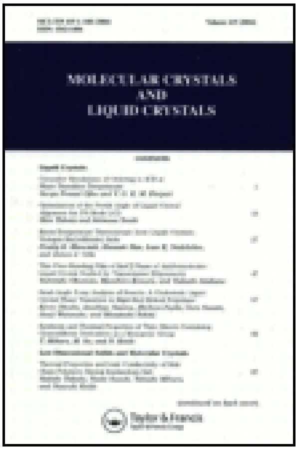

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Thermal Stability of 1-Layer LB Film of Trichloro(Octadecyl)Silane

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Thermal Stability of 1-Layer LB Film of Trichloro(Octadecyl)Silane

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Thermal stability up to 160 °C of monolayers of trichloro(octadecyl)silane (TCOS) and cadmium stearate (CS) on solid substrates are examined by using FT-IR transmission spectroscopy. The changes in wavenumbers and absorbances of CH_2 stretching bands with temperature clearly demonstrate that the 1-layer LB film of TCOS on glass slides are considerably stable and resistant against heating, compared with that of CS.

Keywords: long-chain alkyltrichlorosilanes; Langmuir-Blodgett films; self-assembled monolayers; thermal stability of monolayers; Fourier transform infrared spectroscopy

INTRODUCTION

Many experiments have demonstrated that LB films have a potential for a variety of engineering applications including the areas of electronics and photonics[1]. There are, however, some problems to be solved before applying the films to various functional devices. One of the serious problems is the poor robustness of the LB films against solvent attack, mechanical stimuli, thermal agitation by heating, and so on.

It is well known that long-chain trichlorosilanes spontaneously adsorb to form self-assembled (SA) monolayers on hydroxylic solid surfaces[1]. These monolayers are very stable because of two-dimensional cross-links among the film molecules and of covalent bonds formed with the solid surfaces.

Trichlorosilanes form also spread monolayers on the water surface. We have reported structures of spread monolayers and LB films of long-chain trichlorosilanes [2],[3]. XPS and FT-IR spectroscopic studies revealed that considerable number of residual silanol groups would exist in the spread monolayers, indicating that the molecules can be fixed on the hydroxylic solid surfaces with covalent bonds after transferring monolayers by the condensation reaction. Therefore, 1-layer LB films of long-chain trichlorosilanes are expected to overcome the problems of weakness of usual LB films.

In this paper, we report some results for demonstrating the thermal stability of the 1-layer LB film of TCOS on the solid substrates.

EXPERIMENTAL

1-layer LB films of TCOS and CS were prepared by the conventional vertical dipping method at the so-called solid film regions using a computer-controlled Langmuir trough constructed in our laboratory. Glass slides and CaF_2 plates were used as the solid substrates.

The SA monolayers were formed by immersing glass slides into a 2.5×10^{-3} M solution of TCOS in a mixed solvent of 80 % bicyclohexyl and 20 % carbon tetrachloride at 5 ℃ for overnight. The substrates withdrawn from the silane solution were thoroughly rinsed with carbon tetrachloride and with ethanol for several times. All the silanation reactions were performed in a glovebox under the dry air atmosphere of humidity less than 20 %.

According to the procedure described above, four kinds of monolayers were prepared; 1-layer LB films of TCOS and CS on glass slides, 1-layer LB films of TCOS on CaF_2, and SA monolayers of TCOS on glass slides.

The infrared transmission spectra were recorded with a Nicolet Magna-IR Model 550 spectrometer equipped with a MCT detector at a resolution of 4 cm^{-1}. In order to obtain the FT-IR spectra at elevated temperatures, a sample holder made of copper blocks with heaters connected to a temperature controller was used. The temperature was raised at a rate of 1.0 ℃/min from 30 ℃ to 160 ℃, and the spectra were taken at every 10 ℃ interval. On cooling, however, the holder is allowed to cool and several spectra were measured at random temperatures.

RESULTS AND DISCUSSION

Figure 1 shows the temperature-dependent changes in wavenumbers and normalized intensities of CH_2 stretching bands in infrared spectra of the four monolayer samples. One can evaluate qualitatively the degree of conformational order of hydrocarbon chains in monolayers by the wavenumbers and absorbances of CH_2 stretching bands in FT-IR transmission spectra. If the chains take trans-zigzag conformation with a regular dense packing, the CH_2 antisymmetric and symmetric stretching bands will appear at around 2918 and 2848 cm^{-1}, respectively, with higher intensities, while the wave numbers of these bands will shift upward and their peak intensities decrease with increasing the conformational disorder and/or decreasing the molecular density.

Figure 1 reveals that in all monolayers, the film molecules take trans-zigzag conformation before heating, but the disorder of the hydrocarbon chains are induced with increasing temperature.

By comparing the thermal profiles of 1-layer LB film of CS (a) with that of TCOS (b), it is evident that the content of disorder introduced by temperature increase in the TCOS monolayer is much less than that in the CS monolayer. Furthermore, the wavenumbers and the absorbance of the TCOS monolayer almost return to its initial values when the sample is cooled down to 30 °C. These facts indicate that the conformational disorder introduced at higher temperature disappears and the highly ordered conformation is recovered again by cooling. On the other hand, CS monolayer can not regain its initial structure by cooling. These results clearly demonstrate the thermal resistance of the 1-layer LB monolayer of TCOS.

The thermal profile of the SA monolayer of TCOS (c) and that of the LB film of TCOS (b) resemble each other, indicating that the TCOS molecules in the LB film must form two-dimensional siloxane networks which anchor to the glass surface like in the SA monolayer. When a CaF_2 plate is employed as the substrate (d), the thermal resistance of the TCOS monolayer is reduced compared with those on glass substrates. This may be due to the lack of covalent bonds between the film molecules and the solid surface. However, since the monolayer of TCOS must take a two-dimensional polymer structure, its thermal stability is much improved than that of the CS monolayer.

CONCLUSIONS

It becomes clear that TCOS monolayers on glass slides are considerably resistant against temperature increase. This may be due to the two-dimensional polymer structure and the covalent bond formation with the glass surface. Construction of thermally stable monolayers by LB technique will extend the area of monolayer applications.

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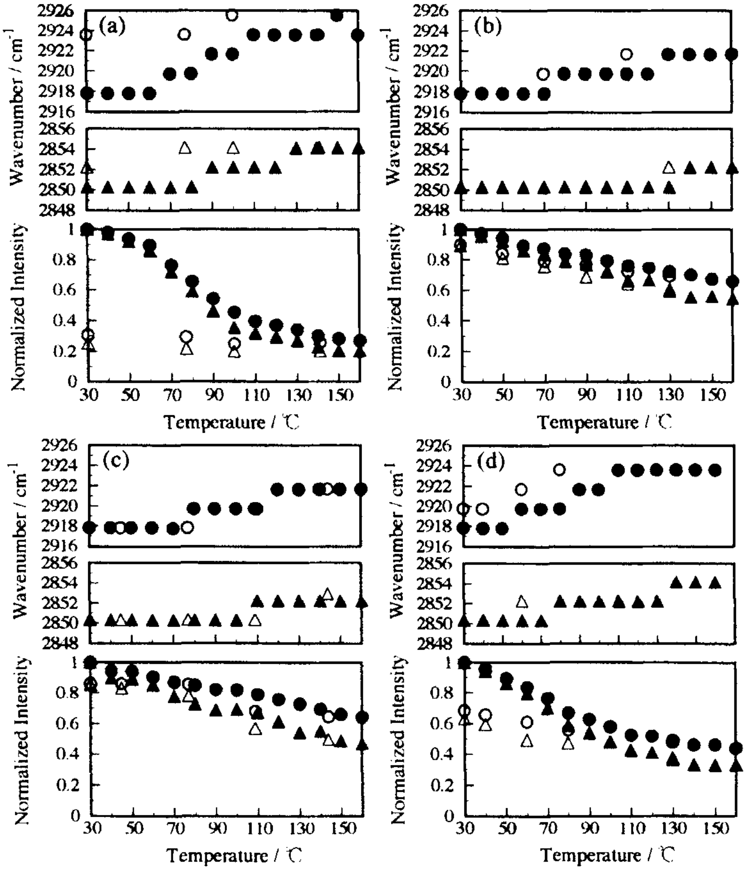

FIGURE 1 Thermal profiles of wavenumbers and normalized intensities of CH_2 antisymmetric (νa) and symmetric (νs) stretching bands; (a) 1-layer LB film of CS on glass slide, (b) 1-layer LB film of TCOS on glass slide, (c) SA monolayer of TCOS on glass slide, and (d) 1-layer LB film of TCOS on CaF_2. Symbols ; ●:νa(CH_2),▲:νs(CH_2) at heating,○:νa(CH_2),△:νs(CH_2) at cooling.

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