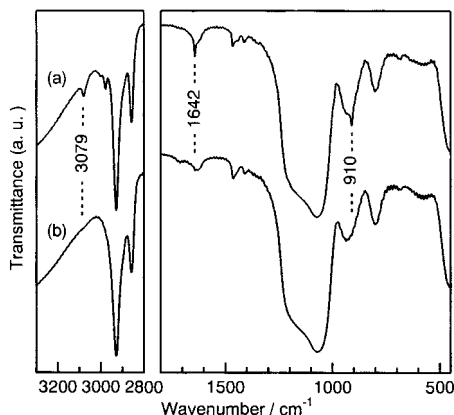


Figure 2. FT-IR spectra of the hybrid films dispersed in KBr pellets. (a) before and (b) after UV irradiation.

the d spacing of the film exhibits a value nearly equal to that of the film derived from octyltrialkoxysilane–tetraalkoxysilane system.¹⁰

The film exposed to the UV light still maintained the structural order with a slight decrease in the d value in the XRD pattern (Figure 1c). The TEM image (Figure 3) of the film shows well-defined stripe patterns which exactly correspond to the d spacing determined by the XRD result. The evidence for the vinyl polymerization was revealed by the substantial decrease in the IR absorption bands ascribed to the terminal double bonds (Figure 2b). In contrast to the polymerization of self-assembled alkenylsiloxane monolayers,¹³ the interlayer organic chains in this system were arranged in a bilayer assembly. Consequently, polymerization should proceed either within layers or between adjacent layers.¹⁴ The resulting hybrid film exhibited a remarkable increase in the scratch resistance if compared with the film before the organic polymerization. This behavior is in accordance with previous studies on the stabilization of the organic molecular assemblies, such as LB monolayers, surfactant micelles, or liquid crystals, by polymerization.¹⁵

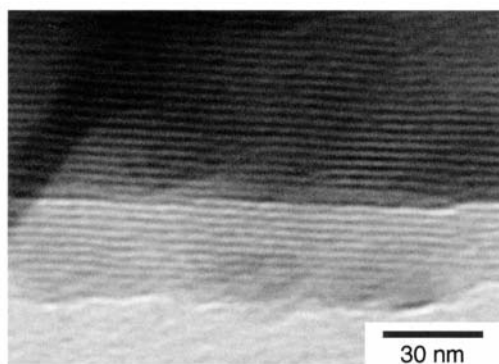


Figure 3. TEM image of the hybrid film after the organic polymerization. (The film was scraped from the substrate and powdered for the observation.)

All these results indicate the formation of inorganic–organic hybrid films with a lamellar structure in which the siloxane layers and the organic polymer are linked by Si–C bonds. Hybrid films thus obtained are a new class of materials and of great interest from a wide range of materials chemistry. With regard to the silica–organic polymer nanocomposites, intercalation of organic polymers into the interlayer spaces of crystalline layered silicates

has attracted much attention for the possibility to provide new properties.¹⁶ Covalent bonding between organic moieties and silica interlayers can also be attained by using a silane coupling agent such as γ -methacryloxypropyltrimethoxysilane.¹⁷ However, the present approach is quite different in utilizing the molecular self-assembly of organoalkoxysilane–tetraalkoxysilane system, which enabled the morphological control into the transparent thin films available for various applications.

In summary, inorganic–organic layered hybrid films consisting of organic polymer assemblies attached covalently to the silica layers were successfully prepared by the self-organization of hydrolyzed organoalkoxysilanes and the photopolymerization of the terminal double bonds in the organic chains. This synthetic approach provides a new methodology for the construction of artificial polymer hybrid systems, leading to the advances in the sol–gel technology to generate a wide range of functional materials. Further characterization of the microstructure as well as the physical properties of the hybrid films are now in progress and will be reported subsequently.

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- In this system, the degree of the polycondensation largely affects the structural order and the transparency of the film. The ¹H and ²⁹Si-NMR measurements of the reaction mixture revealed that the ethoxy groups in both of the alkoxy silanes were almost hydrolyzed within 15 min, and a variety of oligomeric species were present in the precursor solution reacted for 2 h. Higher degree of polycondensation suppressed the self-organization during the deposition, leading to the formation of disordered film. Furthermore, self-organization into the ordered film was associated with the evaporation of the solvent and water. Therefore, the surrounding temperature and relative humidity should be carefully controlled for the reproducible deposition of well-ordered films. In this report, the films were deposited at around 25 °C under the relative humidity of 50%.
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