

## Peculiar Wettability Based on Orientational Change of Self-assembled Hemispherical PAMAM Dendrimer Layer

Tomohiro Fukuda,<sup>1</sup> Erino Matsumoto,<sup>1</sup> Nobuhiko Yui,<sup>1</sup> and Yoshiko Miura\*<sup>1,2</sup>

<sup>1</sup>School of Materials Science, Japan Advanced Institute of Science and Technology, 1-1 Asahidai, Nomi, Ishikawa 923-1211

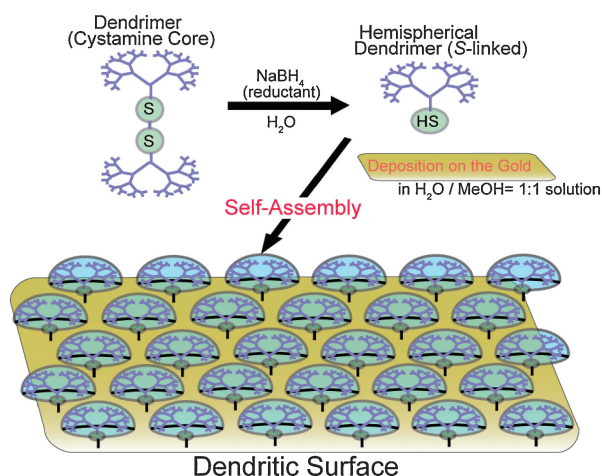
<sup>2</sup>Department of Chemical Engineering, Faculty of Engineering, Kyushu University, 744 Motoooka, Nishi-ku, Fukuoka 819-0395

(Received May 12, 2010; CL-100463; E-mail: miuray@chem-eng.kyusyu-u.ac.jp)

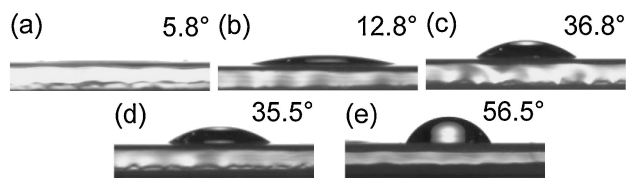
Self-assembled monolayers of hemispherical poly(amidoamine) dendrimer were prepared on a gold substrate via Au–S bond. The dendrimer layer with succinic acid showed strong wettability resulting from the densely packed hydrophilic group and 3-D structure. In this report, we suggest that dendrimer is an attractive tool for the design of surface properties and has the possibility to control the surface not only chemically but also physicochemically.

The design of surface properties is important to fabricate various materials and devices including biomaterials. The surface modification by well-defined polymers receives much attention due to use of the applicability and the uniformity.<sup>1</sup> In particular, the dendrimers are advantageous because of the well-defined 3-D nanostructure.<sup>2</sup> Barnard et al. reported pattern formation of dendrimer films and has accomplished various patterns of dendrimer clusters.<sup>3</sup> It was also reported the preparation and the characterization of self-assembled monolayer (SAM) of poly(amidoamine) (PAMAM) dendrimer.<sup>4</sup> In this report, we focus on the control of surface roughness using PAMAM dendrimers with cystamine core. The dendrimer SAM provides nanoscale roughness leading to various physical and mechanical properties. In this report, we found interesting surface properties resulting from hemispherical PAMAM dendrimer SAM on a gold substrate via Au–S bond formation.

Each dendrimer had a cystamine core which was cleaved into two hemispherical PAMAM dendrimers with a sulfanyl terminus (S-linked dendrimer) by reduction (Figure 1). Subsequently, each S-linked dendrimer formed SAM on the gold



**Figure 1.** Schematic illustration for the preparation of dendrimer SAM.

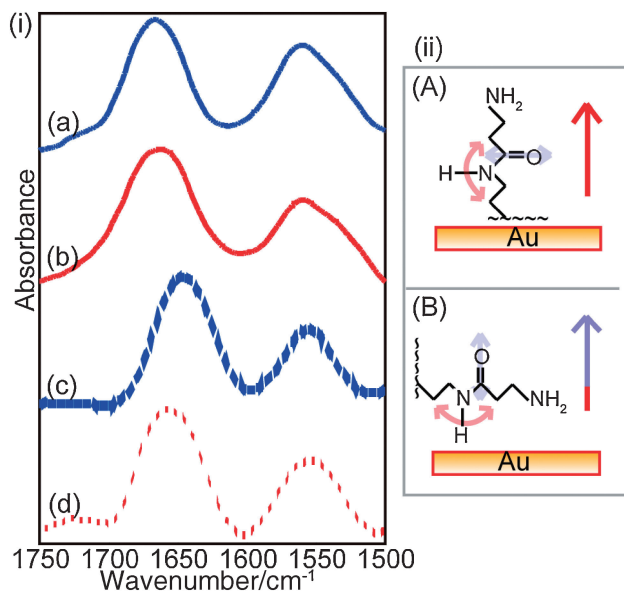


**Figure 2.** The values and pictures of water contact angles on (a) SA-G4, (b) SA-G1, (c) A-G4, (d) MUA, and (e) MPA immobilized gold substrates.<sup>6</sup>

substrate via Au–S bond, giving the rough surface composed of hemispherical dendrimer.<sup>5</sup> The SAM formation was confirmed by Fourier transform infrared reflection adsorption spectroscopy (FTIR-RAS), X-ray photoelectron spectroscopy (XPS), and quartz crystal microbalance analysis<sup>5</sup> and was described in this article as for FTIR-RAS.

We prepared SAMs of S-linked dendrimer with succinic acid (SA-) and amine (A-) terminus. The SAMs of mercaptoundecanoic acid (MUA) and sulfanylpropionic acid (MPA) were also prepared as controls. The water contact angles are represented in Figure 2. Interestingly, the water contact angle of SA-G4 SAM surface was 5.8° and much lower than those on SAMs of MUA (35.5°) and MPA (56.5°). The high density of carboxylic acid which the dendrimer molecules provided contributed to hydrophilicity. In the case of other S-linked dendrimers, the water contact angles on SA-G1 and A-G4 were 12.8 and 36.8°, respectively. This suggests that the dendrimer SAMs (SA-G4 and SA-G1) with succinic acid had a tendency to represent very low contact angles, even though the dendrimer SAM with amine terminus did not. In addition, higher generation dendrimer SAM (SA-G4) showed more hydrophilic than that of lower generation. The contact angles on dendrimer SAMs of other generations followed the same trend. Briefly speaking, higher generation S-linked dendrimer SAM with succinic acid termini had potential for the formation of very hydrophilic surfaces on the gold substrate. This experiment was carried out under the neutral pH condition, and it was possible to change the results under another treatment or condition due to the different net charge of dendrimer SAMs.

Meanwhile, since it is known that the surface wettability is closely related to the change of the surface free energy,<sup>7</sup> the energies of the substrates were calculated by the Owens–Wendt method with diiodomethane contact angle goniometry.<sup>5,8</sup> The energy on SA-G4 surface was 247 mN m<sup>-1</sup>, which was larger than those of others (243 (SA-G1), 210 (A-G4), 221 (MUA), and 173 mN m<sup>-1</sup> (MPA)). The periphery functional group was also related to the surface free energy and wettability. We carefully investigated the carbanion (COO<sup>-</sup>Na<sup>+</sup>) by FTIR and XPS spectra, but the Na<sup>+</sup> was not detected.<sup>5</sup>



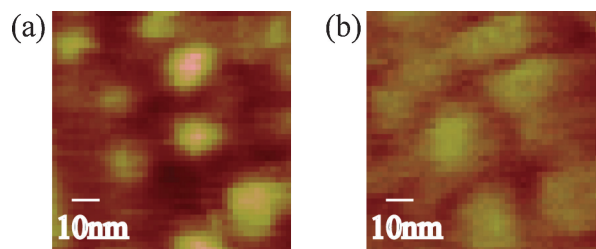
**Figure 3.** (i) The spectra of (a) SA-G4 and (b) A-G4 with FTIR-RAS (solid lines) and (c) SA-G4 and (d) A-G4 with transmission mode (dashed lines). (ii) Vibration of dendrimer with perpendicularly adsorbed (A) and parallel-adsorbed (B).

It is noteworthy that the water contact angles of SA-G4 and A-G4 were totally different, although the hydrophilicities of amine and carboxylic acid are almost the same. Physical surface properties such as wettability are known to be dependent on not only the functional group at the interface but also the structure of SAM.

The orientation of SAM on the metal substrate frequently determined the structure of SAM, which was investigated by FTIR-RAS.<sup>9</sup> The amide regions of G4-dendrimer SAMs spectra are illustrated in Figure 3(i) (solid line: (a) and (b)). FTIR-transmission spectra of PAMAM dendrimers were also investigated using KBr pellet and are illustrated (dashed line: (c) and (d)). The wavenumbers (amide I/amide II) where top peaks of amide I and amide II emerged were at  $1667\text{ cm}^{-1}/1561\text{ cm}^{-1}$  (SA-G4) and  $1663\text{ cm}^{-1}/1560\text{ cm}^{-1}$  (A-G4) with FTIR-RAS and also emerged at  $1647\text{ cm}^{-1}/1554\text{ cm}^{-1}$  and  $1656\text{ cm}^{-1}/1555\text{ cm}^{-1}$  with FTIR-transmission. The top peak ratios of amide I/amide II were 1.26 on SA-G4 SAM and 1.60 on A-G4 SAM with FTIR-RAS, respectively, while the peak ratios in KBr dispersion were 1.83 on SA-G4 and 1.72 on A-G4.

The peak ratio of SA-G4 in FTIR-RAS was much smaller than that in the transmission spectrum, suggesting the specific orientation of SA-G4 on the substrate. In the RAS mode, the only absorbance vertical to the substrate is observed. Therefore, the amide I (C=O stretching) presumably inclined to orient parallel to the substrate even if the peak ratio decreased (Figure 3(ii) (A)). Furthermore, the change of peak ratio indicated that each dendritic outgrowth of SA-G4 possibly oriented to the substrate vertically, due to C=O bond remaining perpendicular to the substrate, resulting in the effective display of hydrophilic groups.

On the other hand, A-G4 in FTIR-RAS was similar to that in transmission spectra, suggesting random orientation to the substrate. It was reported PAMAM dendrimer with amine



**Figure 4.** Phase images of (a) SA-G4 and (b) A-G4 immobilized gold substrates with the tapping-mode AFM.

terminals and an ethylenediamine core attached to the gold substrate via Au–N bond.<sup>4</sup> In our research, not only sulfanyl but also the terminal amine group of A-G4 dendrimer had affinity for the gold substrate and attached with random orientation. Therefore, it was impossible for the dendrimer with amine terminals to attach to the substrate maintaining hemispherical state, due to multibond formation, in contrast to dendrimer with succinic acid terminals. In the case of A-G4, the coverage of hydrophilic groups on the surface was considered to be insufficient, resulting in the ineffective display of hydrophilic groups.

Morphological investigation was carried out for backing up the assumption above. Apparent spherical image was observed on SA-G4 surface (Figure 4a), although the image on A-G4 was not (Figure 4b). The diameter of the sphere was 10–14 nm on SA-G4 and was smaller than that on A-G4 (18–22 nm). Each spherical image was assumed to be corresponding to monolayer formation of dendrimer because it corresponds to the molecular size. The images also represented the monolayer deposition. Moreover, a phase image contrast, which is contributed to phase delay, is higher on SA-G4 than that on A-G4. Phase delay enlarges in the cases of a powerful interaction and a soft sample. Low contrast on A-G4 emerged, which suggested that single molecule of A-G4 combined with a gold substrate rigidly and formed a squashed layer, contrast to SA-G4. On the other hand, the result showed that SA-G4 maintained hemispherical state and had 3-D structure.

The dendrimers have been reported to form monolayer with peculiar shape, leading to the difference of surface roughness. In addition, surface roughening such as fractal surface formation is effective in order to emphasize surface properties,<sup>7</sup> and the 3-D rule structure of dendrimer is suited to roughening. SA-G4 SAM demonstrated rougher surface because SA-G4 maintained its shape with larger aspect ratio on the substrate due to the poor multibond formation, while A-G4 formed a squashed monolayer resulting from Au–N bond. For the immobilization of larger numbers of hydrophilic molecules, SA-G4 SAM also had an advantage of effective use on a limited surface (See the term of QCM analysis.<sup>5</sup>). That is, the larger aspect ratio of the surface emphasized surface properties, resulting in superhydrophilicity with the SA-G4 SAM. Furthermore, the control of surface roughness with the change of aspect ratio was possible to acquire other functions. Meli et al. reported that the aspect ratios of immobilized molecules determined the surface wettability model.<sup>10</sup> The control of these models is necessary to design a desirable surface.

At last, we also evaluated the bioinertness of the surface to the proteins because of the correlation with hydrophilic interface

and found that SA-G4 surface presented stronger bio-inertness than the plain surface of MUA.<sup>5</sup>

In conclusion, we prepared the rough surface of a PAMAM dendrimer SAM via self-assembly and found the surface having peculiar wettability. We believe that the nanopatterning by using certain size of molecule such as dendrimer is useful technique for the development of desirable surface.

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