

# Interaction of a Pyridyl-Terminated Carbosiloxane Dendrimer with Metal Ions at the Air-Water Interface

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**Abstract** - A new class of carbosiloxane dendrimer (G4-48PyP) terminated with 4-pyridylpropanol was synthesized and its possible application to functional thin films was examined through metal complexation and Langmuir-Blodgett (LB) technique. The highly concentrated periphery pyridyl groups of G4-48PyP were exposed on aq. aluminum ions at the air-water interface. The monolayers showed stability up to ca. 50 mN/m of surface pressure. When the subphase became acidic or alkaline, the monolayers changed to condensed phase. The presence of aluminum ions also caused reduction of the molecular area. The macroscopic images of the monolayers were monitored by Brewster angle microscopy (BAM) and only the images of dendrimer aggregates could be observed after the monolayer collapse. The surface images of the monolayer LB film were scanned by atomic force microscopy (AFM). The convex structures of single and aggregate molecules were directly observed. The structures of Langmuir-Blodgett (LB) films were characterized by FT-IR, UV-Vis, and X-ray photoelectron spectroscopy (XPS). The UV-Vis spectrum of the aluminum ion-complexed LB film showed additional band around 670nm, which was not found in the spectra of dendrimer itself or aq. aluminum ions. XPS spectra also supported the incorporation of aluminum ions into the LB films.

**Keywords:** carbosiloxane dendrimer; 4-pyridylpropanol; monolayer; BAM; UV-Vis; XPS; AFM

## 1. 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 [1-3]. Meanwhile, the Langmuir-Blodgett (LB) technique provides featured ultrathin films of nm-sized thickness and ordered molecular structure [4]. Since Saville *et al.* first reported the spreading characteristics of poly(ether) dendrimers by their generations [5], several kinds of dendrimers have been investigated on the aggregation mechanism and the control of molecular assembly. For examples, poly(amidoamine) dendrimers [6,7], diarylethene dendrimers [8], carbosilane dendrimers [9], dendritic diblock copolymers [10], fullerene-glycodendron conjugates [11], and azobenzene dendrimers [12] have been spread over a water surface, and their Langmuir and LB film properties examined. We have also constructed a report on the spreading behaviors of a

carbosiloxane dendrimer on aq. metallic subphase [13]. Particularly, the functional LB films of dendrimers, photochromic property [8], excitation energy transfer [14], and biosensing property [11] have been investigated.

We report here on the dendrimer-metal ion interaction at the air-water interface and characterization of the LB film, including additional visible absorption by dendrimer-metal complexes. A new class of pyridyl-terminated carbosiloxane dendrimer (G4-48PyP) was synthesized, and aluminum ion was employed as a subphase metal ion. The dendritic pyridine-aluminum complex was expected to demonstrate the photoluminescent functionality. The stability and spreading behaviors of the monolayers on water subphase were evaluated by surface pressure-area isotherms and BAM. The chemical and multilayer structures of the aluminum ion-complexed LB films were characterized by XPS and UV-Vis spectroscopy. The surface monolayer structures of the LB films were scanned by AFM.

## 2. Experimental

### 2.1 Synthesis of G4-48PyP

A carbosilane dendrimer terminated with 4-pyridinepropanol (G4-48PyP) was synthesized from the

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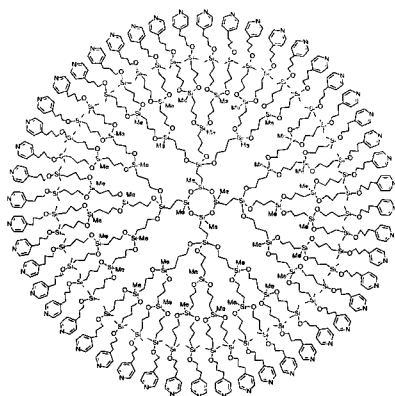
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precursor chloric dendrimer as previously described [15]. The chemical structure was determined from FT-IR,  $^1\text{H}$ -NMR, UV-Vis, MALDI-MS, and elemental analysis.



**Fig. 1** Chemical structure of a carbosiloxane dendrimer G4-48PyP

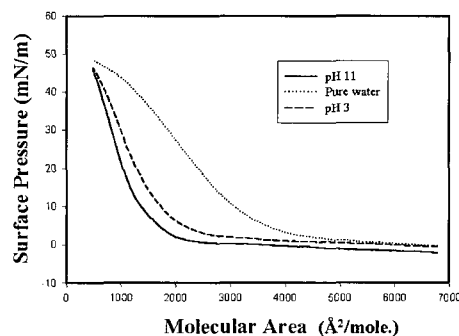
## 2.2 Characterization of Langmuir monolayer and LB film

Film balance system KSV 2000 system 3 was employed for measuring surface pressure as a function of molecular area and for LB transfer of monolayer by the vertical mode (trough surface size,  $960\text{ cm}^2$ ). The macroscopic images of monolayers on water surface were monitored from Mini BAM (Nanofilm Technologie GmbH). The employed substrates were FP-010 filters for XPS, and silicon wafers for XRD and AFM. XPS spectra were obtained on an ESCALAB 250 XPS spectrometer (V.G Scientifics). The UV-Vis spectra were obtained from a Shimadzu UV-3100S spectrophotometer. The molecular surface morphology of the LB film was scanned using an AFM (Nano Scope IV, Digital Instrument).

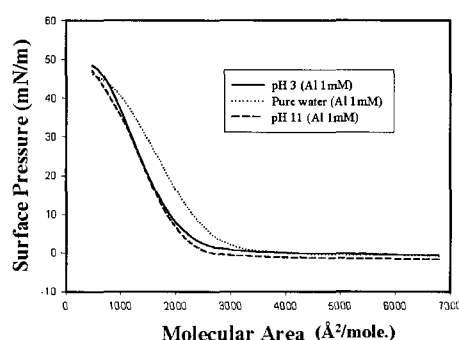
## 3. Results and Discussion

### 3.1 G4-48PyP monolayers at the air-water interface

The highly concentrated pyridyl groups of G4-48PyP periphery were exposed on aq. aluminum ions and the surface pressure-area isotherms were obtained as shown in Fig. 2. A highly diluted chloroform solution ( $0.01\text{ mM}$ ) of G4-48PyP was employed as stock solution for complete monolayer spreading. The surface pressure-area isotherms of G4-48PyP showed a greatly expanded phase on pure water. The isotherms were dependent on subphase pH. When the subphase pH became acidic (pH 3) and alkaline (pH 11), the isotherms displayed a largely condensed monolayer phase. The increased affinity of pyridyl dendrimer periphery toward acidic or alkaline subphase was supposed to be related with the reduced molecular area.



**Fig. 2** Surface pressure-area isotherms of G4-48PyP monolayers on water subphases with different pH.



**Fig. 3** Surface pressure-area isotherms of G4-48PyP monolayers on aq. aluminum subphases with different pH.

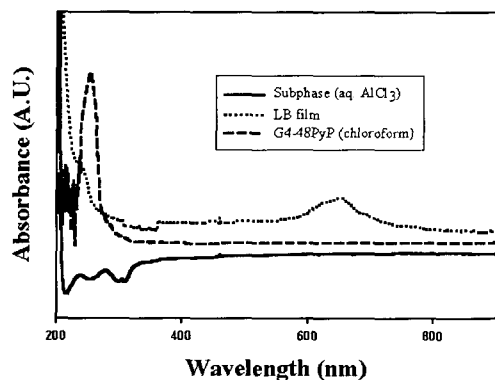
When aluminum ions were dissolved in water subphase, the monolayer phase showed a reduced molecular area in pure water (Fig. 3). However, in the cases of subphases with adjusted pH, the presence of aluminum ions caused an increase in the molecular areas. The incorporation of aluminum ions between dendrimers is thought to be one of the factors affecting phase change. However, the addition of aluminum ions in the acidic or alkaline subphases had little effect.

The images of Brewster angle microscopy were clearly developed when the aluminum ions were introduced in the subphases following the collapsing point. During the monolayer compression below the collapse point, noticeable structures were not seen. The aggregate size observed by BAM was larger in pure water than those in acidic and alkaline subphases.

### 3.2 Characteristics of G4-48PyP LB films

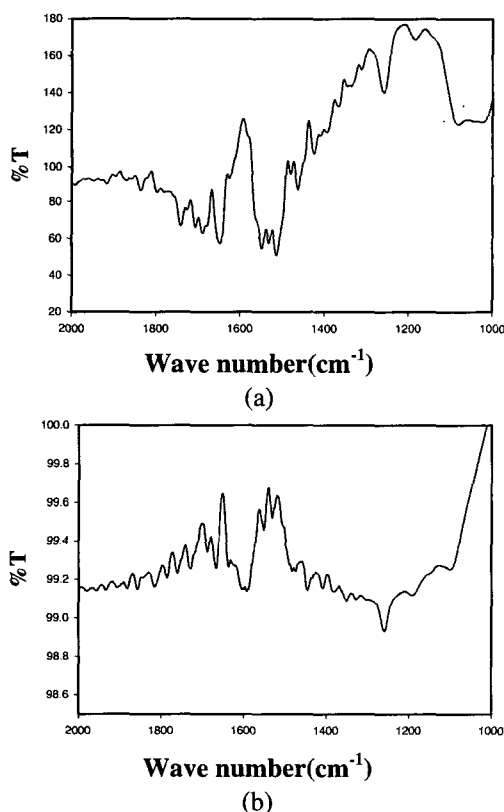
The UV-Vis spectrum of the G4-PyP LB film deposited from aq. aluminum subphase is shown in Fig. 4 together with those from the chloroform solution of G4-PyP and aq. aluminum subphase itself. The UV-Vis spectrum of the aluminum ion-complexed LB film displays additional band around  $670\text{ nm}$ , which is not found in the spectra of the dendrimer solution or aq. metal ions. The additional band is attributed to

the formation of pyridyl-aluminum complexes; however, their structures are not yet fully understood.



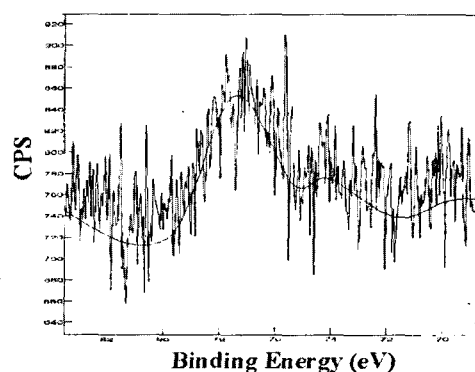
**Fig. 4** UV-Vis absorption spectra of aq.  $\text{AlCl}_3$  only, chloroform solution of G4-48PyP and the G4-48PyP LB film deposited from aq.  $\text{AlCl}_3$  subphase.

Although the noisy bands of hydrated waters caused difficulty in resolving the FT-IR spectra band patterns, we could determine the band difference between G4-48PyP and aluminum ion-complexed G4-48PyP LB film as shown in Fig. 5. However, the assignment of the FT-IR bands to specific vibrational modes remains unclear at this point.



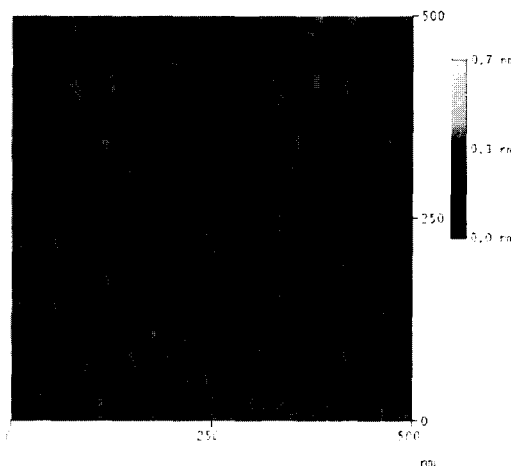
**Fig. 5.** FT-IR absorption spectra of G4-48PyP LB films deposited (a) from pure water subphase and (b) from aq.  $\text{AlCl}_3$  subphase (pH 11.0).

The interaction between pyridyl group and aluminum ion at the air-water interface was quantitatively characterized by XPS measurement of the resulting LB film. The Al 2p XPS spectrum is shown in Fig. 6. Interestingly, increased numbers of aluminum ions were detected in the LB film deposited from a higher pH subphase. The numbers of aluminum ions were counted to be 84 (pH 11), 70 (pure water), and 42 (pH 3) per dendrimer molecule. Considering the peripheral pyridyl numbers of 48, more than this number of Al ions was detected in alkaline pH. Of course, only some of the ions are thought to be involved in the formation of complexes.



**Fig. 6** Al 2p XPS spectrum of G4-48PyP LB film deposited from aq.  $\text{AlCl}_3$  subphase (pH 11.0).

Fig. 7 shows an AFM image of the monolayer LB film deposited from aq. aluminum subphase of which pH was not adjusted. Some larger convex structures are seen together with small dot structures. The convex structures were not observed in acidic or alkaline cases. The large convex structures are considered as two-dimensional dendrimer aggregates. The small dot structures with a diameter of ca. 6 nm seem to be molecular dendrimers.



**Fig. 7.** AFM image of the G4-48P LB film deposited from aq.  $\text{AlCl}_3$  subphase (pH 3.0).

#### 4. Conclusion

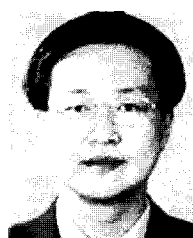
In this study, a new class of carbosiloxane dendrimer containing pyridyl periphery was successfully spread to monolayer on a water surface. The additional visible absorption by the aluminum-complexed LB film indicates the possible application as photoluminescent and electroluminescent materials. Further investigation on the metal-dendrimer complexes is expected for functional thin film materials.

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