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Monolayer Properties of a 4-Pyridinealdoxime-Containing Carbosilane Dendrimer

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Monolayer Properties of a 4-Pyridinealdoxime-Containing Carbosilane Dendrimer

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A carbosilane dendrimer terminated with 4-pyridinealdoxime (G4-48PyA) was synthesized and its monolayer properties on aq. aluminum subphase were examined. G4-48PyA was not totally spread to monolayer and the surface pressure-area isotherms were dependent on the subphase ion and pH. The aggregated images of the monolayers were monitored by Brewster angle microscopy and those structures were also confirmed in the LB film by atomic force microscopy. The UV spectra showed that the pyridinealdoxime moiety was hydrolyzed from the dendrimer upon spreading on water subphase. The incorporation of the aluminum ions into the LB film was found by X-ray photoelectron spectroscopy.

Keywords: carbosilane dendrimer; 4-pyridinealdoxime; monolayer; BAM; XPS; AFM

INTRODUCTION

The regularly branched treelike structure of dendrimers led to a number of applications such as capsules for controlled release, energy transfer funnels, polyfunctional initiators and catalysts, and thin film coatings. Meanwhile, Langmuir-Blodgett (LB) technique provides featured ultrathin films of nm-sized thickness and ordered molecular structure. Spreading behaviors of

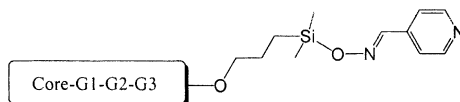
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dendrimers have been investigated to elucidate the aggregation mechanism and control the molecular assembly^[1]. However, the dendrimers containing pyridinealdoxime moieties, which are thought to play as ligands to metals, have not been examined on monolayer behaviors partly because of their synthetic difficulty and structural instability.

In this paper, we report the monolayer properties of a pyridinealdoxime-containing dendrimer (G4-48PyA) at the air-water interface and in the LB film. Specifically, the hydrolytic behavior of G4-48PyA on water surface and the incorporation of aluminum ions into the LB film from the subphase were characterized.

EXPERIMENTAL

A carbosilane dendrimer terminated with 4-pyridinealdoxime (G4-48PyA) was synthesized from the precursor chloric dendrimer according to the literature^[2]. The chemical structure was determined from FT-IR, ¹H-NMR, UV-Vis, MALDI-MS, and elemental analysis.



G4-48PyA terminal structure

A film balance system NLE-LB200-MWC (Nippon Laser and Electronics) was used for obtaining the surface pressure-area (π -A) isotherm and LB deposition. BAM images were obtained from Mini BAM (Nanofilm Technologie GmbH). XPS (V.G. Scientific) and AFM (APCP-PSIA) were employed to determine the aluminum concentration in the LB film and to characterize the image of LB monolayer.

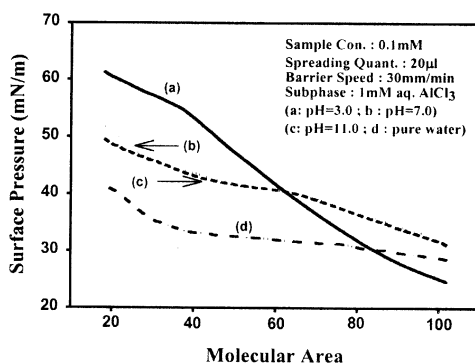


FIGURE 1 Surface pressure-area isotherms of G4-48PyA.

RESULTS AND DISCUSSION

The highly concentrated pyridinealdoxime groups of G4-48PyA were exposed on aq. aluminum ions in subphase and the surface pressure-area (π -A) isotherms were obtained as shown in Fig.1. G4-48PyA was not totally spread to monolayer and the π -A isotherm of G4-48PyA showed very expanded phase on pure water. Although the monolayer was still consisted of aggregated islands, which was evidenced from BAM and AFM images, the π -A isotherm showed rather condensed phase by introduction of aluminum ions into the subphase than on pure water. The isotherms were dependent on subphase pH, the highest surface pressure was obtained when the subphase was going to acidic pH. Upon the spreading, the spontaneous increase of surface pressure was found even in decreasing the spreading amount as 5 μ l in the employed trough. The BAM images were clearly developed when the aluminum ions were introduced in the subphase after the collapse point. The aggregated area observed by BAM was increased on acidic and alkaline

subphase. The very wavy images were found in neutral pH subphase.

The UV spectra of the LB film revealed that the absorption band of G4-48PyA itself at 250 nm in organic media was disappeared when the LB film was fabricated. The hydrolysis of the aldoxime moiety is one of the possible explanations. Although the noisy bands of hydrated waters made the FT-IR spectra difficult to resolve the band patterns, we could find the change of functional groups from the spectra. The interaction between pyridinealdoxime moieties and aluminum ions at the air-water interface was quantitatively characterized by XPS measurement of the resulting LB film. Interestingly, the aluminum ions were much detected in the LB film deposited from neutral pH subphase. It was estimated that, when the subphase was going to acidic or alkaline, the aldoxime structure was easily hydrolyzed and not coordinated to metal ions. The AFM image of the LB film is shown in Fig. 2.

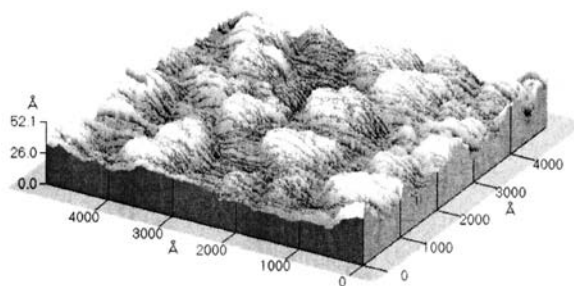


FIGURE 2 AFM image of G4-48PyA LB film.

Acknowledgments.

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