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Formation of organized adsorption layers by amphiphilic dendrimers

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Abstract

The formation of organized adsorption films by amphiphilic AB-type surface-block dendrimers (generation $G = 3,4$) with hydroxyl group/n-hexyl group terminals on solid substrates has been investigated by atomic force microscopy, contact angle, and surface plasmon resonance. Then the surface characteristics have been compared with those of symmetric poly(amido amine) dendrimer (PAMAM). While the adsorption film of PAMAM is rather flat, surface-block dendrimers form bilayers and their accumulation because of their amphiphilic character. Dendrimers in bilayer, which is formed by pairing between hydrophobic blocks, take 'pancake' structure. Adsorption film surface has hydrophilic character, suggesting the hydrophilic OH terminal block faced to the solution. The amount of adsorption is more for the third-generation dendrimer than for the fourth-generation dendrimer, and the adsorption proceeds more for surface-block dendrimers than for PAMAM in relation to the hydrophobicity of dendrimers. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Poly(amido amine) dendrimer; Amphiphilic dendrimer; Surface block dendrimer; Atomic force microscopy; Contact angle; Surface plasmon resonance; Bilayer; Organized adsorption layer

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1. Introduction

In the recent decade, various kinds of functional dendrimers have been synthesized, and their physicochemical properties have been investigated in objectives of industrial, medical, and pharmaceutical applications [1–5]. Many investigations are carried out in bulk solutions, and some are concerned with film construction. Watanabe and Regen [6] have demonstrated the multilayer construction by using dendrimers as building block. Coen et al. [7] have examined the morphology of self-assembled ultrathin films of dendrimers on mica. Sheiko et al. [8,9] have investigated adsorption structure and aggregation process of dendrimers on substrates. Wells and Crooks [10] and Tokuhisa and Crooks [11] have reported the preparation of the dendrimer surface

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linked on self-assembled monolayers and the chemical sensibility of the surface for vapor-phase probe molecules. Chemisorbed adlayers of organothiol dendrons on gold have been investigated by Gorman et al. [12]. Bo et al. [13] prepared self-assembled monolayer of dendron-thiol on metal surfaces. Zhang et al. [14] reported growth strategies of dendritic multilayer film on solid substrates. Dendrimer-modified surfaces have been used as platforms for the deposition of colloidal particles [15]. Tsukruk et al. [16] have composed $(AB)_x$-type molecular films by self-assembly of two dendrimers with opposite charges using electrostatic layer-by-layer deposition. Dendrimer layers at air/water and fine particle/water interfaces have been studied by Saville et al. [17], Sheiko et al. [18], Esumi and Goino [19], and Kampf et al. [20].

The physicochemical properties of dendrimers depend remarkably on their structural characteristics. Among functional dendrimers, amphiphilic dendrimers behave as units of molecular organization. Copolymers with a dendritic head and a linear polymer tail, both having different solvent affinities, have been synthesized as a group of amphiphilic dendrimers [2,20–25]. These dendrimers are called head-tail-block dendrimers. Linear-dendritic ABA-type amphiphilic copolymers have also been synthesized [26]. Another type of amphiphilic dendrimers, layer-block dendrimers, consist of a dendritic core encapsulated by a shell, which is occupied by functional terminals [27] or polymer chains [28–30] with opposite solvent affinity against the cores. Amphiphilic star copolymers with dendritic groups at the periphery have also been reported [31,32]. The third group is amphiphilic surface-block dendrimers [2,33–35].

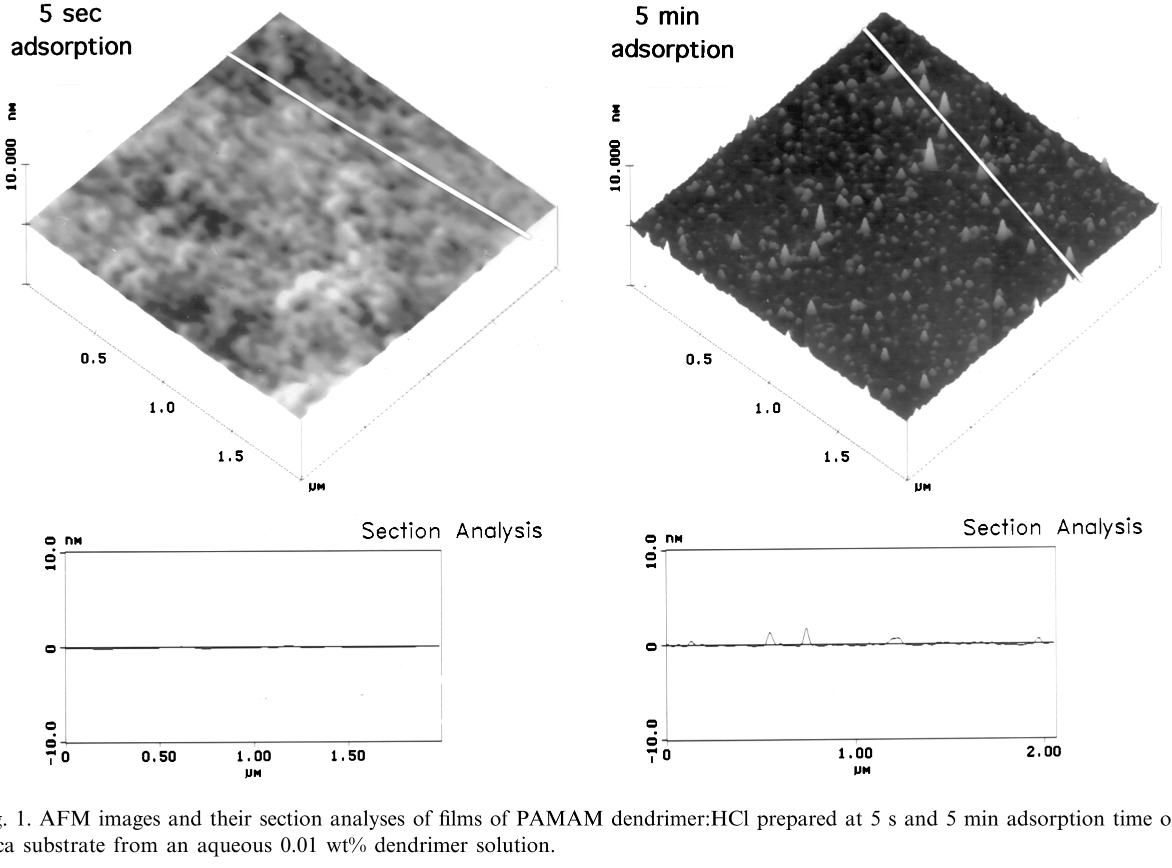


Fig. 1. AFM images and their section analyses of films of PAMAM dendrimer:HCl prepared at 5 s and 5 min adsorption time on mica substrate from an aqueous 0.01 wt% dendrimer solution.

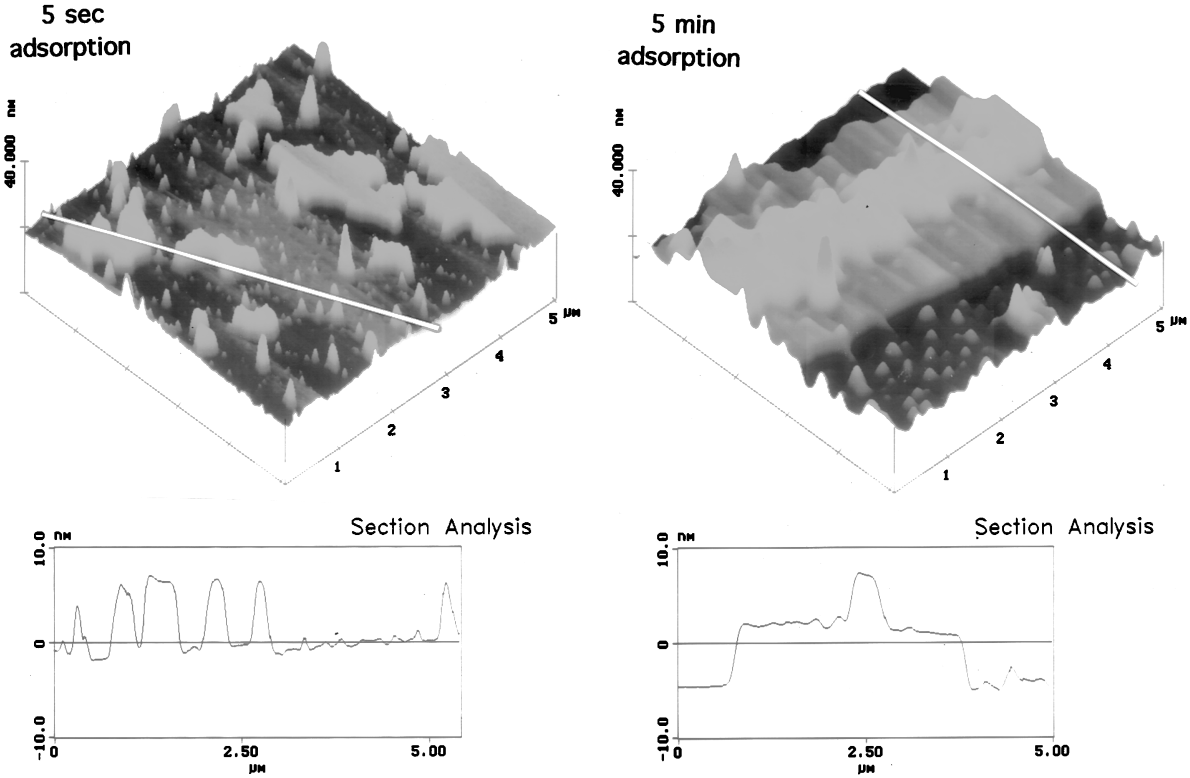
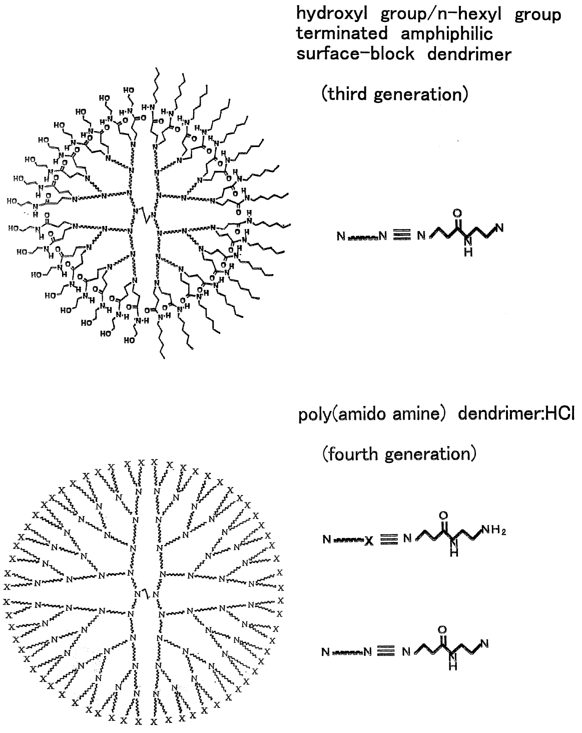


Fig. 2. AFM images and their section analyses of films of surface-block dendrimer ($G = 3$) with hydroxyl group/*n*-hexyl group terminals prepared at 5 s and 5 min adsorption time on mica substrate from an aqueous 0.01 wt% dendrimer solution.

This kind of dendrimer can take a spherical shape but the surface character of one hemisphere is different from that of another.

In the present paper, the formation of organized adlayers on solid substrates is investigated for dendrimers belonging to the third group, and the surface characteristics are compared with those of symmetric poly(amido amine) dendrimer (PAMAM). The surface tension of the amphiphilic AB-type surface-block dendrimers (generation $G = 3$) with hydroxyl group/*n*-hexyl group terminals (see Chart 1) displays break points at critical micelle concentrations (cmc), while the fourth-generation homolog has less surface activity [35]. It should be noticed that there is no remarkable surface tension decrease with increasing PAMAM dendrimer concentration up to 1 wt% [36]. This enables us to expect an organized structure formation at the interface for the surface-block dendrimer.



2. Experimental

PAMAM dendrimer ($G = 4$):HCl was prepared from PAMAM dendrimer with amino terminal groups by adding an excess amount of HCl followed by reprecipitation from methanol to diethyl ether [1]. Surface-block dendrimers ($G = 3,4$) with hydroxyl group/n-hexyl group terminals were synthesized by a divergent/divergent method with a half-protected initiator core. The dendrimers consist of hydrophilic surface-hydroxyl-substituted poly(amido amine) dendrimer fragment and hydrophobic surface-n-hexyl-substituted poly(amido amine) dendrimer fragment. The detail of the synthesis is described elsewhere [34,35].

Aqueous amphiphilic dendrimer solutions of 0.01 wt% which is below cmc [35] were prepared. Freshly cleaved mica substrate was dipped into the solution. After a constant time, the substrate was picked up from the solution and dried. A similar specimen was also prepared for PAMAM dendrimer:HCl. The dendrimer-adsorbed mica substrates were supplied for atomic force microscopic (AFM) observation and contact angle measurement.

AFM observation was carried out on a Digital Instrument NanoScope III apparatus by the tapping method. Contact angles were evaluated on photographs: 0.17 g of water was dropped onto the dendrimer-adsorbed mica substrate. Photograph of a water droplet was taken by Olympus camedia digital camera C-1400L. Surface plasmon resonance (SPR) spectroscopic examination was performed on a biosensor analytical system (Nippon Laser & Electronics Lab.). Aqueous dendrimer solution (0.01 wt%) was filled in a solution cell on a gold-evaporated glass substrate, and the reflectance under 670 nm wavelength laser light

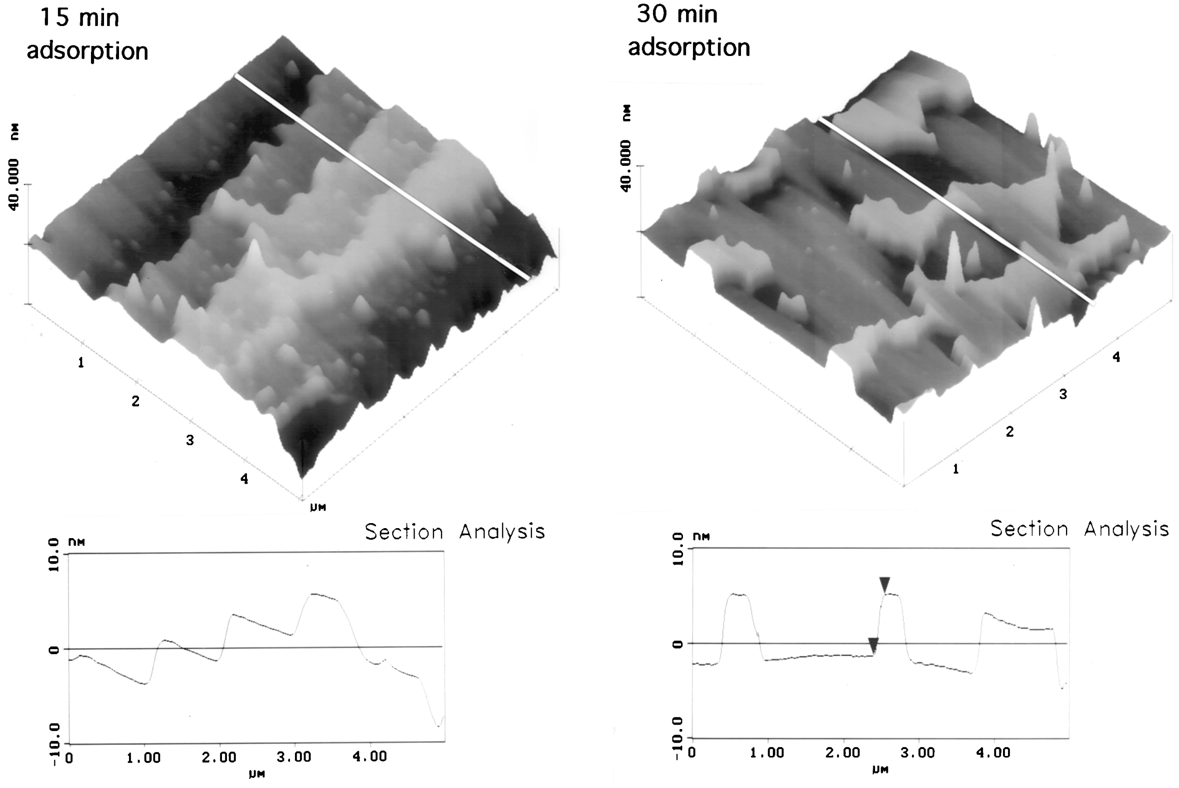


Fig. 3. AFM images and their section analyes of films of surface-block dendrimer ($G = 3$) with hydroxyl group/n-hexyl group terminals prepared at 15 and 30 min adsorption time on mica substrate from an aqueous 0.01 wt% dendrimer solution.

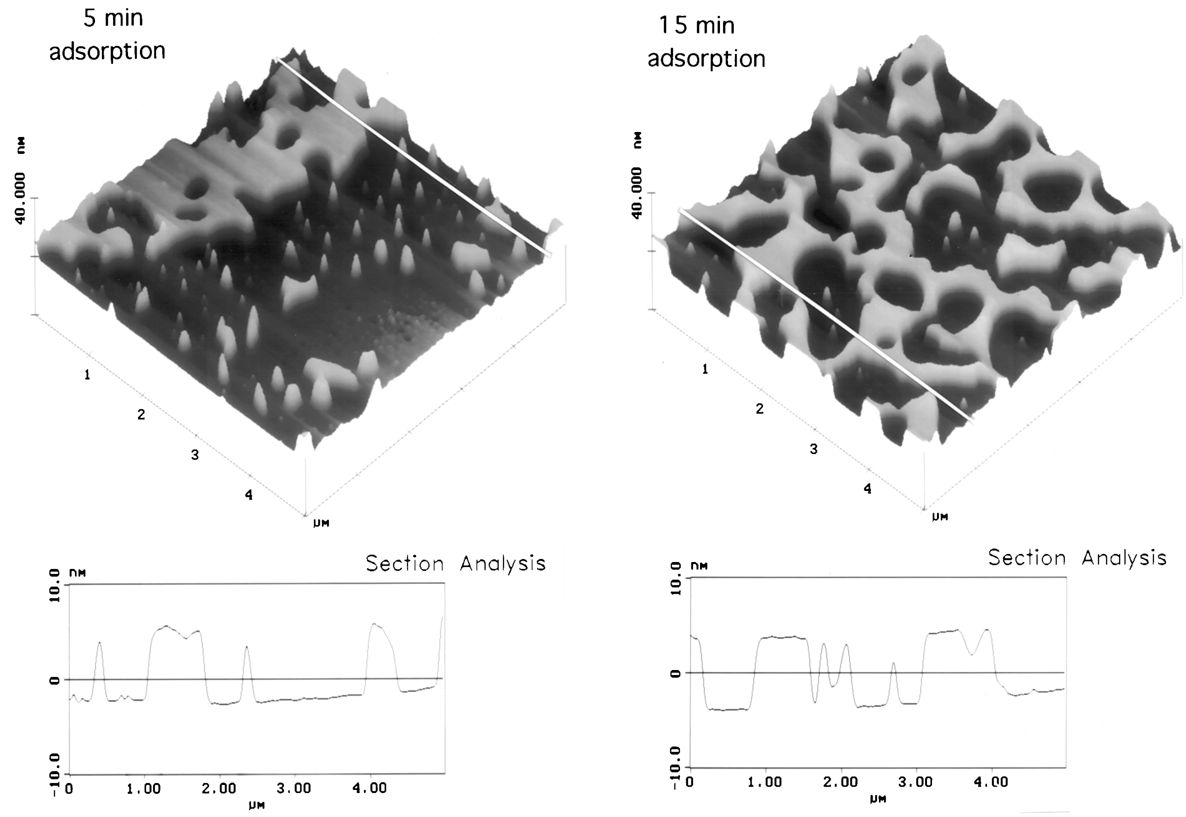


Fig. 4. AFM images and their section analyses of films of surface-block dendrimer ($G = 4$) with hydroxyl group/n-hexyl group terminals prepared at 5 and 15 min adsorption time on mica substrate from an aqueous 0.01 wt% dendrimer solution.

was monitored as a function of adsorption time. SPR spectra as a function of angle were observed at the adsorption equilibrium condition.

3. Results

3.1. AFM image of dendrimer-adsorption films

The adsorption films of dendrimer on mica substrate prepared from an aqueous PAMAM dendrimer:HCl solution of 0.01 wt% concentration were examined by AFM and displayed in Fig. 1. Dendrimer was adsorbed on mica even after 5 s. The surface was uniformly flat, as seen in section analysis. However, no ordering of molecules was observed. The flat adsorption surfaces were also obtained even after additional adsorption time up to 30 min, although slight roughness increased with increasing the time.

AFM images for surface-block dendrimer-adsorbed mica substrates are given in Figs. 2–4. For the third-generation dendrimer, many islands were observed on an image of the surface after 5 s. Although size and shape of islands were different each other, their height was almost constant at 5.6–6.5 nm, as evaluated from section analysis in Figs. 2 and 3. The island size increased with increasing adsorption time, and larger domains of the adsorbed layer were formed. Moreover, a layer was accumulated on the layer, as seen in an image after 5 min adsorption. Whereas there were

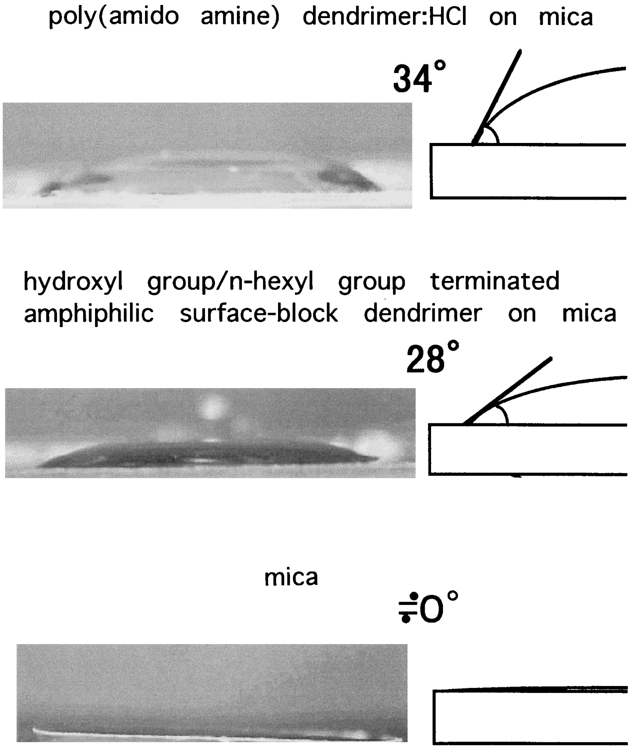


Fig. 5. Photographic images of water droplets on mica and dendrimer-adsorbed mica.

four layers at least after 15 min adsorption, only one step was observed on flat surface after 30 min (see Fig. 3). That is, after long immersion, the adsorption surface becomes rather homogeneously flatter. This indicates that the flatter surface is free-energetically preferable and is reached at the equilibrium state.

AFM images for the fourth-generation surface-block dendrimer presented the one-step layer existence at every adsorption time from 5 s to 30 min, and the occupation of the layer domains was rather independent of the increasing adsorption time (see Fig. 4). The layers after 30 min had small hills. The layer thickness was about 7.2–7.5 nm but the hill height was only half of the layer height.

3.2. Contact angle for dendrimer-adsorption films

Fig. 5 shows photographs of water droplets on mica and dendrimer-adsorbed mica. The contact

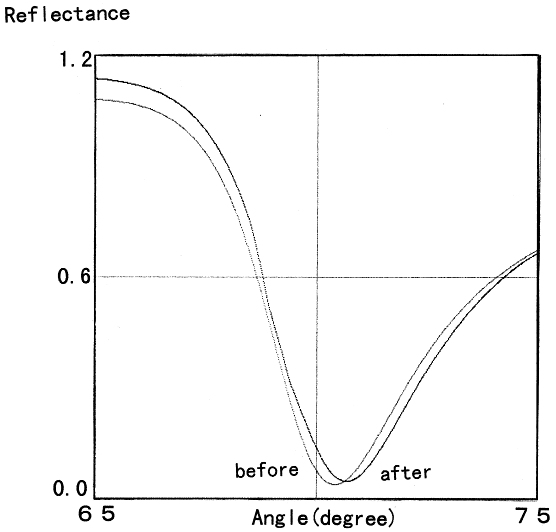


Fig. 6. SPR reflectance vs. angle curves before and after 150 min adsorption time from an aqueous surface-block dendrimer ($G = 3$) solution of 0.01 wt%.

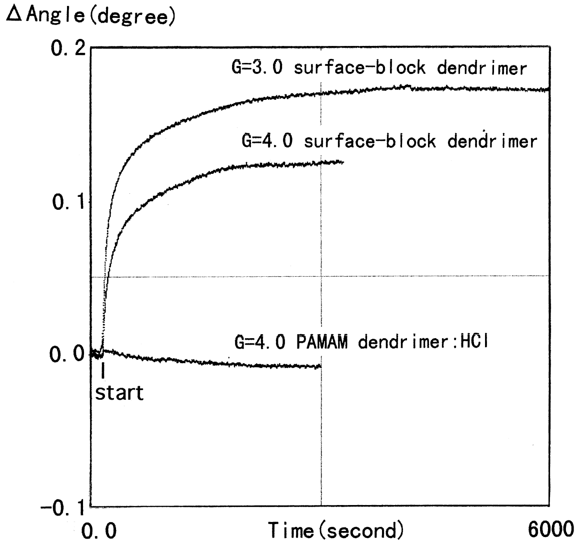


Fig. 7. SPR reflectance angle shift as a function of adsorption time from aqueous solutions of PAMAM dendrimer:HCl and surface-block dendrimers ($G = 3,4$) with hydroxyl group/n-hexyl group terminals.

angle was evaluated as schematically represented in Fig. 5. The contact angle on mica was nearly null, and those for PAMAM dendrimer:HCl and surface-block dendrimer ($G = 3$) on mica were 34° and 28°, respectively. These values imply that three surfaces are hydrophilic.

3.3. SPR of dendrimer adsorption

The reflectance versus angle curve after 150 min adsorption for an aqueous surface-block dendrimer ($G = 3$) solution at 0.01 wt% is compared with the curve without adsorption of dendrimer in Fig. 6. The reflectance curve after adsorption was meaningfully shifted from the curve without adsorption. The angle shift is plotted as a function of adsorption time in Fig. 7. The SPR angle for PAMAM dendrimer:HCl was shifted until a constant value soon after the adsorption started. However, the shift was less.

On the other hand, the SPR angle for the third-generation surface-block dendrimer was shifted initially rapid and, after that, gradually with adsorption time. Then the adsorption equilibrium was reached after 60 min. Although the fourth-generation surface-block dendrimer behaved similar to the third-generation dendrimer, the equilibrium for the fourth-generation was reached more early and at smaller shift value. However, the angle shift at equilibrium was much larger for both surface-block dendrimers than for PAMAM dendrimer:HCl. This means the larger amount of adsorption of surface-block dendrimers.

4. Discussion

Amphiphilic head-tail copolymers with a dendritic head and a linear polymer tail, concentric layer-block copolymers with dendritic core or dendritic periphery, and AB type surface-block dendrimers are known as amphiphilic copolymers with dendritic block, since two blocks exhibit different affinities with solvent. The main characteristics of the amphiphilic copolymers are the formation of molecular assemblies. Van Hest et al. [21] have synthesized linear polystyrene-poly(propylene imine) dendrimer block copolymers (PS-dendr-$(NH_2)_n$), which form spherical micelles, micellar rods, and vesicles in aqueous solutions. On the other hand, wormlike micelles or large network structures due to clustering of the aggregates are observed in aqueous solutions, at pH 14, of acid-functional linear polystyrene-poly(propylene imine) dendrimer block copolymers (PS-dendr-$(COOH)_n$) [22]. Surface-block dendrimers have also synthesized, and NMR, DSC, solubility of pyrene, and surface tension have been investigated [2,33–35]. However, the formation of molecular assemblies have never been reported. In the present paper, the formation of an adsorption layer on substrate from a solution of surface-block dendrimer was elucidated.

It is apparent from AFM images that adsorption surfaces of PAMAM dendrimer:HCl is uniformly flat, although there is no ordering of dendrimers, as schematically illustrated in Fig. 8. On the other hand, AB-type surface-block dendrimers ($G = 3,4$) with hydroxyl group/n-hexyl group terminals form adsorption layers. Each layer for the third-generation surface-block dendrimer have a similar height of 6.0 ± 0.5 nm each.

This height is larger than dendrimer diameter and less than double of the diameter, since the calculated value is 4.4 ± 1.6 nm in average. It is confirmed from this result that the surface-block dendrimers form bilayer on mica substrate and the dendrimer structure must be transformed like 'pancake'. Although the layer formation profile of the fourth-generation dendrimer seems similar to that of the third-generation, the layer thickness of 7.35 ± 0.15 nm is thicker than that of the third-generation. However, this value is reasonable, when 'pancake' bilayers of dendrimers with the calculated 5.05 ± 1.75 nm diameter are imaged.

Fig. 8 represents schematically the organized adsorption layers of the surface-block dendrimers. Hydrophilic blocks of surface-block dendrimers adsorb in contact with hydrophilic substrate. Then the first bilayer of the surface-block dendrimers with 'pancake' structure is formed by pairing between hydrophobic blocks. Thus hydrophilic blocks are faced to solution. With the proceeding of adsorption, another bilayer is accumulated with coupling between hydrophilic blocks. As a result, hydrophilic blocks must always be faced to solution, as elucidated from contact angle result that the adsorbed surface of surface-block dendrimers must be hydrophilic.

The morphology of dendrimer films has been visualized by AFM for carbosilane dendrimer and terminal-substituted carbosilane dendrimer [7–9,16,18]. Carbosilane dendrimers adsorbed onto flat solid substrates yield either monolayer or bilayer films, depending on their interactions with the substrate [8,9]. Self-assembled ultrathin films of mesogen-substituted carbosilane dendrimer display different morphology on mica, depending on concentration of dendrimers in solution and dendrimer generation [7]. In the present work, the

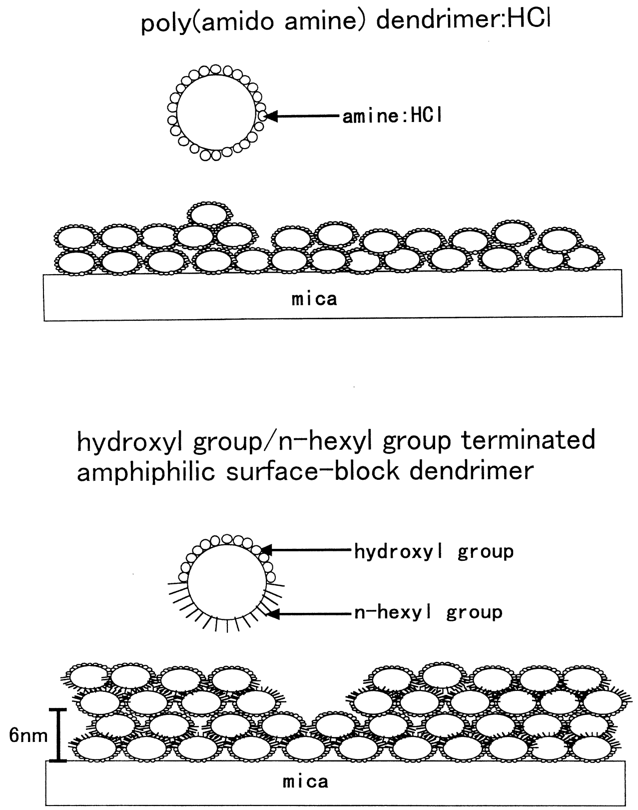


Fig. 8. Schematic illustration of adsorption of PAMAM dendrimer:HCl and surface-block dendrimer ($G = 3$) on substrates.

difference of morphology depending on adsorption time and dendrimer generation was clarified for the surface-block dendrimer.

The adsorption structure of ‘pancake’ or ellipsoidal type due to compression in monolayer films on a flat substrate have been estimated for composit dendrimer layers of $(AB)_x$ type [16]. Average thickness of a molecular layer in multilayer films is much smaller than the diameter of ideal spherical dendrimers. The model of molecular ordering in dendrimer films assumes compressed dendrimer of oblate shape with the axial ratio in the range from 1:3 to 1:6. Similar structural change has been reported for arborescent graft polystyrene deposit films on mica substrate [37]. The structural transition to prolate ellipsoid occurs for polyether dendrimers in Langmuir films [17]. The dendrimer compression has also been discussed for PAMAM dendrimer sandwiched between two glass substrates in contact [38].

It was confirmed from the present work that the surface-block dendrimer can form a bilayer accumulation on mica substrate, different from PAMAM dendrimer:HCl. This behavior must be related to the structural characteristics, that is, amphiphilic character. On the other hand, the adsorption amount of surface-block dendrimers on gold-evaporated glass substrate is drastically different from PAMAM dendirmer:HCl, as elucidated from the SPR reflectance angle shift. It is assumed from surface force measurement that PAMAM dendrimers with hydroxyl terminals adsorb less than monolayer on glass [38]. Therefore, abundant adsorption of surface-block dendrimers has also to result from amphiphilic character. The adsorbed amount of PAMAM dendrimers on silica particles is increased with increasing generation [19], different from the generation dependence on adsorption of the present surface-block dendrimer. The adsorption of the third-generation surface-block dendrimer is much more than that of the fourth-generation. However, it should be noticed that the order of the adsorption, PAMAM < fourth-generation < third-generation, is same to the order of surface activity estimated from surface tension decrease [35,36]. This may be the order of the hydrophobicity of dendrimers, since the hydrophilic particles are stably dispersed in solution rather than adsorb on air/water interface or water/substrate interface. In this connection, PAMAM dendrimer is highly hydrophilic and the fourth-generation dendrimer has hydrophilic OH groups more than the third-generation dendrimer.

It must be noted that the fourth-generation surface-block dendrimer forms partly monolayer hills on bilayers after 30 min adsorption. The hill must be the accumulation of monolayer, since the height is half of bilayers. This means the stronger hydrophilic attraction force between bilayer and monolayer of the fourth-generation dendrimers than of the third-generation because of a greater amount of terminal OH groups, which will connect dendrimers by hydrophilic hydrogen-bonding interaction.

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