Nanofrictional Properties of Dendron Langmuir–Blodgett Films

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The nanofrictional properties of Langmuir–Blodgett (LB) films of three dendrons (G2-COOH, G3-COOH, and G4-COOH) are characterized using atomic force microscopy/friction force microscopy (AFM/FFM). The result shows that the frictional responses of LB films of three dendrons decrease with increasing generation. The origin of the frictional differences measured from these LB films is also discussed.

Extensive interest has recently been attracted to the synthesis[1] and the applications[2] of dendrons in nanotechnology and material science, because of their precisely controlled structures at the molecular level and many unique properties.[1c,3] In such material sciences, dendrons are ideal nanoscale building blocks for a wide range of interfacial materials.[4] Some studies show that dendron films have been just beginning to receive attention concerning their adhesive frictional behavior and related potential applications.[5] These films are generally fabricated in process such as molecular deposition, self-assembly technologies. In comparison with these methods, previous studies of well-ordered Langmuir–Blodgett (LB) films of dendrons indicate that LB deposition can offer a means to alter and control molecular order and orientation in films.[6] However, there are limited reports of the nanofrictional property of thin film fabricated using LB technique. In this study, we prepared LB films of Fréchet-type poly(benzyl ether) dendrons (the insert in Figure 1) bearing a strongly hydrophilic carboxyl moiety at the focal point, and investigated the surface morphologies and nanofrictional characterization using AFM/FFM. The obtained results could provide helpful information to understand the nanofrictional properties of the dendron LB films, which is important to the potential applications of dendron ultrathin films in information storage materials and microelectromechanical systems.[5c]

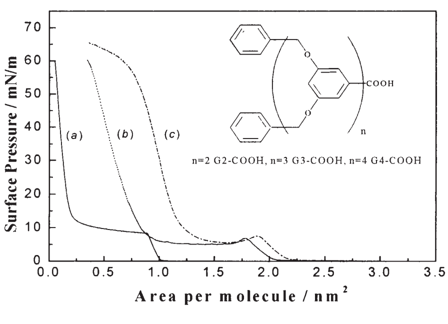

Figure 1. Representative surface pressure versus molecular area (π-A) isotherms of dendrons at the air-water interface at 20 °C. (a) G2-COOH, (b) G3-COOH, and (c) G4-COOH.

The used dendrons were synthesized according to the methods reported previously.[3a,5c] The π–A isotherms and Langmuir–Blodgett films transfer experiments were performed on a KSV minitrough LB system (KSV Instruments, Finland) at room temperature (20 °C). The LB films were deposited onto newly cleaned mica plate at a typical rate of 5 mm·min^{-1} (vertical dipping) under a constant surface pressure of 20 mN·m^{-1}. According to the method described previously,[7] the AFM/FFM investigations were conducted using a Nanoscope IIIa AFM (Digital Instruments, Santa Barbara, CA) under ambient conditions (in air, at 20 °C, and relative humidity of 40–50%). All frictional forces were measured with the same tip (commercial V-shaped Si_3N_4 cantilever, normal spring constant 0.32 N·m^{-1}) on 4 different regions of each samples over a scan size 1.2 μm × 1.2 μm at a constant scan rate of 2 Hz. Before and after each force measurement, AFM images of the sample surface were taken to ascertain the absence of spurious contamination or damage resulting from the force measurement.

Representative π–A isotherms of three dendrons at the air-water interface at 20 °C are shown in Figure 1. The appreciable difference in the π-A isotherms between G3-COOH, G4-COOH, and G2-COOH can be observed. The G3-COOH and G4-COOH have similar isotherms, characterized by an increase in the surface pressure, followed by a peaked collapse transition and then a flat roof, indicating a nucleation and growth process. Further compression results in the formation of solid film. The G2-COOH isotherm also has a flat roof, but not a peaked collapse transition, which indicates that the nucleation process of G2-COOH with surface pressure increase is much slower than those of G3-COOH and G4-COOH.[8] Nevertheless, these three dendrons form solid films at the air-water interface and can be compressed into the LB films under the pressure of 20 mN·m^{-1}.

The surface morphologies of single-layer LB films transferred onto mica under 20 mN·m^{-1} were imaged using tapping-mode AFM. Figure 2a shows many discotic domains of the G2-COOH film. Distinct phenomena are observed for the LB films of G3-COOH and G4-COOH in Figures 2b and 2c, respectively. The G4-COOH LB film shows much more homogenous and flat than

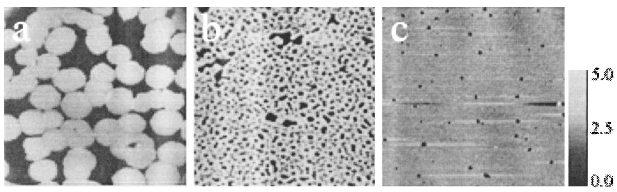

Figure 2. The tapping-mode AFM images of one-layer LB films of three dendrons transferred on mica under the surface pressure of 20 mN·m^{-1}. Scan size: 5.0 μm × 5.0 μm. Height scale: 5 nm. (a) G2-COOH, (b) G3-COOH, and (c) G4-COOH.

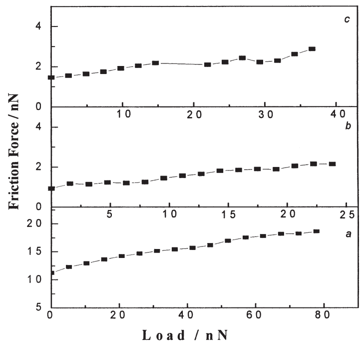

Figure 3. Representative friction-load curves in the increasing load region for one-layer LB films of three dendrons on mica. (a) G2-COOH, (b) G3-COOH, and (c) G4-COOH.

those of G2-COOH and G3-COOH. The surface coverages are 65.9%, 86.3%, and 92.7% for the LB films of G2-COOH, G3-COOH, and G4-COOH, respectively.

The nanofrictional characterization of one-layer LB films of three dendrons on mica was tested in contact mode AFM. Some representative results of friction verse load curves are shown in Figure 3. It can be deduced that the values of relative friction coefficient are 0.122, 0.054, and 0.05 for G2-COOH, G3-COOH, and G4-COOH, respectively. G2-COOH LB film exhibits significantly high bearing-loading property with load up to 80 nN while low friction and low-bearing capacity are observed for the other two. These results suggest that the average frictional responses of LB films of the three dendrons decrease as increasing generation. This may be ascribed to the difference in surface order and film quality of dendron films.[9] In the case of G2-COOH LB film, it is expected that there must exist defects or disorder and low coverage in the overall film, which were observed using AFM in Figure 2a. These defects or disorder give rise to additional channels of energy dissipation and hence enhance higher coefficient of friction.[9b] The G3-COOH and G4-COOH LB films, bearing higher surface coverage and little surface defects affecting the friction, have a better nanofrictional performance. Moreover, the previous studies show that local packing density of the chemical moieties influences the frictional response of the monolayer.[9a,9c] However, in this work, the apparent surface area per terminal group, derived from the π-A isotherms, is 0.055, 0.11, and 0.078 nm^2 for G2-COOH, G3-COOH, and G4-COOH, respectively. These values imply that the occupied packing density per terminal groups is almost the same at the air-water interface. Therefore, in the case of dendron LB film measured, the surface order and film quality may play more important roles in the nanofrictional properties.

To further understand the nanofrictional properties of the three LB films, the roughness was also obtained in contact-mode AFM. The surface roughnesses (RMS) are 1.622 nm for G2-COOH LB film, 0.673 nm for G3-COOH, and 0.200 nm for G4-COOH, respectively. It is apparent that G4-COOH LB film appears much flatter, and thus has lower friction coefficient and better lubrication property than G2-COOH and G3-COOH LB films.

In summary, G4-COOH LB films exhibit more flat and featureless film relative to the other two. Because of increasing surface coverage or surface roughness of LB film, the friction responses of LB films of G2-COOH, G3-COOH, and G4-COOH decrease with increasing generation. The further work is in progress involving nanowear or microwear properties.

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References

1 a) S. M Grayson and J. M. J. Fréchet, *Chem. Rev.*, **101**, 3819 (2001). b) M. Kobayashi, S. Machida, S. Takahashi, K. Horie, H. Yoshikawa, and H. Masuhara, *Chem. Lett.*, **2002**, 394. c) T. Mizutani, M. Ikegami, R. Nagahata, and T. Arai, *Chem. Lett.*, **2001**, 1014.

2 a) J. C. M. Van Hest, D. A. P. Delnye, M. W. P. Baars, M. H. P. Van Genderen, and E. M. Meijer, *Science*, **268**, 1592 (1995). b) G. J. Deng, Q. H. Fan, X. M. Chen, D. S. Liu, and A. S. C. Chan, *Chem. Commun.*, **2002**, 1570.

3 a) J. M. J. Fréchet, *Science*, **263**, 1710 (1994). b) K. Kasuga, T. Akita, N. Matsuura, M. Handa, and T. Sugimori, *Chem. Lett.*, **2002**, 966. c) K. Kasuga, N. Matsuura, K. Inoue, M. Handa, T. Sugimori, K. Isa, and M. Nakata, *Chem. Lett.*, **2002**, 352.

4 D. C. Tully and J. M. J. Fréchet, *Chem. Commun.*, **2001**, 1229.

5 a) L. A. Baker, F. P. Zamborini, L. Sun, and R. M. Crooks, *Anal. Chem.*, **71**, 4403 (1999). b) S. C. Strret, A. Rar, J. N. Zhou, W. J. Liu, and J. A. Barnard, *Chem. Mater.*, **13**, 3669 (2001). c) D. C. Tully, A. R. Trimble, J. M. J. Fréchet, K. Wilder, and C. F. Quate, *Chem. Mater.*, **11**, 2892 (1999). d) T. Imae, K. Funayama, K. Aoi, K. Tsutsumiuchi, M. Okada, and M. Furusaka, *Langmuir*, **15**, 4076 (1999).

6 a) M. Liebau, H. M. Janssen, K. Inoue, S. Shinkai, J. Huskens, R. P. Sijbesma, E. W. Meijer, and D. N. Reinhoudt, *Langmuir*, **18**, 674 (2002). b) G. L. Cui, Y. Xu, M. Z. Liu, F. Fang, T. Ji, Y. M. Chen, and Y. F. Li, *Macromol. Rapid. Commun.*, **20**, 71 (1999).

7 J. Li, C. Wang, G. Shang, Q. Xu, Z. Lin, J. Guan, and C. Bai, *Langmuir*, **15**, 7662 (1999).

8 P. M. Saville, J. W. White, C. J. Hawker, K. L. Wooley, and J. M. J. Fréchet, *J. Phys. Chem.*, **97**, 293 (1993).

9 a) S. Lee, Y.-S. Shon, R. Colorado, Jr., R. L. Guenard, T. R. Lee, and S. S. Perry, *Langmuir*, **16**, 2220 (2000). b) B. Bhushan, A. V. Kulkarni, V. N. Koinkar, M. Boehm, L. Odoni, and C. Martelet, *Langmuir*, **11**, 3189 (1995). c) Y.-S. Shon, S. Lee, R. Colorao, Jr., S. S. Perry, and T. R. Lee, *J. Am. Chem. Soc.*, **122**, 7556 (2000).