The Construction of Layered Architectures of Dendrimers — Adsorption Layers of Amino-terminated Dendrimers on 3-Mercaptopropionic Acid Self-assembled Monolayer Formed on Au

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Abstract

Adsorption kinetics of amino-terminated poly(amido amine) dendrimer (PAMAM) and poly(trimethyleneimine) dendrimer (PTMI) from aqueous solutions onto 3-mercaptopropionic acid (MPA) self-assembled monolayer (SAM) on Au films have been investigated by surface plasmon resonance sensor and surface enhanced infrared absorption spectroscopy. The adsorption kinetics at high dendrimer concentrations does not obey Langmuir adsorption mechanism but passes 2-step adsorption process, which includes monolayer adsorption and additional adsorption on it. Further consideration indicates the difference on the adsorption structure between two dendrimers: PAMAM dendrimer adsorbs with "the hemi-micellar structure" because of the electrostatic and hydrogen-bonding interactions between amine of PAMAM and carboxylate of MPA SAM, while the adsorption structure of PTMI dendrimer is "the hourglass type" or "the conical type" due to no hydrogen-bonding interaction between dendrimer interior and MPA SAM.

Keywords: Dendrimer, poly(amido amine) dendrimer, poly(trimethyleneimine) dendrimer, adsorption, self-assembled monolayer, 3-mercaptopropionic acid, surface plasmon resonance sensing, surface-enhanced infrared absorption spectroscopy, electrostatic interaction, hydrogen-bonding

1. Introduction

Two-dimensionally organized systems of dendrimers have been prepared as Langmuir or Gibbs monolayer at air-water interface and adsorption layer on solid substrate or self-assembled monolayer[1].

In this work, the adsorption kinetics of dendrimers from aqueous solutions onto 3-mercaptopropionic acid (MPA) self-assembled monolayers (SAM) prepared on Au surfaces is investigated by surface plasmon resonance (SPR) sensor and surface enhanced infrared absorption (SEIRA) spectroscopy. Two dendrimers focused here, poly(amido amine) dendrimer (PAMAM) and poly(trimethyleneimine) dendrimer (PTMI), possess amino terminals and electrostatically bind on MPA SAM. The adsorption behavior is compared with and discussed.

2. Experimental Section

MPA and dendrimers were purchased from Aldrich Chemical Co. Ethanol was purchased from Wako Pure Chemical Industries, Ltd.

SPR sensing was examined at 30 °C on a biosensor analytical system from Nippon



Fig. 1. Film thickness of adsorbed PAMAM and PTMI dendrimers on MPA SAM as a function of time on adsorption-desorption cyclic process. \bigcirc , start of adsorption; \square , start of desorption.

Laser & Electronics Lab, as described before[2]. MPA SAM was prepared on an Au-evaporated (44nm in thickness) glass substrate from 2.0mM ethanol solution. The SAM-adsorbed substrate was equipped in a SPR solution cell and used for the measurement. The shift of SPR angle under laser light radiation at 670nm wavelength was monitored as a function of adsorption time. After the adsorption equilibrium was reached, desorption process was proceeded by exposing the adlayer to water. The adlayer thickness was evaluated from a spectrum of SPR reflectance vs. incident angle according to the Fresnel relation[2]. Attenuated total reflective (ATR) SEIRA spectra were recorded at room temperature (~25) on a Bio-Rad FTS 575C FT-IR spectrometer equipped with a surface enhanced attachment with a band resolution of 4cm⁻¹. Au island film of 15 nm in thickness on a hemispherical silicon prism was prepared as described before[3]. MPA-SAM was prepared in an ATR solution cell and used for the adsorption of dendrimers from aqueous solutions. A SEIRA spectrum of an ATR cell filled water was used as a background.





Fig. 2. Kinetics analysis for initial adsorption process of PAMAM dendrimer on MPA SAM. $\blacklozenge \blacktriangle \diamondsuit$, observed; -----, calculated by eq. (1); -, calculated by eq. (3).

3. Results and Discussion

Figure 1(a) shows the film thickness of adsorbed PAMAM dendrimers as a function of time on adsorption-desorption cyclic process. Film thickness at equilibrium on the initial adsorption process depends on the concentration of PAMAM dendrimer but not linear to the concentration. On the process of desorption, while the desorption is extremely less in the cases of 0.001 and 0.01 wt% solutions, about half of dendrimers desorb from the adlayer from a 0.1wt% solution. The adsorption-desorption profile is almost reproducible. It should be noted that the film thickness after desorption is nearly same for 0.01 and 0.1wt% solutions. These results indicate that the strong monolayer adsorption is attained at around 3.5nm in thickness. At the high dendrimer concentration 0.1wt%, of additional adsorption occurs but it is easy desorbed in water. Similar adsorptiondesorption behavior was observed for a PTMI dendrimer, as seen in Fig. 1(b). The monolayer formation is accomplished with a thickness of about 2.5nm, which is thinner



Fig. 3. Kinetics analysis for initial adsorption process of PTMI dendrimer on MPA SAM. $\blacklozenge \blacktriangle \diamondsuit$, observed; -----, calculated by eq. (1).

than that of PAMAM dendrimer, relating to the difference of dendrimer size.

The kinetics for initial adsorption of dendrimer was analyzed on the basis of the Langmuir (monolayer) adsorption equation[4]

 $I = I_1 \{1 - \exp(k_{1,obs} t)\}$ (1) where I and I_1 are film thickness at time t and at equilibrium, respectively, and $k_{1.obs}$ is an apparent rate constant. The theory suggests that the apparent rate constant becomes large with the concentration C as follows;

$$k_{1 \text{ obs}} = k_{a}C + k_{d} \tag{2}$$

where k_a and k_d are intrinsic rate constants of adsorption and desorption, respectively.

The $k_{1.obs}$ values of 0.015 and 0.012sec⁻¹ were evaluated from the curve fitting, as shown in Fig. 2(a), for adsorption of PAMAM dendrimer from 0.001 and 0.01wt% solutions, respectively. The values are inconsistent with the theoretical assumption, although the calculated curves fairly fit with the observed ones.

The contribution of additional adsorption beside monolayer formation must be included, especially, in a case of 0.1 wt% solution, as estimated from the adsorptiondesorption cyclic process in Fig. 1. Then, a 2-step adsorption mechanism described by[5]

$$I = \sum_{i=1}^{2} I_i \{1 - \exp(k_{i \text{ obs }} t)\}$$
(3)

must be applied. It can be supported from Fig. 2(b) that the adsorption of dendrimer from a 0.1wt% solution follows on a 2-step mechanism.

The adsorption of PTMI dendrimer deviates from the Langmuir adsorption kinetics even at low concentrations like 0.001 and 0.01wt% (see Fig. 3). Although the adsorption mechanism at 0.1wt% seems to obey the Langmuir kinetics, it is suggested from the film thickness in Fig. 1



Fig. 4. Absorbance increase of a CH_2 wagging vibrational band, as a function of time, of a PTMI dendrimer adsorbed from an aqueous 0.01wt% solution on MPA SAM. \blacklozenge , observed; ----, calculated by eq. (1); -, calculated by eq. (3).

that there must be additional adsorption on monolayer on the adsorption process. Thus, the adsorption of PAMAM and PTMI dendrimers on MPA SAM does not follow a simple Langmuir adsorption kinetics, at least, except a 0.001wt% PAMAM solution.

The adsorption kinetics was examined even from time-resolved ATR-SEIRA spectroscopy. The increase of absorbance of a CH₂ wagging vibration band at 1282cm⁻¹ for PTMI dendrimer adsorbed from an aqueous 0.01wt % solution is plotted as a function of adsorption time in Fig. 4. The increase is obedient to the 2-step adsorption mechanism but not the Langmuir type. This result is equivalent with the kinetics analysis on SPR spectroscopy, where there is the slight additional adsorption over the monolayer adsorption for a case of the initial adsorption from a 0.01wt% solution.

Figure 5 shows infrared absorption spectra of PAMAM and PTMI dendrimers, in equilibrium, adsorbed from aqueous solutions. Amide I band of PAMAM dendrimer is weaker than amide II. This tendency is enhanced for the adsorption in a concentrated solution, and both bands shift to low wavenumber region for the adsorption in a D_2O solution. It should be (a) PAMAM



Fig. 5. ATR-SEIRA spectra, at adsorption equilibrium, of PAMAM and PTMI dendrimers on MPA SAM.



Fig. 6. Adsorption models of PAMAM and PTMI dendrimers on MPA SAM.

noticed that the solution pH was 7.1 and 8.4 for 0.001 and 0.01wt% solutions, respectively. For PTMI dendrimer, although there is no variation of absorbance depending on the concentration, carboxylic acid of MPA changes to carboxylate species during the adsorption process as same as in a case of PAMAM dendrimer, indicating the electrostatic interaction between MPA and dendrimer.

From these results, we can assume the adsorption structure of dendrimers on MPA SAM. PAMAM dendrimer adsorbs with "the hemi-micellar structure" (see Fig. 6(a)) due to the electrostatic and hydrogenbonding interactions between terminal amino and interior amide groups of PAMAM dendrimer and carboxylate of MPA SAM, as estimated from infrared absorption spectroscopy. This tendency depends on dendrimer concentration or solution pH. On the other hand, PTMI dendrimer adsorbs by only the electrostatic interaction between terminal amine of PTMI dendrimer and carboxylate of MPA SAM. Then the adsorption structure of PTMI dendrimer should be "the hourglass type" or "the conical type", which are illustrated in Figs. 6(b) and 6(c), respectively.

4. Conclusions

The adsorption behavior on carboxylateterminated SAM was compared with two dendrimers which have poly(amido amine) and poly(trimethyleneimine) interiors and common amino terminals. The adsorption kinetics for both dendrimers deviates from Langmuir theory. Although the electrostatic interaction is a main driving force of the adsorption on MPA SAM, there is additional adsorption on dendrimer monolayer. On the other hand, the adsorbed structure is different between dendrimers depending on interior structures because of the additional interaction between SAM and PAMAM dendrimer.

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