

**Figure 3** Changes in the tensile shear adhesive strength with the grafted amount for grafted LDPE and HDPE plates.

Failure- ○, Δ : cohesive failure, ●, ▲ : substrate failure (substrate breaking)

Sample- ● : ungrafted LDPE plate, ▲ : ungrafted HDPE plate, ○, Δ, ●, ▲ : grafted LDPE and HDPE plates

bonding is responsible for an increase in the adhesive strength. In addition, the grafted layers enriched in grafted PMAA chains formed on the HDPE plates also can facilitate interdiffusion leading to the entanglements of grafted PMAA chains.

The substrates were broken at 8 mmol/cm<sup>2</sup> and 20 mmol/cm<sup>2</sup> for HDPE-g-PAA and HDPE-g-PDMAEMA plates, respectively. It can be safely said that the substrate breaking at lower grafted amounts can be considered to come from higher mobilities of grafted polymer chains in the grafted layers highly swollen in water, since the photografting of DMAEMA onto the HDPE plates leads to the formation of the grafted layers with higher water absorptivities. In addition, cohesive properties of grafted PAA chains mentioned above would also be favorably influenced in the increase in adhesive properties.

The adhesive strength can go up to over the ultimate strengths of the used substrates at a lower grafted amount under the conditions where grafted polymer chains can get close to each other and interact through the grafted layers swollen in water. It is of great interest that the adhesive strength higher than the ultimate strength of LDPE and HDPE plates is obtained by heat-pressing the grafted LDPE and HDPE plates immersed in water without any adhesives. The procedure is expected to contribute much to the functionalization of widely used polymer materials and their reusabilities.

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## INTERMOLECULAR INTERACTION AND ADSORPTION PROPERTIES OF POLY(AMIDO AMINE) DENDRIMER WITH OH-TERMINAL

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5th- and 6th-generation poly(amido amine) dendrimer with OH terminal was synthesized. The measurement and analysis of surface interactions and forces were carried out between dendrimer layers adsorbed on glass beads from the aqueous solution. On the inward process of force measurement for the 10<sup>-7</sup> wt% aqueous solution of the 5th-generation dendrimer, the repulsive interaction force decreased at 12 hours adsorption and then increased after 30 hours. On the outward process, the adhesion force which appeared at 12 hours disappeared after 30 hours. Same behavior was observed at shorter adsorption time for the more concentrated solution and for the higher-generation dendrimer. The adsorption mechanism depending on adsorption time was discussed.

## INTRODUCTION

Recently, dendrimers with the regularly branched dendritic structure are focused as novel nanoparticles, and their synthetic and physicochemical investigations have been reported.<sup>1,2)</sup> One of characteristic properties of dendrimers is the doping ability of small molecules to their sponge-like interior. The property can induce the remarkable functions, such as molecule segregation, drug delivery, and gene carrier, different from linear polymers. The globular shape of dendrimers which are recognized as unimolecular micelles is also valuable to be remarked, because the molecular interaction between them in solution bulk and their molecular arrangement on surfaces should be different from linear polymers. In this work, dendrimers with amido amine unit were constructed, the intermolecular interaction and adsorption properties were investigated, and the additional functionality of dendrimers was discussed.

## EXPERIMENTAL SECTION

5th- and 6th-generation poly(amido amine) dendrimer with OH terminal (Fig. 1) was synthesized by reacting the 4.5th- and 5.5th-generation poly(amido amine) dendrimer having terminal methyl ester groups with 2-aminoethanol. Dendrimer was dissolved in ultra-pure (Mili-Q) water at adequate concentrations.

Dynamic light scattering measurement was carried out at 25 °C on an Otsuka Electric DLS 700 spectrometer equipped with ALV-5000 analyzer. The instrument was operated by a 30° scattering angle. The microscopic observation was performed at room temperature (~25 °C) by a Digital Instruments NanoScope III atomic force microscope (AFM). The surface tension was measured at 25 °C by a drop weight method.

The surface force was measured at room temperature (~25 °C) on an Anutech MASIF. Two glass beads were set on piezo tube and teflon-sheathed bimorph, respectively. The movement of upper glass surface was measured by linear variable displacement transducers (LVDT) attached to piezo tube, and the movement of lower glass surface was measured as a displacement of bimorph. The force run was carried out on "inward" and "outward" processes. The force  $F$  divided by average radius of curvature of glass beads  $R$  was calculated as a

function of separation between two glass surfaces  $H_{ss}$ .

**RESULTS**

Diffusion coefficients of the dendrimer in aqueous 1 wt % solutions were determined by dynamic light scattering measurement, and the hydrodynamic diameters were calculated from an Einstein-Stokes equation. The observed values, 7.8 and 8.1 nm for the 5th- and 6th-generation, respectively, were consistent with ones calculated by Corey-Pauling-Koltum (CPK) model,<sup>2)</sup> as seen in Table 1.

Figure 2 shows an AFM image which was observed for a specimen prepared by dropping a tiny amount of 1 wt % solution of the 5th-generation dendrimer on mica freshly cleaved, draining extra solution, and drying. The spherical particles of about 8 nm diameter in average existed, consistent with the observation from the dynamic light scattering.

The surface tension measured by a drop weight method for aqueous solutions of the 5th-generation dendrimer decreased slightly at concentrations above  $10^{-2}$  wt %, as seen in Fig. 3. This means low surface activity or less adsorption on air-water interface, in contrast with a case of amphiphilic poly(2-methyl-2-oxazoline)-block-poly(amido amine) dendrimer which has a hydrophobic globular head and a hydrophilic linear tail. However, the adsorption behavior on the solid substrate from the solutions differs from that on the air-liquid interface, as describe below.

The surface force measurement was carried out for aqueous  $10^{-7}$  and  $10^{-3}$  wt % solutions of the 5th-generation and a  $10^{-3}$  wt % solution of the 6th-generation. As seen in Fig. 4, for aqueous  $10^{-7}$  wt % solutions of the 5th generation, the force-separation curves on the inward

Table 1. The observed and calculated diameters of dendrimer (in nm unit).

generation	observed	calculated
5	7.8	4.4 - 8.6
6	8.1	5.2 - 9.6

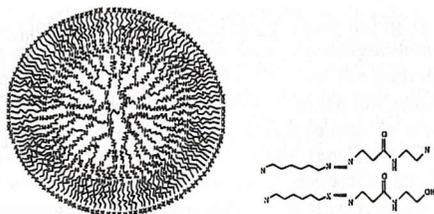


Fig. 1. Chemical structure of the 5th-generation poly(amido amine) dendrimer with OH terminal.

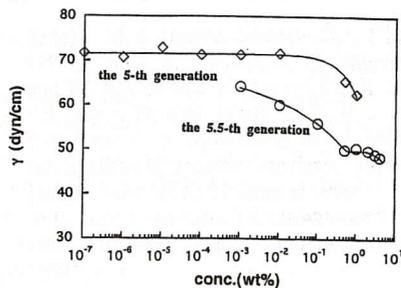


Fig. 3. Surface tension as a function of concentration for the 5th-generation dendrimer in water. Figure includes data for amphiphilic dendrimer.<sup>2)</sup>

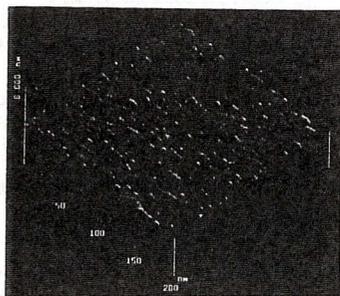


Fig. 2. An AFM photograph of the 5th-generation dendrimer deposited on mica.

and outward processes at 2 hours adsorption were both same as that between glass surfaces. The repulsive force at the inward process decreased at 12 hours adsorption, while the jump-out occurred at the outward process. For the 30 hours adsorption, the repulsive force increased at the inward process, and the same repulsive curve was observed even at the outward process, but the jump-out was not. These three types of force curves are denoted as A, B, and C.

Three types of force curves were also observed for  $10^{-3}$  wt % solutions of the 5th- and 6th-dendrimer. However, the adsorption time where B and C types occurred was shorter at higher concentrations and higher generation, as seen in Table 2. The numerical values of the adhesion forces to be the jump-out forces are also included in Table 2. The adhesion forces ( $\sim 2$  mN/m) for the 5th-generation were independent of concentration but weaker than that for the 6th-generation.

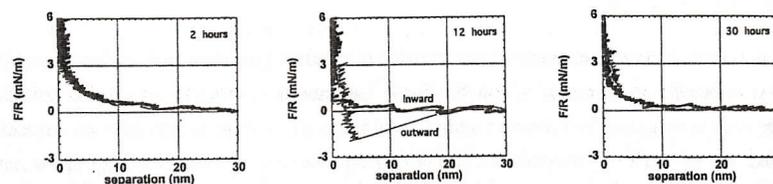


Fig. 4. Force vs. separation curves for 2, 12, and 30 hours adsorption from a  $10^{-7}$  wt% solution of the 5th-generation dendrimer.

Table 2. The classification of force-separation curves. The numerical values in bracket represent the adhesion forces in unit of mN/m.

adsorption time (h)	generation		
	5	6	
1	A	B(2.4) A	
2	A	B(1.2)	B(5.0)
4		B(2.2)	B(4.0)
6	A		
12	B(1.9)	C	C
30	C		

- A : no or less adsorption
- B : adsorption (coverage < 1)
- C : adsorption (coverage  $\geq 1$ )

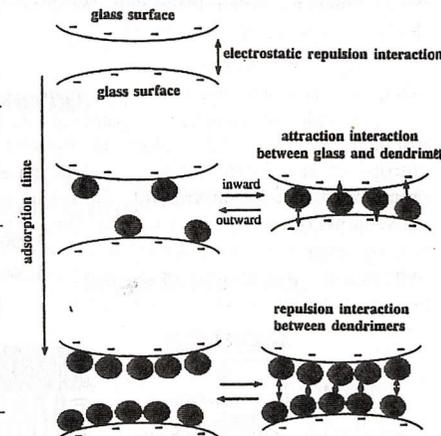


Fig. 5. An adsorption profile of poly-(amido amine) dendrimer on glass substrate.

**DISCUSSION**

The force-separation curves can be classified into three types, depending on adsorption time. Type A at initial adsorption is equivalent to that between glass surfaces. In this case, dendrimer molecules adsorb no or very few amount on glass surfaces. In the type B at medium adsorption time, the repulsive force is weaker than that between glass surfaces at the inward process and the adhesion force occurs at the outward process. In this adsorption time, dendrimers are adsorbed on glass surfaces but the coverage is far less than unity. Then the

electrostatic repulsion force between glass surfaces diminishes apparently, because the real contact surface is no longer at the glass surfaces. At the contact situation, the monolayer of dendrimers is adsorbed between glass surfaces, inducing the adhesive attraction force between dendrimers and glasses. In the type C at long adsorption time, where both glass surfaces are covered by dendrimers adsorbed, the repulsive force reacts between dendrimer layers. An adsorption profile of poly(amido amine) dendrimer on glass substrate is illustrated in Fig. 5.

The interaction force  $F = -(\partial V_{ss}/\partial H_{ss})_{T,P}$  between two spheres at constant temperature  $T$  and pressure  $P$  is related to the interaction potential  $V_{pp}$  between two flat plates by  $F/R = \pi V_{pp}$  under the Derjaguin's approximation. When two plates covered by adsorbed polymers approach each other, the interaction potential is the sum of the repulsion term  $V_R$ ,  $V_{VR}$ , and  $V_M$  and the attraction term  $V_A$ . The electrostatic potential  $V_R$  is negligible in the case of the adsorption of nonionic dendrimer.

The mixing or osmotic effect  $V_M$  and the volume restriction effect  $V_{VR}$  in the steric repulsion potential are expressed by

$$V_M = 2(2\pi/9)^{3/2}v^2RT(\alpha^2-1)\langle h^2 \rangle \cdot 3\pi^{1/2}(6H_{pp}^2/\langle h^2 \rangle - 1)\exp(-3H_{pp}^2/\langle h^2 \rangle) \quad (1)$$

and

$$V_{VR} = 2vkT \cdot 2(1-12H_{pp}^2/\langle h^2 \rangle)\exp(-6H_{pp}^2/\langle h^2 \rangle) \quad (2)$$

respectively, for linear polymers.<sup>3)</sup>  $v$  is the number of loops and tails per unit area or the amount of polymer adsorbed,  $\alpha$  is the expansion of the chains,  $\langle h^2 \rangle^{1/2}$  is the root mean square end-to-end distance of a chain,  $H_{pp}$  is the distance between two plates,  $R$  is the gas constant, and  $k$  is the Boltzmann constant. If the plates are thick in comparison with the interplate distance, the van der Waals potential  $V_A$  is written by

$$V_A = -A/(12\pi H_{pp}^2) \quad (3)$$

where  $A$  is the Hamaker attraction constant.

The calculated interaction potentials are plotted as a function of the distance in Fig. 6. It can be recognized that the volume restriction repulsion, due to the decrease of configurational entropy of an adsorbed polymer on the approach of a second polymer, and the osmotic repulsion, due to the mixing of the adsorbed polymeric clouds, are effective on the interaction between dendrimer layers, since the contribution of van der Waals attraction is less. In other words, the interaction potential between dendrimer layers is mainly steric repulsion. This indicates that poly(amido amine) dendrimer with repulsive intermolecular interaction can be utilized as a surface-improvement agent promoting the dispersion stability of fine particles in medium.

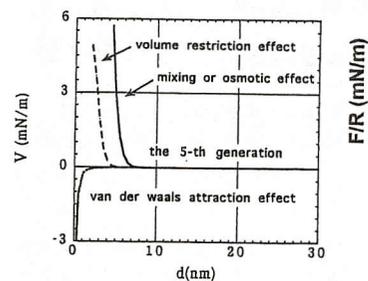


Fig. 6. Calculated interaction potential between plates covered by adsorbed dendrimer.

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## INTERACTIONS BETWEEN POLY(L-LYSINE) BRUSH LAYERS STUDIED BY SURFACE FORCES MEASUREMENT

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## INTRODUCTION

Interactions between apposing surfaces in solvents can be measured directly at the nanometer resolution using a surface forces apparatus,<sup>1)</sup> which affords information on polymers and other molecules on substrate surfaces. In order to elucidate behavior of ionizable polypeptides in water, we prepared terminally anchored poly(L-lysine) monolayers (brushes) by the Langmuir Blodgett method, and subjected them to the surface forces measurement. Steric components of force profiles obtained were analyzed quantitatively to give the elastic compressibility moduli of the polypeptide brushes in different conformations, and compared with those of the poly(glutamic acid) brushes.<sup>2,3)</sup>

## EXPERIMENTAL

Poly(L-lysine) amphiphiles (2C18-PLL( $n$ ), C18H37N(CH2)3NH-(CO-CH(NH2)-CH2) $n$ -H, polymerization degree,  $n = 41, 77$ ) bearing the poly(L-lysine) group as a hydrophilic part and a dioctadecyl group as a hydrophobic tail were prepared by the NCA method.<sup>4)</sup>

Scheme I: 2C18-PLL( $n$ )  $n = 41, 77$

The surface pressure-area isotherm measurements and LB films deposition were performed by use of a computer-controlled film balance system (USI system, FSD-50). The conformation and the orientation of poly(L-lysine) in LB films were determined by Fourier transform infrared (FT-IR) spectroscopy (Perkin Elmer, System 2000) using the combination of the transmission (TS) (CaF2 plates as substrates) and the reflection (RAS) (gold-deposited

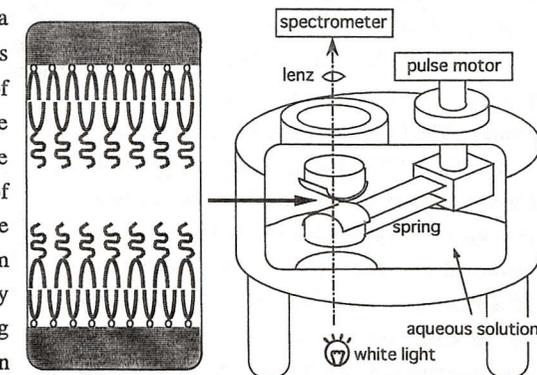


Fig. 1 Schematic pictures of a surface forces apparatus and brush layers on mica surface.