

In Situ Investigation of Adlayer Formation and Adsorption Kinetics of Amphiphilic Surface-Block Dendrimers on Solid Substrates

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The adlayer formation and adsorption kinetics of third- and fourth-generation (G3 and G4) amphiphilic surface-block dendrimers with amino and *n*-hexyl terminals (amino/hexyl), hydroxyl and *n*-hexyl terminals (hydroxyl/hexyl), and *N*-acetyl-D-glucosamine and *n*-hexyl terminals (glucosamine/hexyl) on solid substrates were investigated using atomic force microscopy, contact angle, surface plasmon resonance spectroscopy, and surface-enhanced infrared absorption spectroscopy. The amino/hexyl and hydroxyl/hexyl dendrimers formed dimer-unit layers on a solid surface, but the whole adlayer of the glucosamine/hexyl dendrimers displayed a rather flat surface, while the adlayer surface of each dendrimer was always hydrophilic. The time dependence of the adlayer formation, which was monitored in situ, obeyed two-step adsorption kinetics, namely, fast and slow adsorption steps. The adsorption amount at the adsorption equilibrium decreased in the order of hydroxyl/hexyl > amino/hexyl > glucosamine/hexyl dendrimers, and the adsorption amount of the third-generation species was greater than that of the fourth-generation species. The linear dependence of the whole adlayer thickness on the concentration of hydroxyl/hexyl dendrimers was obtained at the equilibrium state. The molecular orientation of the hexyl chains in the adlayers was in the order of amino/hexyl > hydroxyl/hexyl > glucosamine/hexyl dendrimers.

Introduction

Different kinds of dendrimers, such as linear polymer–dendrimer hybrids,^{1–10} star dendrimers,^{11–14} surface-block dendrimers,^{1,15–19} core–shell block dendrimers,^{20–24} and

polymer dendrons,^{25,26} have been synthesized and characterized. Surface-block dendrimers take a spherical shape where the surface character of one hemisphere is different from that of the other. Amphiphilic surface-block dendrimers, especially, consist of surface blocks with different affinities for solvents, where one is hydrophilic and the other is hydrophobic.^{1,15–19} In previous work, the amphiphilic characteristics of the surface-block poly(amido amine) (PAMAM) dendrimer with hydroxyl and *n*-hexyl terminals in comparison with those of the symmetric PAMAM dendrimers have been reported.^{17–19} The surface tension of the surface-block dendrimers (generation G = 3) has a significant break point at the critical micelle concentration (cmc), while the fourth-generation (G4) homology displays less surface activity.¹⁷ On the other hand, there is no remarkable surface tension decrease with increasing PAMAM dendrimer concentration up to

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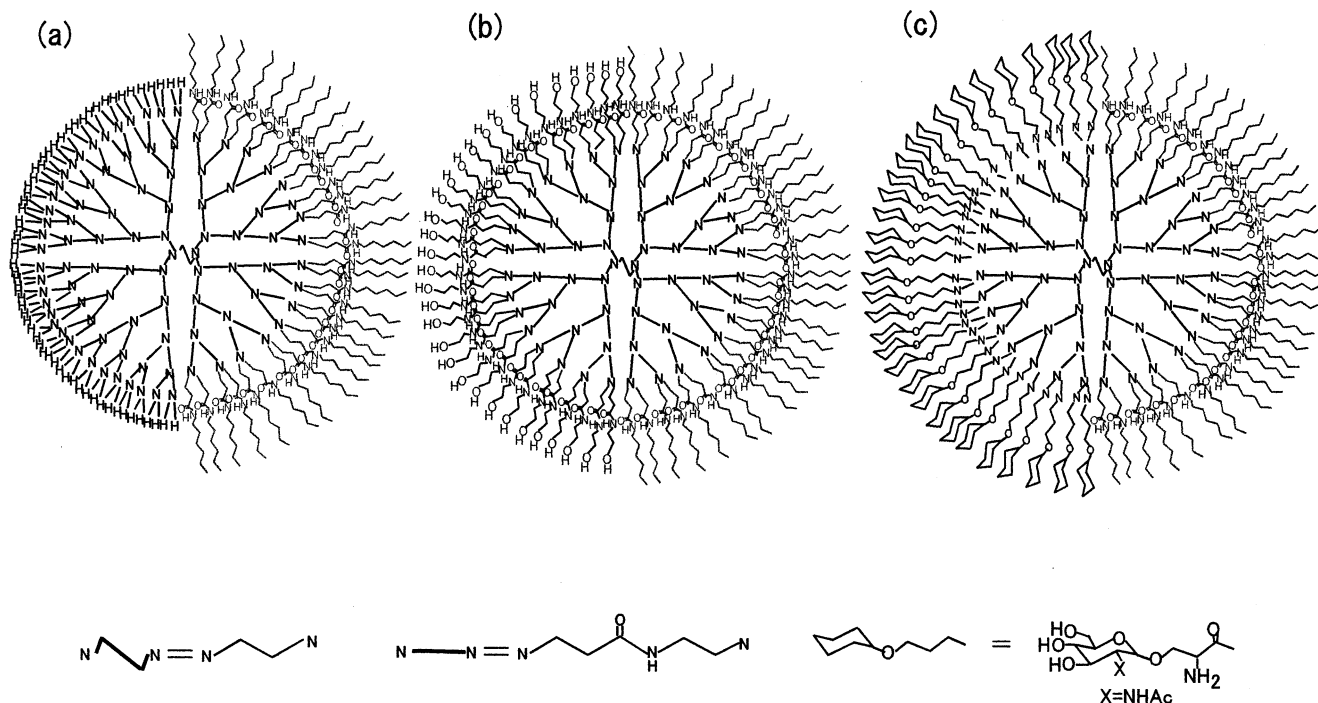


Figure 1. Chemical structures of dendrimers: (a) G4 amino/hexyl PAMAM dendrimer; (b) G4 hydroxyl/hexyl PAMAM dendrimer; (c) G4 glucosamine/hexyl PAMAM dendrimer.

1 wt %.¹⁸ This suggests that the surface-block dendrimers form an organized structure at the interface.¹⁰

In this study, the adlayer formation and adsorption kinetics of amphiphilic surface-block dendrimers with different hydrophilic moieties on solid substrates have been investigated in situ, and the effects of the hydrophilic moieties are discussed. Surface-block PAMAM dendrimers with amino and *n*-hexyl terminals and *N*-acetyl-D-glucosamine and *n*-hexyl terminals have been newly synthesized and utilized for comparison with a derivative with hydroxyl and *n*-hexyl terminals. These dendrimers (see Figure 1) are, hereafter, abbreviated as amino/hexyl, glucosamine/hexyl, and hydroxyl/hexyl dendrimers. Surface plasmon resonance (SPR)²⁷ and surface-enhanced infrared absorption (SEIRA)^{28,29} spectroscopy are both useful for the in situ investigation of adlayer formation and adsorption kinetics. The adlayer thickness and molecular orientation can be determined exactly from SPR and SEIRA spectroscopy. The kinetics is measured using SPR and attenuated total reflective (ATR) SEIRA instruments with a flow cell attachment and analyzed on the basis of adsorption kinetics models.

Experimental Section

G3 and G4 surface-block dendrimers were synthesized from a half-protected initiator core using a divergent/divergent method as follows.^{17–19} After the first divergent step, the terminal methyl ester groups of *core-Z*-protected PAMAM dendrimers were allowed to react with hexylamine to form the hexyl surface-block moiety.¹⁶ After deprotection of the *core-Z* group, the second divergent dendrimer construction was carried out to generate a terminal methyl ester type surface-block dendrimer of generations 2.5 and 3.5. By reactions of the terminal methyl ester type surface-block dendrimer with ethylenediamine and with ethanolamine, amino/hexyl and hydroxyl/hexyl surface-block den-

drimers (Figure 1a and Figure 1b, respectively) were obtained. Glucosamine/hexyl surface-block dendrimers (Figure 1c) were synthesized by the reaction of the amino/hexyl dendrimer with acetylated *N*-acetyl-D-glucosamine-substituted serine *N*-carboxyl anhydride (glycoNCA), followed by deprotection with hydrazine monohydrate.³⁰ The G4 PAMAM dendrimer hydrochloride (PAMAM·HCl dendrimer) was prepared from the PAMAM dendrimer with amino terminals by adding an excess amount of HCl and by precipitating from methanol/diethyl ether.³¹

Dendrimers were dissolved in water at a concentration of 0.01 wt %. Since this concentration was far below the cmc, dendrimers were dispersed as individual molecules in the solutions.

A freshly cleaved mica substrate was dipped into the aqueous solution of a dendrimer. The dendrimer-adsorbed substrate was dried and used for atomic force microscopic (AFM) observation and contact angle measurement at room temperature. The AFM observation was performed in the tapping mode on a Digital Instruments NanoScope III apparatus. The contact angle was evaluated from a photograph just after a water droplet was dropped on the dendrimer-adsorbed substrate. Photographs were taken using an Olympus Camedia digital camera C-1400L and a Nikon digital camera COOL PIX 950.

SPR spectroscopic examination was carried out at 30 °C on a biosensor analytical system (Nippon Laser & Electronics Lab.). The solution cell on a gold-evaporated glass substrate was filled with the aqueous solution of a dendrimer, and the SPR angle shift under 670 nm wavelength laser light was monitored as a function of the adsorption time until the adsorption equilibrium was reached. The reflectance versus the incidence angle curve was taken at the equilibrium adsorption. The curve was fitted using the standard Fresnel theory for the four-layer model.^{27,32} The first layer is a silicon prism with $\epsilon_r = 2.29$ and $\epsilon_i = 0$, where ϵ_r and ϵ_i are the real and imaginary parts, respectively, of a complex dielectric constant. The second and third layers are the gold islands and the adsorbate, respectively. The fourth layer is an aqueous medium, for which $\epsilon_r = 1.77$ and $\epsilon_i = 0$. The parameters for the gold layer were obtained from the best fit to the SPR spectrum from a system without an adlayer: the dielectric

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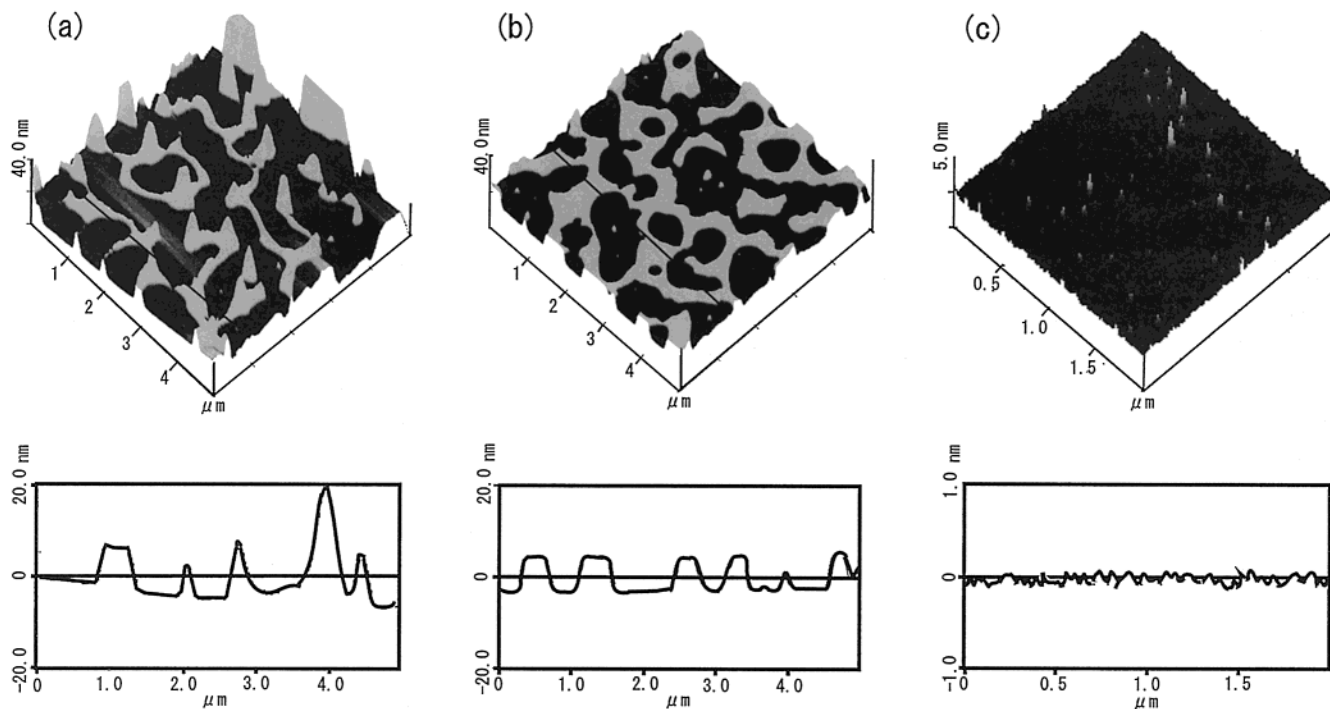


Figure 2. Atomic force microscopic images of G4 dendrimers adsorbed for 15 min on mica from aqueous 0.01 wt % solutions. Their section analyses are drawn in the bottom. (a)–(c) denote dendrimers in Figure 1.

Table 1. Parameters for Dendrimer Structure, Solution Property, Adlayer Film, and Adsorption Kinetics

dendrimer	unit adlayer thickness, nm	contact angle, deg	whole adlayer thickness, nm	first cmc, ^a wt %	second cmc, ^a wt %	IR intensity ratio ^b	number of total CH ₂ (hexyl CH ₂)	number of CONH	k_{obs} , s ⁻¹	$k_{1,\text{obs}}$, s ⁻¹	$k_{2,\text{obs}}$, s ⁻¹
G4 amino/hexyl	7	30	8			12	594 (160)	124	0.0112	0.0026	0.0361
G3 hydroxyl/hexyl	6		14	0.07	0.5			60	0.0035	0.0014	0.0118
G4 hydroxyl/hexyl	7	28	10	~0.5		5	594 (160)	124	0.0036	0.0015	0.018
G3 glucosamine/hexyl		39		0.1	0.7	7					
G4 glucosamine/hexyl		39		0.5	5	2	658 (160)	156	0.0048	0.0027	0.0169
G4 PAMAM-HCl		34				1.4	498 (0)	124			

^a From refs 16 and 17. ^b Amide I/CH₂ antisymmetric stretching band.

constant was $\epsilon_r = -13.3$ and $\epsilon_i = 2.20$, and the thickness varied between 44.2 and 44.7 nm. Then, the dielectric constant $\epsilon_r = 1.80$ for the adlayer and the adlayer thickness were simultaneously evaluated from the best fit to the SPR spectra for all the solutions of the dendrimers examined. The adlayer thickness obtained was used for replotting the angle shift versus adsorption time curves as the adlayer thickness versus adsorption time curves.

Fourier transform infrared (FT-IR) spectra were recorded at room temperature using a Bio-Rad FTS 575C FT-IR spectrometer equipped with a cryogenic mercury–cadmium telluride (MCT) detector. The reflection–absorption (RA) spectra were taken using a Harrick reflectance attachment with a 70° incidence angle. The substrate, which was prepared by evaporating Cr at 150 nm thickness and then Au at 250 nm thickness on a glass plate, was used for the RA measurement. The transmission SEIRA spectra were measured on a gold-island CaF₂ window, which was prepared by evaporating Au at 10 nm thickness at a rate of 0.05 Å/s under a pressure below 3×10^{-4} Pa in an Evaporator SD-240 (Shinku of Technology, Nagoya, Japan) apparatus.³³ The dendrimer-adsorbed gold-island CaF₂ window was prepared by filling with an aqueous solution of the dendrimer on the window for 15 min, draining the solution, and drying the window. The dendrimer-adsorbed substrates were supplied for the FT-IR measurement. The ATR-SEIRA spectra were measured on a Kretschmann type flow ATR cell attachment using water as the background. The measurement was carried out for 2000 sets at 256 times accumulation and a 4 cm⁻¹ resolution for background and transmission mode, and it was at 4 times accumulation and a 4 cm⁻¹ resolution for the ATR mode.

Results and Discussion

Layer Formation Observed by Atomic Force Microscopy and Contact Angle. The formation of adsorption films organized by the amphiphilic surface-block dendrimers on solid substrates was investigated by AFM observation and contact angle measurement. Dendrimers were adsorbed on mica substrates from aqueous 0.01 wt % solutions. Figure 2 shows AFM images of adlayers of G4 dendrimers after 15 min adsorption. G4 amino/hexyl dendrimers formed layers of 7 nm in thickness. Similar layer images of 7 nm in thickness were obtained for the adlayer of G4 hydroxyl/hexyl dendrimers. Images for G3 hydroxyl/hexyl dendrimers resembled those for the G4 species except for the unit layer thickness. The unit adlayer thickness of G3 hydroxyl/hexyl dendrimers was 6 nm, as listed in Table 1. The adsorption proceeded with time. Islands with constant thickness were initially formed, and then these increased in size and associated into adlayer domains with the same thickness. Finally, the accumulated layers with a rather uniform surface were formed after a long adsorption time or at adsorption equilibrium. On the other hand, the adlayer surfaces of G3 and G4 glucosamine/hexyl dendrimers were always rather flat like that of PAMAM-HCl dendrimers.¹⁹

The contact angle measurement was carried out for adlayer films on mica. The contact angle was 28–39° for the three surface-block dendrimers, as shown in Table 1.

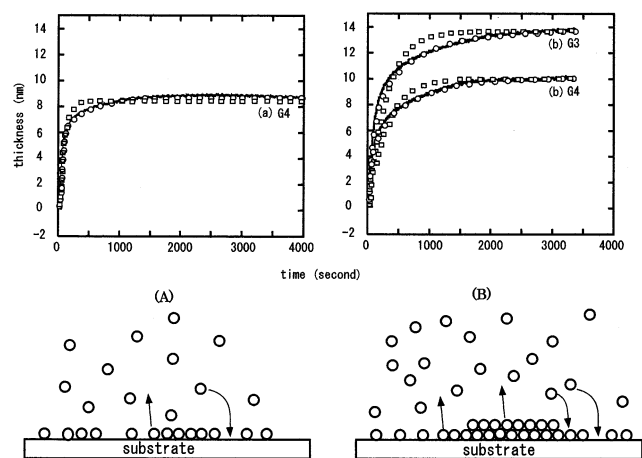


Figure 3. (Top) Whole adlayer thickness variation as a function of adsorption time for aqueous 0.01 wt % solutions of G3 and G4 dendrimers: (a) amino/hexyl PAMAM dendrimer; (b) hydroxyl/hexyl PAMAM dendrimer. Calculated values based on Langmuir adsorption kinetics (\square) and two-step adsorption kinetics (\circ) are also included. (Bottom) Schematic illustration of Langmuir adsorption (A) and two-step adsorption (B).

The low contact angle values indicate the hydrophilicity of the surface, although they were larger than that of the bare mica surface, which displayed almost zero contact angle. This implies that the hydrophilic terminals of the dendrimers are exposed at the outermost layer and the hydrophobic alkyl terminals are not. This indicates that the substrates are covered by dendrimers, the hydrophilic terminals of which are located at the exterior of the adlayer. Since the mica surface is also hydrophilic, the hydrophilic terminals of the adsorbed dendrimers must be directed to the mica surface, suggesting the formation of a dimer-unit adlayer. Therefore, the adlayer thickness of the amino/hexyl and hydroxyl/hexyl dendrimers in the AFM images must be double the dendrimer size. Since the unit adlayer thickness listed in Table 1 is larger than the PAMAM dendrimer diameter estimated from the Corey–Pauling–Koltun (CPK) model and previous experiments^{34,35} but less than double the diameter, the dendrimers in the adlayer must be collapsed and in the “pancake” structure.

Whole Adlayer Thickness Determined by SPR. The increase in adlayer thickness as a function of the adsorption time was obtained from the SPR time course and is shown in Figure 3 for aqueous 0.01 wt % solutions of amphiphilic surface-block amino/hexyl and hydroxyl/hexyl dendrimers. The adsorption equilibrium of the surface-block dendrimers on the Au substrate was reached after 30–50 min. The whole adlayer thickness at equilibrium was 8 nm for G4 amino/hexyl dendrimers and 14 and 10 nm, respectively, for G3 and G4 hydroxyl/hexyl dendrimers (Table 1). The adsorption amount of G4 hydroxyl/hexyl dendrimers was more than that of G4 amino/hexyl dendrimers but less than that of G3 hydroxyl/hexyl dendrimers. The effect of the generation originates in the hydrophobicity–hydrophilicity balance or amphiphilicity of the dendrimers. The fraction of hydrophobic hexyl groups is less in G4 species than in G3 species, and this is elucidated from the comparison of the critical micelle concentrations (cmc’s),^{16,17} as listed in Table 1. The cmc’s of G4 species are always higher than those of G3 species.

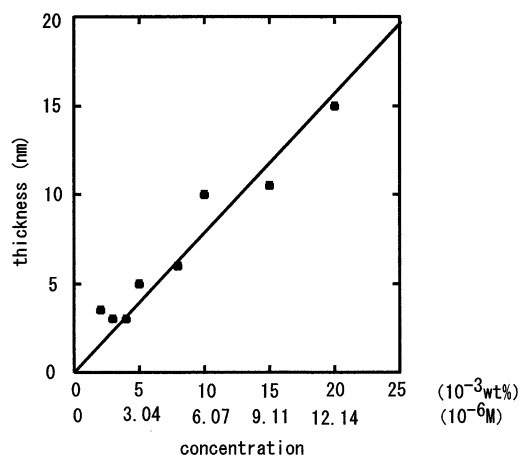
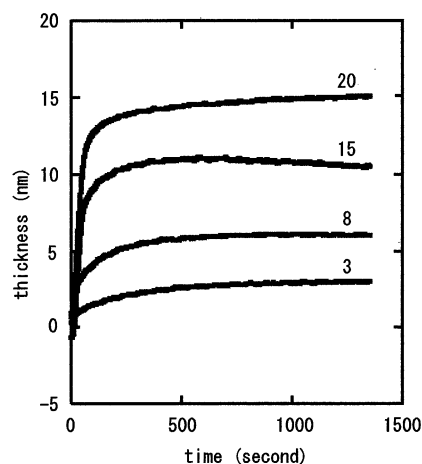


Figure 4. Whole adlayer thickness as a function of adsorption time at different dendrimer concentrations (top) and whole adlayer thickness at adsorption equilibrium as a function of dendrimer concentration (bottom) for aqueous solutions of G4 hydroxyl/hexyl PAMAM dendrimer. Numbers in the top figure denote dendrimer concentrations in units of 10^{-3} wt %.

It is obvious from the unit and whole adlayer thicknesses (Table 1) that more than one layer of unit adlayers were equilibrated to aqueous solutions of G3 and G4 hydroxyl/hexyl dendrimers, while the whole adlayer of amino/hexyl dendrimers was nearly comparable to one unit adlayer. This indicates the stronger adsorption ability of hydroxyl/hexyl dendrimers compared with amino/hexyl dendrimers. This may result from stronger hydrogen bonding between hydroxyl groups and amide groups of hydroxyl/hexyl dendrimers in neighboring adlayers than that between amino groups and amide groups of amino/hexyl dendrimers.

The SPR time courses were measured at various concentrations of G4 hydroxyl/hexyl dendrimers in aqueous solutions. Figure 4 (top) shows the curves of whole adlayer thickness versus adsorption time. The adlayer thickness reached an equilibrium state after 10–30 min, depending on the dendrimer concentration. The whole adlayer thickness was lower than the unit adlayer thickness (7 nm) for aqueous solutions below 10×10^{-3} wt %. This result indicates that the whole solid surface is not covered by the adsorption of the unit layer. The whole adlayer thickness at the equilibrium state was plotted against the dendrimer concentration in Figure 4 (bottom). The thickness increased in proportion to the concentration, in accordance with Henry’s adsorption theory. The adsorption-to-desorption profile was examined for an aqueous 0.01 wt % solution of G4 amino/hexyl

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Table 2. Positions (in cm^{-1}) and Assignments of IR Absorption Bands for Adlayers Prepared by 15 min Adsorption from Aqueous 0.01 wt % Solutions of G4 Surface-Block and PAMAM-HCl Dendrimers^a

amino/hexyl dendrimer, transmission SEIRA	hydroxyl/hexyl dendrimer		glucosamine/hexyl dendrimer, transmission SEIRA	PAMAM-HCl dendrimer, transmission SEIRA	assignment
	IR-RA	transmission SEIRA			
3252m	3293m	3258m	3258m	3220vw	amide A
3059w	3077w	3070w	3069w	3054vw	amide B
2917m	2929m	2918m	2918m	2918m	CH ₂ antisymmetric stretching
2848w	2853m	2849m	2850m	2849m	CH ₂ symmetric stretching
1635s	1653s	1640s	1636s	1640m	amide I
1540s	1559s	1548s	1540s	1545w	amide II
1458m	1457w	1457w	1456w	1439w	CH ₂ scissoring
w	1437w	1433w			
1341m	1369w	1359w	1399w		CH ₂ wagging
w	1200w	1190w			amide III
		1149w			
1029m	1058m	1066w			C-C stretching (trans)

^a s, strong; m, medium; w, weak; vw, very weak.

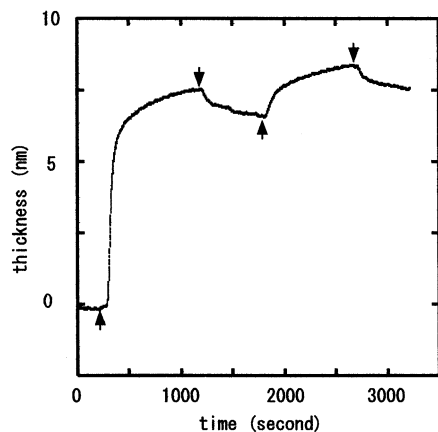


Figure 5. An adsorption-to-desorption profile for an aqueous 0.01 wt % solution of G4 amino/hexyl PAMAM dendrimer. The symbols \uparrow and \downarrow denote starting points of adsorption and desorption, respectively.

dendrimers, for which the formation of a unit adlayer was suggested by the results of the AFM and SPR. As shown in Figure 5, the amount of desorption was rather less in comparison with total adsorption, indicating the strong adsorption of dendrimers on the substrate.

Molecular Orientation Evaluated from Infrared Absorption Spectroscopy. The advantages of the use of SEIRA spectroscopy are not only the strong enhancement of band intensity but also the surface selection rule.^{33,36} By the selection rule of both IR-RA and transmission SEIRA spectroscopy, although the substrates utilized are coated by thick and island Au films, respectively, only vibrational bands with transition moments perpendicular to the metal surface are enhanced by the electric field normal to the surface. On the contrary, those parallel to the metal surface are minimized. Therefore, the molecular orientation on the surface can be determined. The surface enhancement effect on an island Au substrate is superior to the reflection-absorption effect on a thick Au substrate.³³ In the case of the surface-block dendrimers, the intensity of the transmission SEIRA spectrum was almost double that of the IR-RA spectrum.

Transmission SEIRA spectra, which were measured for adlayers after adsorption for 15 min from aqueous 0.01 wt % solutions, were compared among G4 surface-block dendrimers and a PAMAM-HCl dendrimer, as shown in Figure 6. The band positions and their assignments are listed in Table 2. The assignments were carried out

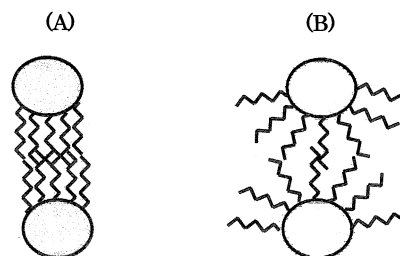
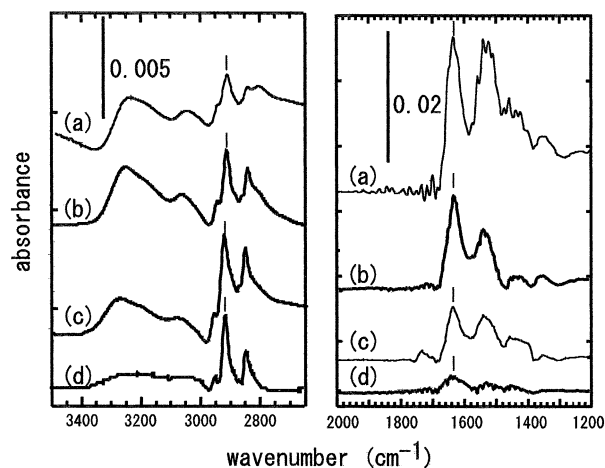


Figure 6. (Top) Transmission SEIRA spectra of dendrimer adlayers (at 15 min adsorption) prepared from aqueous 0.01 wt % solutions. (a)–(c) denote dendrimers in Figure 1. (d) G4 PAMAM-HCl dendrimer. (Bottom) Schematic illustration of hexyl groups in coupled surface-block dendrimers: (A) bilayer arrangement; (B) radial arrangement.

according to the literature.^{37,38} The spectrum profile for the PAMAM-HCl dendrimers was similar to that previously reported for the G4 PAMAM dendrimers with amino terminals.³⁸ Imae et al.¹⁹ have reported that the adsorption proceeds in greater amount for the surface-block hydroxyl/hexyl dendrimers than for the PAMAM-HCl dendrimers, due to the hydrophilicity of the latter. As shown in Figure 6, the amide A, B, I, and II bands of the hydroxyl/hexyl dendrimers were very strong in intensity in comparison with those of the PAMAM-HCl dendrimers, and this was related to the adsorption amount. The intensity ratio of the amide I and II bands, the transition dipole moments

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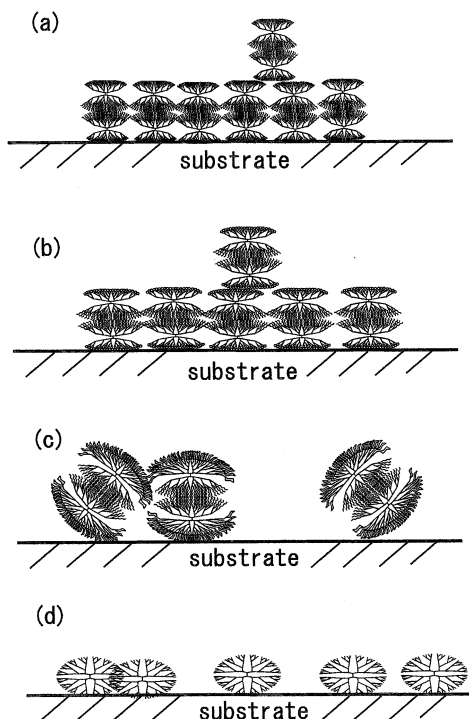


Figure 7. Schematic illustration of G4 dendrimers adsorbed on a substrate. (a)–(d) denote dendrimers described in Figure 6.

of which are directed along nearly the C=O and the chain axes, respectively, was similar to that of the disordered case,³⁷ suggesting that the poly(amido amine) branches should be less oriented. A similar result has been reported by Zhao et al.³⁸ The CH₂ antisymmetric and symmetric stretching bands were observed at ~2918 and ~2849 cm⁻¹, respectively. While a G4 PAMAM·HCl dendrimer has 498 CH₂ groups, a G4 hydroxyl/hexyl dendrimer has 594 CH₂ groups, 160 of which belong to the hexyl groups (see Table 1). Nevertheless, the intensities of the CH₂ antisymmetric and symmetric stretching bands for the hydroxyl/hexyl dendrimers were comparable to those for the PAMAM·HCl dendrimers. This implies a decrease in the intensities of the CH₂ stretching bands for the hydroxyl/hexyl dendrimers. Thus, the alkyl chains in the terminal hexyl groups must be arranged in a direction almost normal to the Au surface, as illustrated in Figure 6A, rather than radially as in Figure 6B.

A similar orientation of hexyl groups was assumed even for amino/hexyl and glucosamine/hexyl dendrimers, although the orientation degree differs from dendrimer to dendrimer. When the intensity of the CH₂ antisymmetric stretching band is compared with that of the amide I band, the ratio can be a measure of the hexyl chain orientation. The intensity ratios are listed in Table 1, and the numbers of CH₂ and CONH are also included. The ratio for amino/hexyl dendrimers was far larger than that for PAMAM·HCl dendrimers. If amino/hexyl dendrimers take a similar adsorption structure to that of PAMAM·HCl dendrimers, the ratio must be decreased, because the number of CH₂ groups in the former is larger than that in the latter. However, the SEIRA result is contrary to that expectation. The selection rule of SEIRA spectroscopy suggests normal orientation of the *n*-hexyl chains in amino/hexyl dendrimers. From the band intensity ratio, one can note that the orientation of the *n*-hexyl groups was in the order of amino/hexyl dendrimers > hydroxyl/hexyl dendrimers > glucosamine/hexyl dendrimers.

Figure 7 illustrates the plausible adsorption models of dendrimers on substrates. Amino/hexyl dendrimers form bilayers with hexyl groups that are oriented almost perpendicularly to the surface. Hydroxyl/hexyl dendrimers also form bilayers, but the hexyl groups of this dendrimer are oriented less than that of amino/hexyl dendrimers. The poly(amido amine) moiety of amino/hexyl dendrimers must be oriented more than that of hydroxyl/hexyl dendrimers, since the intensities of amide I and II for amino/hexyl dendrimers were almost same, and different from the disordered case.³⁷ The adsorption structure of glucosamine/hexyl dendrimers is rather less clear because of the lesser information on the orientation of the poly(amido amine) interior and hexyl terminal groups. It is assumed from the hydrophilic surface block with a large structural hindrance that the glucosamine/hexyl dendrimers may form dimers but be less oriented, as illustrated in Figure 7. This is not the case for the lower generation, G3 glucosamine/hexyl dendrimers, since the orientation ratio for G3 dendrimers was 3.5 times larger than that for G4 homology because of the loose hydrophilic periphery.

Adsorption Kinetics. An investigation of the adsorption kinetics using SPR spectroscopy has been reported for the self-assembled monolayer formation, adsorbate adsorption, and antigen–antibody reaction on substrates.^{19,39–47} The resultant kinetics profiles were analyzed on the basis of different adsorption models.^{48–52} A well-known model is the Langmuir monolayer adsorption,⁴⁸ where adsorbate A occupies adsorption sites S on the substrate through interaction, according to the adsorption reaction



where k_a and k_d are the intrinsic rate constants of adsorption and desorption, respectively. When the equilibrium state is maintained between the adsorption and desorption processes, a monolayer array in equilibrium is formed on the substrate, as illustrated in Figure 3A. Then the surface coverage θ at the finite time t is described as

$$\theta = \frac{k_a C}{k_a C + k_d} \{1 - \exp(-k_{\text{obs}} t)\} \quad k_{\text{obs}} = k_a C + k_d \quad (2)$$

where C is the concentration of adsorbate A in the solution. Equation 2 was used for reproducing the observed adsorption curves of surface-block dendrimers. The reproducibility was lower, as seen in comparison of the observations with calculation in Figure 3, which was

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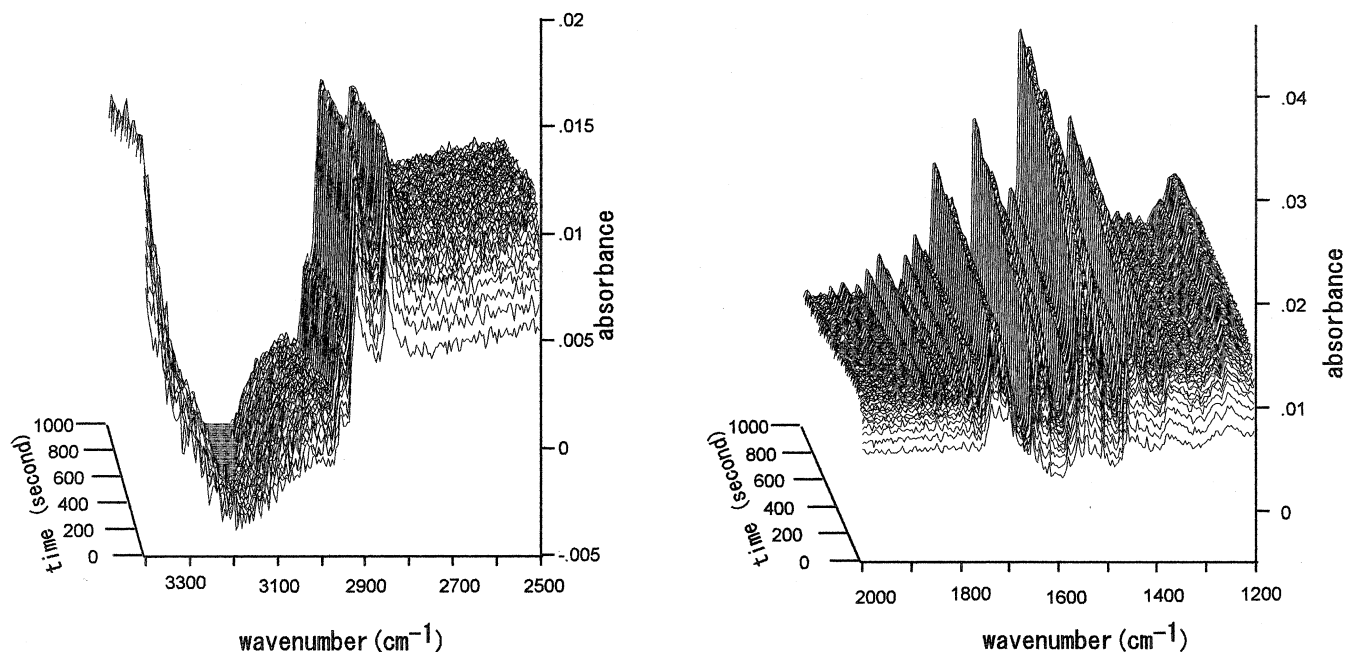
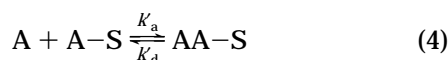


Figure 8. Time-resolved ATR-SEIRA spectra for an aqueous 0.01 wt % solution of G4 glucosamine/hexyl PAMAM dendrimer.

carried out with the optimum parameters in Table 1. It should be noted as an important condition that amino/hexyl and hydroxyl/hexyl dendrimers raise the accumulation of the unit layer, as discussed above.

One of authors (T. I.) and her collaborators^{36,47,53} have investigated the adsorption kinetics of a cationic surfactant on thiol self-assembled monolayers (SAMs). The adsorption kinetics of a cationic surfactant on the hydrophobic SAM did not obey a simple Langmuir adsorption model, since the cationic surfactant was additionally adsorbed on the adsorbed monolayer. Such an adsorption mechanism can be applied to the present systems.

Suppose that the first layer is formed on the adsorption sites *S* and that the additional multilayer is added onto it as illustrated in Figure 3B. For simplification, the second layer formation only is taken into account. This assumption is applicable to the systems reported in Figure 3, since the whole adlayer thickness is, at most, double the unit adlayer thickness. Then the adsorption reaction of adsorbate *A* on a substrate is described by



where the rate constants of adsorption and desorption of the first layer are k_a and k_d , respectively, and those of the second layer are k'_a and k'_d , respectively. The surface coverage θ at an adsorbate concentration C is written as⁵³

$$\theta = I_1\{1 - \exp(-k_{1,obs}t)\} + I_2\{1 - \exp(-k_{2,obs}t)\} \quad (5)$$

where I_1 , I_2 , $k_{1,obs}$, and $k_{2,obs}$ are functions of the adsorbate concentration and rate constants. When the optimum parameters given in Table 1 were used, the kinetics curves observed were sufficiently reproduced, as shown in Figure 3. The objective surface-block dendrimers form the accumulation of the unit adlayer. If dimers as a unit of the adlayer are formed in solution, the dimer is regarded as

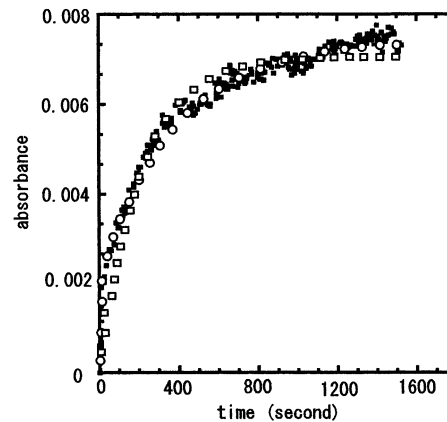


Figure 9. Absorbance of an amide II band as a function of adsorption time for an aqueous 0.01 wt % solution of G4 glucosamine/hexyl PAMAM dendrimer. Calculated values based on Langmuir adsorption kinetics (□) and two-step adsorption kinetics (○) are also included.

an adsorbate. The dendrimer concentration (0.01 wt %) investigated in the present paper was lower than the first cmc (Table 1), above which small aggregates such as dimers are formed.⁵⁴ Therefore, dimer formation did not occur in the present case. Then, the adsorption of a counterpart of the molecule adsorbed on a site should be very fast, since the unimolecular height was not observed on AFM images. In this case, a couple of molecules may be assumed to be an adsorbate.

A time-resolved ATR-SEIRA spectrum was measured for an aqueous 0.01 wt % solution of G4 glucosamine/hexyl dendrimers and is shown in Figure 8. The intensities of all absorption bands increased with the adsorption time. The intensity of the amide II band, which is one of the bands marked as an indicator of adsorption, was plotted as a function of the adsorption time in Figure 9. The adsorption kinetics eqs 2 and 5 were used to obtain the best fit to the observed one. The calculated values using the optimum parameters listed in Table 1 are included in

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Figure 9. The two-step adsorption kinetics was again adequate in comparison with the Langmuir kinetics. When the apparent rate constants in two-step adsorption kinetics were compared among dendrimers, the first rate constant was 1 order larger than the second.

Conclusions

In the present work, adlayer fabrication of three amphiphilic surface-block dendrimers on solid substrates which were different from those of previous studies^{55–66}

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was reported and compared with that of PAMAM dendrimer hydrochloride. The adlayer of surface-block dendrimers consisted of a couple of molecules, whose hydrophobic hexyl terminals were toward the interior and hydrophilic terminals toward the exterior. The whole adlayer thickness and the molecular orientation in the adlayer depended on the hydrophilic surface-block and the generation. These results are consistent with our concept of a nano-organized system with hydrophobic and hydrophilic layers and corresponding pockets.¹⁰

Adsorption kinetics of amphiphilic surface-block dendrimers was also investigated. The adsorption monitored in situ did not obey the Langmuir adsorption kinetics but did fit the two-step mechanism, namely, fast and slow adsorption steps. There are very few kinetics reports of dendrimer adsorption on solid substrates. Redox-active dendrimers containing ferrocenyl or ruthenium moieties on the periphery were adsorbed on a Pt electrode surface.^{67,68} The time dependence of the surface coverage was well described by the activation-controlled model, namely, the Langmuir adsorption conditions. The adsorption of amphiphilic surface-block dendrimers in the present work is different from this case.

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