

Interactions, Structure, and Stability of Photoreactive Bolaform Amphiphile Multilayers

Guangzhao Mao, Yi-hua Tsao, Matthew Tirrell,* and H. Ted Davis

Department of Chemical Engineering and Materials Science, University of Minnesota,
Minneapolis, Minnesota 55455

Volker Hessel and Helmut Ringsdorf

Institut für Organische Chemie, Universität Mainz, J. J. Becherweg 18–20,
D-55099 Mainz, Germany

Received July 5, 1994. In Final Form: November 7, 1994*

Ultrathin organic multilayer films are appealing to scientists not only because they serve as molecular level models but also because they can be transformed into superlattices through successive deposition of alternating layers of different materials. Cationic bolaform amphiphile and anionic polyelectrolyte multilayers were self-assembled from their aqueous solutions via electrostatic attraction. The bolaform amphiphile layers are photopolymerizable by UV irradiation. The mechanical and surface electrical properties of the multilayer film were studied by surface force measurements, and the surface topography was studied by atomic force microscopy. We observed an average increase in film thickness of 75 Å with each amphiphile and polyelectrolyte double layer deposition, a molecularly smooth first anchoring amphiphile layer, and nonuniform polyelectrolyte layers with a surface roughness of 30 Å. The surface roughness was preserved in the multilayer deposition process and was reduced by adding salt to the polyelectrolyte solution. Photopolymerization increases the integrity of the first anchoring layer as well as the subsequent multilayers. It took less than 5 min to dissolve a monomeric amphiphile film in chloroform, but immersion of the UV-irradiated film in chloroform for 2 h only resulted in partial removal of film materials. The multilayer film is quite fragile especially for the first few layers. Controlling of the monolayer structure by selective variation of the amphiphile chemical structure may help to optimize the photopolymerization process.

Introduction

Ultrathin organic multilayer films are appealing to scientific researchers not only because they serve as molecular level models but also because they can be transformed into superlattices through successive deposition of alternating layers of different materials.^{1–3} In many applications, bilayer and multilayer films are preferred and often required: (1) the response from electronic, optical, and electrically active films often increases with the number of layers, such as the quadratic dependence of second harmonic on the number of layers. (2) The precise control of film thickness is essential to the design of dielectric devices. (3) Alternating and conjugated layers secure and enhance the noncentrosymmetric properties of thin films. (4) A passive spacer separation layer is inserted in between two active layers in order to prevent crystallization into centrosymmetric structures. (5) Anchoring and supportive layers are used to modify or eliminate substrate effects on successively deposited films. For example, a nonporous but highly permeable layer is deposited underneath separation membranes to reduce film defects induced by the porous substrate. Anchoring organic layers can provide biocompatibility between a solid substrate and the immobilized biomolecules. (6) A multifunctional device can be built by incorporating different components in different layers such as the interface of a receptor unit with a transducer unit in sensor devices.

Several film preparation methods have been developed to fabricate multilayer films: spin coating,^{4,5} solution casting,^{6,7} vapor phase deposition,⁸ the Langmuir–Blodgett and Schaefer techniques,^{9–15} chemisorption,^{16–19} and physisorption.^{20–24} Sometimes, a combination of two or more of the deposition techniques may produce films of desirable properties.^{25,26} Self-assembly via physical

- (4) Coulon, G. *Macromolecules* **1989**, *22*, 2581.
- (5) Foster, M. D.; Sikka, M.; Singh, N.; Bates, F. S.; Satija, S. K.; Majkrzak, F. *J. Chem. Phys.* **1992**, *96*, 8605.
- (6) Kunitake, T.; Tsuge, A.; Nakashima, N. *Chem. Lett.* **1984**, 1783.
- (7) Okahata, Y.; Taguchi, K.; Seki, T. *J. Chem. Soc., Chem. Commun.* **1985**, 1122.
- (8) Sun, L.; Thomas, R. C.; Crooks, R. M.; Ricco, A. J. *J. Am. Chem. Soc.* **1991**, *113*, 8550.
- (9) Blodgett, K. *Phys. Rev.* **1939**, *55*, 391.
- (10) Langmuir, I.; Schaefer, V. J. *J. Am. Chem. Soc.* **1938**, *57*, 1007.
- (11) Gaines, G. L., Jr. *Insoluble Monolayers at Liquid-Gas Interfaces*; Interscience Publishers: New York, 1966.
- (12) Roberts, G. G. *Langmuir–Blodgett Films*; Plenum Press: New York, 1990.
- (13) Elbert, R.; Laschewsky, A.; Ringsdorf, H. *J. Am. Chem. Soc.* **1985**, *107*, 4134.
- (14) Walsh, S. P.; Lando, J. B. *Langmuir* **1994**, *10*, 246.
- (15) Rubner, M. F. In *Polymers for Electronics and Photonics*; Wong, C., Ed.; Academic Press: New York, 1992; pp 601–631.
- (16) Maoz, R.; Sagiv, J. *Thin Solid Films* **1985**, *132*, 135.
- (17) Bain, C. D.; Troughton, E. B.; Tao, Y. T.; Evall, J.; Whitesides, G. M.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 321.
- (18) Nuzzo, R. G.; Fusco, F.; Allara, D. L. *J. Am. Chem. Soc.* **1987**, *109*, 2358.
- (19) Lee, H.; Kepley, L. J.; Hong, H. -G.; Mallouk, T. E. *J. Am. Chem. Soc.* **1988**, *110*, 618.
- (20) Decher, G.; Hong, J. -D. *Makromol. Chem., Macromol. Symp.* **1991**, *46*, 321.
- (21) Decher, G.; Hong, J. D. *Ber. Bunsen-Ges. Phys. Chem.* **1991**, *95*, 1430.
- (22) Decher, G.; Hong, J. D.; Schmitt, J. *Thin Solid Films* **1992**, *210*, 211, 831.
- (23) Mao, G.; Tsao, Y.; Tirrell, M.; Davis, H. T.; Hessel, V.; Ringsdorf, H. *Langmuir* **1993**, *9*, 3461.
- (24) Cheung, J. H.; Fou, A. F.; Rubner, M. F. *Thin Solid Films* **1994**, *244*, 985.

* Abstract published in *Advance ACS Abstracts*, February 1, 1995.

(1) Swalen, J. D.; Allara, D. L.; Andrade, J. D.; Chandross, E. A.; Garoff, S.; Israelachvili, J.; McCarthy, T. J.; Murray, R.; Pease, R. F.; Rabolt, J. F.; Wynne, K. J.; Yu, H. *Langmuir* **1987**, *3*, 932.

(2) Ullman, A. *An Introduction to Ultrathin Organic Films, from Langmuir–Blodgett to Self-Assembly*; Academic Press: New York, 1991, and the references therein.

(3) Fuchs, H.; Ohst, H.; Prass, W. *Adv. Mater.* **1991**, *3*, 10.

adsorption is a particularly simple means of creating multilayer and multicomponent films. The physical adsorption process allows molecules more freedom to position themselves with respect to the substrate and to each other since no chemical bonds are formed in the process. It needs neither preformation of oriented films nor special equipment. The process is friendly to the environment and can be easily adapted for large scale automation. Electrostatic attraction between layers with opposite surface charges drives surfactant and polyelectrolyte molecules to self-assemble from their aqueous solutions.

Multilayers are three-dimensional materials with defined periodicity perpendicular to the layer plane. A complete reversal of surface active groups using bifunctional molecules is the crucial factor for a periodic self-consistent growth of self-assembled films. The periodic structure of a multilayer film and the in-plane ordering within each layer are closely related to film macroscopic properties and are determined by intermolecular forces. Continuous efforts have been made to address issues pertaining to the multilayer film structure in the past decade.^{2,23,27-35} These issues are the evolution of layer structure from a monolayer film toward a thin multilayer film (<10 layers) and toward a thick film similar to a bulk phase; the propagation of substrate effects, surface roughness, and defects through film growth; the influence of the first anchoring layer and top surface layer on the internal structure and stability of the multilayers; the degree of interpenetration between adjacent layers; and the interlayer and intralayer interactions which determine film stability.

The areas that require most attention concerning thin film application are the improvement of film stability against mechanical, chemical, and thermal degradation and the identification and deletion of defects and inhomogeneity. In general, methods to increase film strength fall into two categories. One can improve film stability either by polymerization and cross-linking of film-forming molecules or by incorporation of materials with high intrinsic integrity, such as polymers and layer-spanning dipolar amphiphiles, through mixing or physical and chemical attachment to the layers.³⁶ Topochemical photopolymerization of phenylenediacrylic acid and cinnamic acid derivatives was only successful for highly ordered molecular assemblies.³⁷⁻⁴⁰ It has been shown that the bolaform phenylenediacrylic acid derivative amphiphile containing two unsaturated bonds can be photopolymerized in mono- and multilayers by a high-pressure Xe/Hg UV lamp.²³ The rate and degree of this type of topochemical polymerization strongly depend on the molecular lattice spacing and crystallization direction of the unit cell.

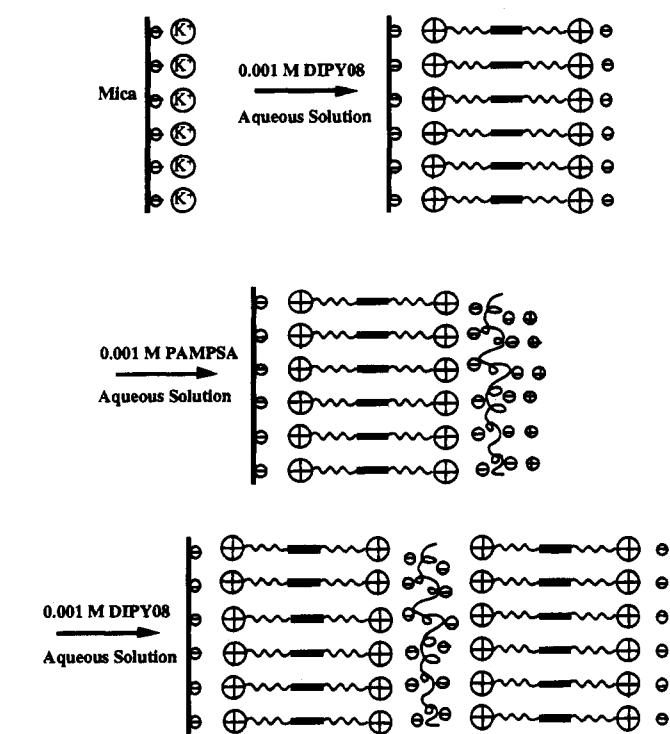


Figure 1. Schematic of the cationic bolaform phenylenediacrylic amphiphile DIPY08 and the anionic polyelectrolyte PAMPSA multilayer self-assembly from their aqueous solutions on mica.

Photopolymerization is expected to reduce the rate of film desorption in an organic solvent. The solvent etching method was used by K. Blodgett to dissolve arachidic acid from LB films made of a mixture of arachidic acid and cadmium arachidate.⁴¹ The remaining cadmium arachidate after solvent etching was called a skeleton film and the etching method was called skeletonization. She found that the optical quality depended on the size of the air spaces in the skeleton films and different solvents have different effects on film materials. The skeletonization method has been used in thin organic film research to selectively remove parts of the film species and to identify defects.⁴²⁻⁴⁴ In our experiments, the chloroform-etched films were imaged by the atomic force microscope. We were able to compare the chemical stability of monomeric and photopolymerized amphiphile films.

We have established the method of alternating self-assembly (Figure 1) of a photoreactive bolaform phenylenediacrylic acid amphiphile with two pyridinium groups in the α and ω positions (DIPY08) (Figure 2) and an anionic poly(sulfonic acid) (PAMPSA).²³ This paper will focus on the interactions, structure, mechanical integrity, and chemical stability of the multilayer system. Six bolaform amphiphile and polyelectrolyte double layers were constructed in the surface force apparatus and their interactions were measured in a stepwise fashion; i.e., force profiles were obtained after each addition of a top amphiphile surface layer before and after UV irradiation. We also studied hysteresis in the force measurements between a bare mica surface and a mica surface with an adsorbed layer. The combination of the surface force measurements and the atomic force microscopy allows us

- (25) Lvov, Y.; Essler, F.; Decher, G. *J. Phys. Chem.* **1993**, *97*, 13773.
- (26) Mao, G.; Tsao, Y.-H.; Tirrell, M.; Davis, H. T.; Hessel, V.; van Esch, J.; Ringsdorf, H. *Langmuir* **1994**, *10*, 4174.
- (27) Bonnerot, A.; Chollet, P. A.; Frisby, H.; Hoclet, M. *J. Chem. Phys.* **1985**, *97*, 365.
- (28) Stroeve, P.; Srinivasan, M. P.; Higgins, B. G.; Kowal, S. T. *Thin Solid Films* **1987**, *146*, 209.
- (29) Kimura, F.; Umemura, J.; Takenaka, T. *Langmuir* **1986**, *2*, 96.
- (30) Spinke, J.; Liley, M.; Guder, H. -J.; Angermaier, L.; Knoll, W. *Langmuir* **1993**, *9*, 1821.
- (31) Maoz, R.; Sagiv, J. *Colloid Interface Sci.* **1984**, *100*, 465.
- (32) Böhm, C.; Seitz, R.; Riegler, H. *Thin Solid Films* **1989**, *178*, 511.
- (33) Schwatz, D. K.; Garnaes, J.; Viswanathan, R.; Zasadzinski, J. A. N. *Science* **1992**, *257*, 508.
- (34) Lvov, Y.; Decher, G.; Möhwald, H. *Langmuir* **1993**, *9*, 481.
- (35) Schmitt, J.; Grünewald, T.; Decher, G.; Pershan, P.; Kjaer, K.; Lösch, M. *Macromolecules* **1993**, *26*, 7058.
- (36) Ringsdorf, H.; Schlarb, E.; Venzmer, J. *Angew. Chem. Int'l. Ed. Eng.* **1988**, *27*, 113, and the references therein.
- (37) Schmidt, G. M. *J. Pure Appl. Chem.* **1971**, *27*, 647.
- (38) Hasagawa, M. *Pure Appl. Chem.* **1968**, *58*, 1179.
- (39) Hakanishi, F.; Fang, P.; Xu, Y. *J. Photopolym. Sci. Technol.* **1991**, *4*, 65.
- (40) Reiser, A.; Egerton, P. L. *Photogr. Sci. Eng.* **1979**, *23*, 144.

- (41) Blodgett, K. B. *Phys. Rev.* **1939**, *55*, 391.
- (42) Sagiv, J. *Isr. J. Chem.* **1979**, *18*, 346.
- (43) Fukuda, K.; Shibasaki, Y.; Nakahara, H.; Endo, H. *Thin Solid Films* **1989**, *179*, 103.
- (44) Sun, L.; Crooks, R. M. *Langmuir* **1993**, *9*, 1951.

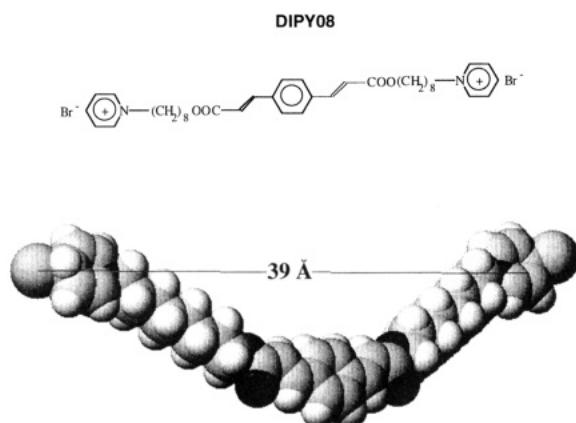


Figure 2. Chemical structure of the bolaform phenylenediacrylic acid derivative DIPY08 and computer-generated molecular conformation of an isolated fully stretched DIPY08 molecule.

to study the film growth, molecular in-plane ordering, polymer chain conformation, film integrity and chemical stability, surface electrical properties, and surface roughness and defects, as well as the effects of the substrate, solution ionic strength, and photoirradiation on multilayer formation.

Experimental Section

Materials. *p*-Phenylenediacrylic acid bis(8-pyridinium-*N*-yl octyl ester) dibromide, i.e., DIPY08 (Figure 2), was synthesized by a general route in three steps.²³ The amphiphile was stored in the solid state and kept away from light as much as possible.

The anionic polyelectrolyte poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPSA) was purchased from Aldrich Chemical Co. in 10 wt % aqueous solution. It was used without further purification.

The salt sodium bromide was ACS-certified grade crystals, received from Fisher Scientific and used without further purification.

The solvent chloroform was Analytical Reagent grade, purchased from Mallinckrodt Specialty Chemicals Co. and used without further purification.

Surface Preparation. Grade 2, muscovite ruby mica, purchased from United Mineral and Chemical, was hand-cleaved and used as the main substrate. Water was filtered through a Millipore purification system and was processed with a Water Prodigy polishing unit from Labconco Corp. Freshly cleaved mica sheets were used for multilayer deposition by a procedure described in Figure 1. A clean mica sheet was first placed in DIPY08 aqueous solution in a small nitric acid-cleaned flask. The DIPY08 concentration used for adsorption (in our case 0.001 mol/dm³) was chosen to be lower than the critical micelle concentration (cmc) of the amphiphile (0.015 mol/dm³) to ensure a fully covered monolayer structure. We did not investigate the effect of solution concentration on amphiphile adsorption. After 30 min to 1 h of incubation, the mica sheet was lifted from the solution with a pair of tweezers holding an edge of the mica and was rinsed by pouring 500 mL of water slowly onto the sheet. After draining the remaining water from the mica sheet, we placed it in 0.001 mol of monomer units/dm³ PAMPSA aqueous solution in the absence or presence of 1 mol/dm³ NaBr and let the adsorption proceed for 30 min to 1 h. The mica was again lifted from the solution and rinsed with 500 mL of water. The above procedures of depositing DIPY08/PAMPSA double layers were repeated to allow multilayers to build up on the mica. The mica surface bearing the adsorbed layers was dried in a laminar hood at room temperature before characterization measurements were carried out.

In order to study the chemical stability of the film, mica sheets bearing the self-assembled amphiphile monolayers, with or without UV irradiation, were immersed in chloroform. The chloroform-etched surfaces were scanned in air at room temperature with the atomic force microscopy.

In the surface force measurements, instead of incubating the mica pieces in the amphiphile solution, drops of the solution

were placed in between two mica pieces. More details will be given in the section where the surface force apparatus is described.

Photopolymerization through UV Irradiation. Photopolymerization of the mica-mounted mono- and multilayers was carried out in a laminar hood or in the surface force apparatus at room temperature by UV irradiation with an intensity of 5–50 mW for up to 1 h using a 200-W Hg/Xe ozone-free lamp purchased from Oriel Corp.

Characterization Methods. (1) **Atomic Force Microscopy (AFM).** The self-assembled layers on mica were visualized by AFM using the Nanoscope III (Digital Instruments) in air at room temperature. In the AFM experiments, mica bearing adsorbed layers was glued onto a stainless steel disk. The AFM apparatus was operated at a minimum force on all the surfaces studied. Si₃N₄ probes from Digital Instruments were used. A 0.7- or a 12-μm scanner was used. Both were calibrated with highly oriented pyrolytic graphite (HOPG; Union Carbide Corp.) or muscovite mica.

(2) **Surface Force Apparatus (SFA).** The forces between mica-mounted bolaform amphiphile/polyelectrolyte layers were measured using the method developed by Israelachvili et al.⁴⁵ SFA enables measurement of surface forces between two smooth mica pieces bearing the adsorbed layers to a precision of 10⁻⁷ N by measuring the deflection of the double cantilever spring with a spring constant of 1.166 × 10² N/m supporting the lower mica surface. The surface separation is determined by the multiple beam interferometry method with an accuracy of better than 5 Å. Data are represented in plots of F/R versus D , where F is the measured surface force, R is the measured mean radius of curvature of the mica surfaces in the region where they are interacting, and D is the surface separation relative to the measured contact position of the bare mica surfaces in water. The quantity F/R is equal to 2π times the free energy per unit area of two interacting flat surfaces.⁴⁶ The cleanliness of mica surfaces is checked by bringing the two surfaces into contact in both air and water. Drops (1.0 cm³) of DIPY08 0.001 mol/dm³ stock solution were injected through a Millipore filter (0.22 μm) in between the two mica surfaces (to limit the amount of amphiphiles consumed). After 1 h of adsorption, the force measurement chamber was rinsed thoroughly with distilled water. The polyelectrolyte PAMPSA (0.001 mol of monomer units/dm³) was added to the aqueous phase in the apparatus with a needleless syringe through a nucleopore polycarbonate membrane filter (0.6 μm). After at least 4 h of mixing and adsorption, the measuring chamber was rinsed three times with distilled water. The temperature was controlled at 298.5 K.

Results

Interactions between a Bare Mica Surface and a Mica Surface Covered with a Monolayer of Phenylendiacrylic Amphiphile DIPY08 before (DIPY08 Monolayer) and after (P-DIPY08 Monolayer) UV Irradiation. We have measured interactions between identical monolayers in aqueous solutions and the results agree well with the DLVO theory.²³ By fitting the experimental data with the DLVO curves, we have been able to obtain information pertaining to surface electrical properties, uncompressed monolayer thickness before reaching the adhesive contact, and compressed bilayer thickness at the adhesive contact. However, interactions between a bare mica surface and a mica surface with the adsorbed monolayer will give an accurate account of the charge sign of a monolayer-covered mica surface, a single monolayer thickness at the adhesive contact, and the integrity of a monolayer film.

In the SFA experiment, drops of DIPY08 stock solution of 0.001 mol/dm³ were allowed to sit on the lower mica surface for 30 min to 1 h. The upper mica surface was kept 2 cm away from the lower mica surface so that it was not in contact with the water droplet during the adsorption. Distilled water filled the measuring chamber to a level just below the upper surface in order to rinse off any nonadsorbing surfactant molecules and was drained

(45) Israelachvili, J. N.; Adams, G. E. *J. Chem. Soc. Faraday Trans 1* **1978**, 74, 975.

(46) Derjaguin, B. V. *Kolloid-Z.* **1934**, 69, 155.

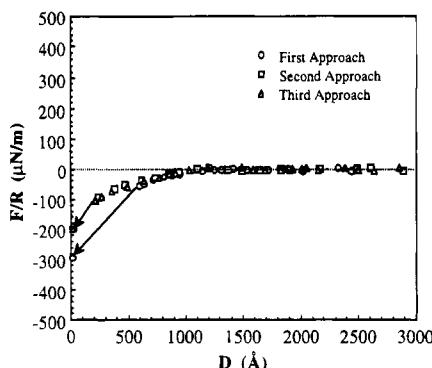


Figure 3. Surface force profiles between a bare mica surface and a monomeric DIPY08 monolayer adsorbed on a mica surface. The open circles, squares, and triangles are data obtained in the first, second, and third approach, respectively. Inward arrows represent inward jumps.

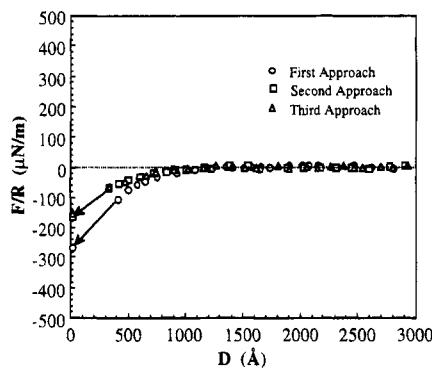


Figure 4. Surface force profiles between a bare mica surface and a photopolymerized DIPY08 monolayer adsorbed on a mica surface. The open circles, squares, and triangles are data obtained in the first, second, and third approach, respectively. Inward arrows represent inward jumps.

immediately. The chamber was filled with distilled water, and the forces between the upper bare mica surface and the lower monolayer-covered mica surface were measured before (Figure 3) and after UV irradiation (Figure 4).

The force between the bare mica and the amphiphile monolayer was purely attractive until the final steric barrier was reached. In the first approach before UV irradiation, the interaction became detectably attractive at 1100 Å and the instability limit of the spring was reached at 600 Å, where the force gradient exceeds the spring constant, k ($dF/dD > k$), and the two surfaces moved rapidly and spontaneously toward each other until reaching the steric barrier at a surface separation of 18 Å. The two surfaces were separated and brought toward each other again. In the second approach, an attractive force was measured from 930 to 220 Å. At 220 Å, the spring stability limit was reached and the two surfaces jumped into an adhesive contact. The magnitude of the attractive force was smaller in the second approach than in the first approach. The final separation was still 18 Å. The third approach was almost identical to the second one.

In the first approach after UV irradiation, an attractive force was measured between 950 and 420 Å. At 420 Å, the two surfaces started to move toward each other spontaneously. The final separation at adhesion was 18 Å. In the subsequent approaches, attractive forces were measured between 900 and 340 Å. The attractive force was reduced to a constant profile after the first approach. The final surface separation remained 18 Å.

For dissimilar surfaces having charges of unlike signs, the electrostatic double layer interaction at large enough surface separations should be attractive regardless of the boundary conditions describing the interaction, i.e.,

interaction at constant surface charge density, constant surface potential, or regulation.⁴⁷ The force profile between a bare mica surface and a mica surface covered with a monolayer of the bolaform amphiphile DIPY08 resembles that of two surfaces with unlike charges at constant surface potentials. Therefore the surface of DIPY08 monolayer must bear positive charges since a bare mica surface is negatively charged in water. A bare mica surface has a charge density of 1 charge per 48 Å² and a surface potential of -100 mV in distilled water. The monolayer surface potential before UV irradiation has been estimated to be 106 mV by fitting the experimental data with the DLVO curve.²³ Therefore, the adsorption of amphiphile DIPY08 is most likely an end-on adsorption which results in a complete reversal of the bare mica surface charge.

In the first approach, the attraction between the bare mica surface and the monolayer surface is reduced after UV irradiation, which supports our argument²³ that photopolymerization promotes counterion binding in order to reduce the repulsion between charged head groups.

The compressed monolayer thickness is 18 Å. A closely packed monolayer with perpendicular molecular configurations with respect to the substrate should have a layer thickness of 39 Å. The monolayer thickness without compression was estimated to be 35 Å by fitting the experimental data with the DLVO curve.²³ Therefore the amphiphile monolayer is quite compressible.

The hysteresis in mica/monolayer interaction indicates changes in monolayer structure upon separation of the two surfaces. In the case of an end-on adsorption, the head group pointing toward the liquid medium is electrostatically attracted to the approaching bare mica surface. "Bridging" occurs when a bolaform molecule adsorbs on both mica surfaces (Figure 5). The monolayer film can be ruptured mechanically upon separation of the two surfaces, which results in partial transfer of the amphiphile monolayer to the bare mica surface. The partial transfer reduces the charge density of both surfaces and therefore reduces the electrostatic attraction. Hysteresis was also observed after UV irradiation. Either photopolymerization is incomplete or the nature of physical adsorption is responsible for the partial transfer of the monolayer from one mica surface to another.

Interactions between Multiple Layers of Bolaform Amphiphile DIPY08. We have reported surface force measurements on bolaform amphiphile mono- and bilayers.²³ We continued multilayer construction of up to six alternating bolaform amphiphile and polyelectrolyte double layers in the surface force apparatus and measured their interactions in distilled water at a constant temperature of 25.5 °C. After each DIPY08 layer deposition, force profiles were measured before (Figure 6) and after UV irradiation (Figure 7). Therefore, during the force measurement, all the amphiphile layers except the top surface layer were photopolymerized. The stability of the multilayer assembly against the external compression in the case of an unpolymerized top layer and a photopolymerized top layer was studied by the surface force measurements.

All the multilayer interaction profiles were repulsive at long range due to electrostatic and structural interactions. The onset of the structural force shifted to longer surface separations after each deposition of polyelectrolyte and bolaform amphiphile double layers. Meanwhile, the electrostatic force was reduced with the multilayer deposition.

Multilayers showed stronger resistance to compression after the surface monolayer was UV irradiated. In fact,

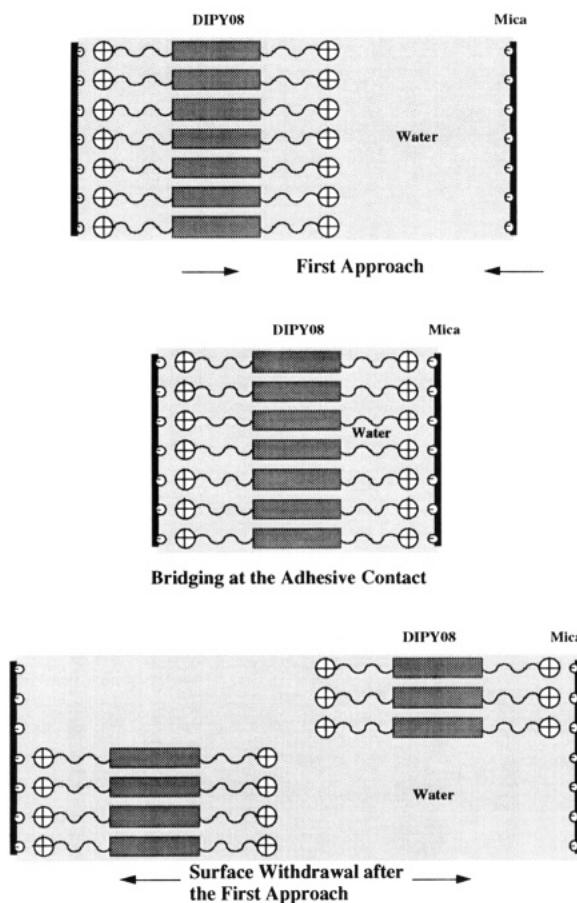


Figure 5. “Bridging” mechanism for the interaction of a DIPY08 monolayer with a bare mica surface. Counterions are omitted for simplicity.

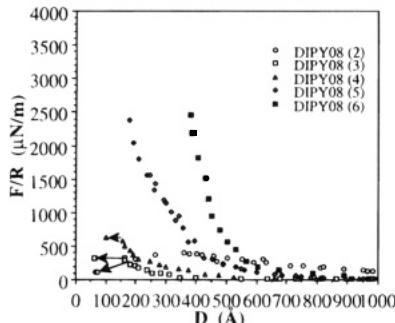


Figure 6. Force profiles between bolaform amphiphile DIPY08 multilayers of monomeric top surface layers in distilled water at 298.5 K. The number of bolaform amphiphile layers deposited on mica is indicated in the legend of each data set. Inward arrows represent inward jumps.

periodicity was more distinct for the multilayers with every layer photopolymerized (Figure 7) than for the multilayers whose surface layers were not photopolymerized (Figure 6). We also observed rapid deterioration upon compression of the multilayer assembly when none of the layers were UV irradiated.

The average amphiphile/polyelectrolyte layer thickness was estimated from Figure 7 by calculating the surface separation before and after deposition of the polyelectrolyte and amphiphile double layers. The bolaform amphiphile and polyelectrolyte double layer thickness was estimated to be 74.5 Å by measuring the average change in surface separation, D , at some constant force between 100 and 500 $\mu\text{N}/\text{m}$. If all the bolaform amphiphile layers assume the same end-on and almost perpendicular configuration as the first monolayer (which has a layer thickness of 35 Å) and there is no interdigitation between

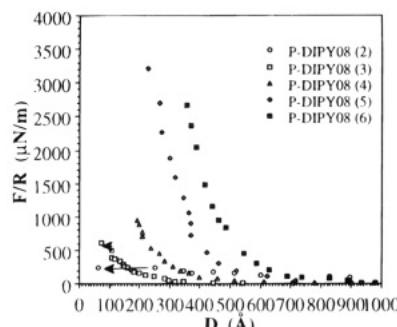


Figure 7. Force profiles between bolaform amphiphile DIPY08 multilayers of photopolymerized top surface layers in distilled water at 298.5 K. The number of bolaform amphiphile layers deposited on mica is indicated in the legend of each data set. Inward arrows represent inward jumps.

layers, the polyelectrolyte layer would have a thickness of 39.5 Å.

Adhesive contacts were reached for the first four bolaform amphiphile layers when they were compressed against each other. Stronger surface pressures were applied in order to bring surfaces into an adhesive contact as the films became thicker. In order to avoid damage to the multilayers, compression was stopped before an adhesive contact was reached for the thicker films.

All the curves shown here were measured during the first approach of two opposing surfaces. Hysteresis, characterized by a shorter range of subsequent force measurements than that of the first compression measurement, was observed in the force measurements of the multilayer system.

AFM Image of Six Bolaform Amphiphile and Polyelectrolyte Double Layers on Mica in Air. In the surface force apparatus, six amphiphile and polyelectrolyte double layers were assembled on mica glued to a lens. The same multilayer surface was taken out for an examination by the atomic force microscope after the surface force measurements. Its AFM image is shown in Figure 8 with a scan area of $4 \times 4 \mu\text{m}^2$. The surface roughness of the multilayer film, which is characterized by the average vertical peak to valley distance, is about 25 Å, smaller than the thickness of the bolaform amphiphile DIPY08 monolayer (35 Å) and the surface roughness of two bolaform amphiphile layers with one polyelectrolyte layer in between (40 Å) (Figure 9). It indicates that the surface roughness was preserved or even reduced in the process of the multilayer deposition.

AFM Images of the Second DIPY08 Layer on a Polyelectrolyte Layer Assembled in the Absence and in the Presence of Salt. Salt influences polyelectrolyte adsorption through electrostatic screening of the charged groups on the polymer chain. The surface of the second DIPY08 layer adsorbed on a polyelectrolyte layer, prepared with 0.001 mol of monomer units/dm³ PAMPSA aqueous solution in the presence of 1 mol/dm³ NaBr (Figure 10), is smoother than the surface of the same DIPY08 layer on a polyelectrolyte layer prepared without the addition of salt (Figure 9). The surface roughness in the presence of salt is less than 10 Å while in the absence of salt is 40 Å. This difference in surface roughness is related to the chain flexibility and conformation change due to salt screening.

AFM Measurements of Chloroform-Etched Monolayers before and after UV Irradiation. AFM images of monomeric and polymeric bolaform amphiphiles showed nearly the same unit cell spacing and slightly better ordering for the polymeric layer.²³ Both monolayers were prepared by immersion in 0.001 mol/dm³ amphiphile aqueous solution for 0.5 h. Both monolayers appeared

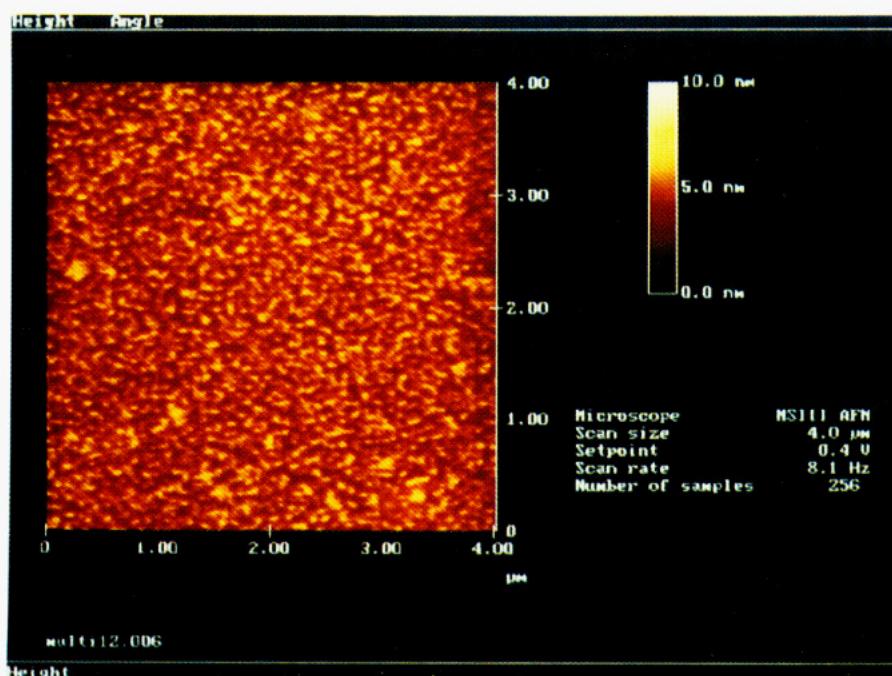


Figure 8. AFM surface view of six bolaform amphiphile and polyelectrolyte double layers on mica in air with a scan area of $4 \times 4 \mu\text{m}^2$. The surface roughness characterized by the average vertical peak to valley distance is 25 Å.

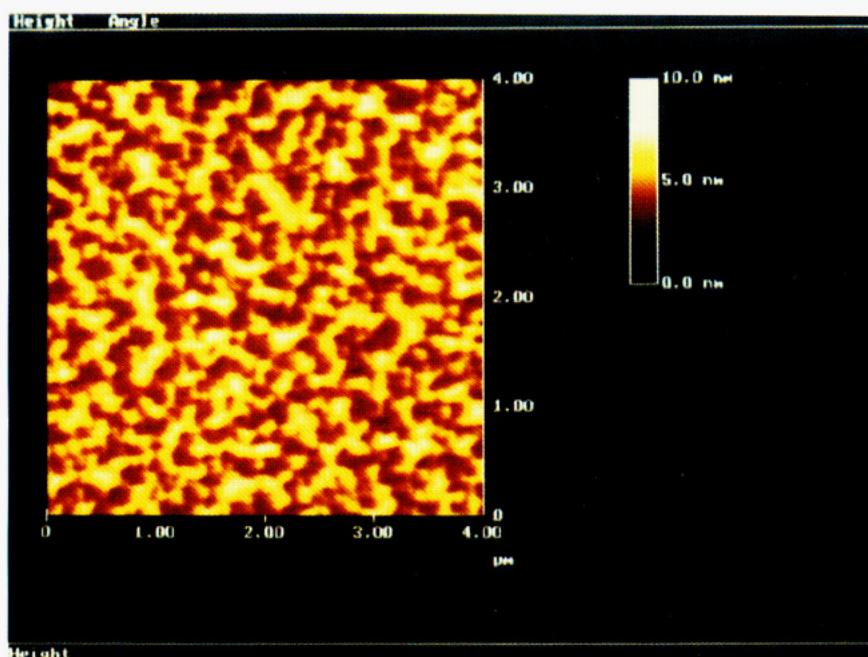


Figure 9. AFM surface view of two bolaform amphiphile layers with one polyelectrolyte layer in between on mica in air with a scan area of $4 \times 4 \mu\text{m}^2$. The surface roughness characterized by the average vertical peak to valley distance is 40 Å.

under the atomic force microscope to be smooth and uniform over tens of microns with no obvious defects. In order to examine film chemical stability and expose film defects, the self-assembled monolayers were immersed in chloroform before the AFM measurements. Chloroform is a good solvent for the organic surfactant and is expected to better differentiate film stability against solvent dissolution than water.

The monomeric film was immersed in chloroform for 5 min and dried in air before its AFM image was taken (Figure 11 a). Its $4 \times 4 \mu\text{m}^2$ AFM image revealed a virtually flat surface with a few scattered aggregates about $0.14 \times 0.14 \mu\text{m}^2$ in size. The average aggregate height is 20 Å, smaller than the thickness of a fully covered, perpendicular, and end-on adsorbed monolayer, which is about 35 Å. The image with molecular resolution of the flat area revealed the bare mica lattice structure with a

unit cell area of 24 \AA^2 (Figure 11 b). We concluded that dissolution of monomeric bolaform amphiphile in chloroform is fast and complete.

Figure 12 a is an AFM image of a photoirradiated bolaform amphiphile monolayer sample immersed in chloroform for 2 h with a scan area of $6 \times 6 \mu\text{m}^2$. Circular holes were revealed in an otherwise flat surface. The size of the holes ranges from 0.36 to $1 \mu\text{m}^2$, but the depth of the holes remains 25 Å. An image with molecular resolution inside the holes reveals mica lattice structure with a unit cell area of 24 \AA^2 (Figure 12 b). We suggest that during the immersion of film in chloroform, dissolution starts at defects and gradually expands isotropically to bigger areas. Thus, defects, either adventitious or intrinsic in nature, previously not seen in the aqueous treatment, can be visualized using the chloroform etching method. The much slower dissolution process of the

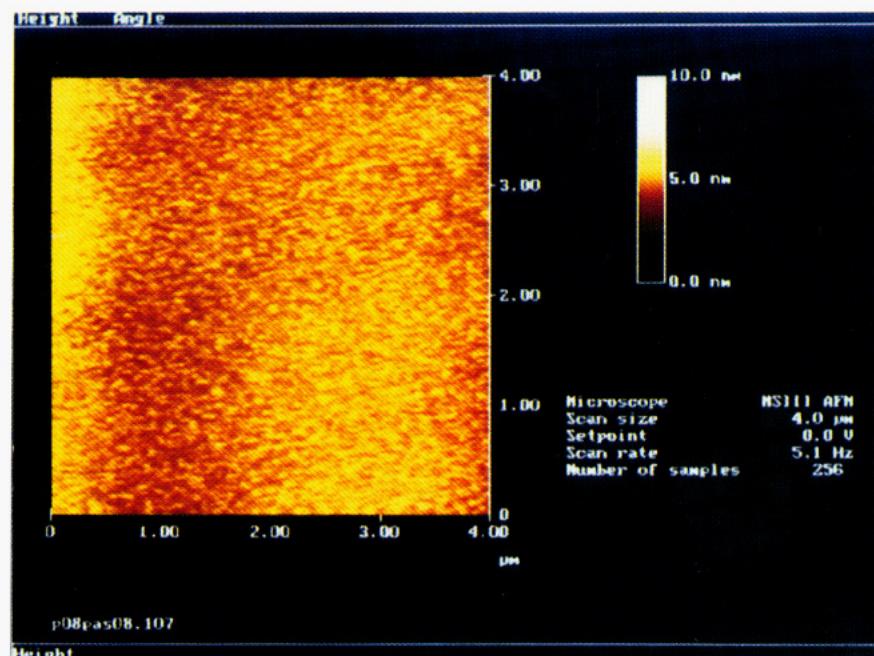


Figure 10. AFM surface view of two bolaform amphiphile layers with one polyelectrolyte layer in between on mica in air with a scan area of $4 \times 4 \mu\text{m}^2$. The polyelectrolyte was adsorbed from the PAMPSA stock solution in the presence of $1 \text{ mol}/\text{dm}^3 \text{ NaBr}$. The surface roughness characterize by the average vertical peak to valley distance is less than 10 \AA .

photoirradiated film corroborates with the notion that photopolymerization in the monolayer film increases the film stability and integrity.

The chemical-etching method also offers the possibility of an independent measurement of film thickness. The AFM determined monolayer thickness, 25 \AA , is smaller than the DLVO-fitted uncompressed film thickness, which is about 35 \AA , measured by SFA. There are a couple of possible explanations. The monolayer might be flattened out due to partial removal of film materials and the weakened attraction between the substrate and the amphiphile molecules in the presence of chloroform. The applied force by the AFM tip might be strong enough to compress the layer and thus gives the thickness of a slightly compressed monolayer.

Discussion

Film and Surface Properties of the Anchoring Amphiphile Monolayers. The first anchoring amphiphile layer on the substrate is the foundation of the subsequent multilayer assembly and possibly a major factor controlling the stability of the multilayer system. First, we discuss the properties of the first anchoring amphiphile monolayer.

In the AFM study, the DIPY08 amphiphile monolayer on mica in air and in water is continuous and uniform over tens of microns. We have measured the monolayer thickness of DIPY08 amphiphile to be 35 \AA by DLVO fitting²³ and the average optical monolayer thickness to be 33 \AA by surface plasmon spectroscopy.²⁶ Another independent measurement of the monolayer thickness was accidentally obtained from the AFM image of a partially dissolved monolayer film. The photopolymerized monolayer thickness was measured by AFM with the chloroform-etching method to be 25 \AA . The computer generated fully stretched molecular configuration has an end-to-end distance of 39 \AA . Molecules might be tilted from the surface normal to establish optimum van der Waals contacts or distorted to accommodate the bulky phenylene groups in the center.

The surface potential determined by DLVO fitting is 106 mV for the monomeric DIPY08 film, slightly higher

than the absolute surface potential of a bare mica surface in water (100 mV). The DLVO-fitted surface potential of a photopolymerized DIPY08 monolayer in distilled water is 71 mV . The pure long-range attraction between the monolayer surface and the bare mica surface indicates that the sign of surface charge is reversed from negative to positive by adsorption of DIPY08 amphiphile. The packing density of DIPY08 monolayer in water has been measured by AFM to be 1 molecule per 30 \AA^2 ,²⁶ while the charge density of a bare mica surface in water is 1 charge per 48 \AA^2 . The adsorption of amphiphile DIPY08 is most likely an end-on adsorption which causes an almost complete reversal of the bare mica surface charge. The end-on adsorption of bolaform amphiphiles is desirable in applications that require an effective reversal of substrate surface charge or a maximum exposure of functional surface groups.

In the SFA experiment, the mica separation of a pair of opposed monolayers at an adhesive contact in the presence of water is surprisingly small (25 \AA) compared to the thickness (78 \AA) of a bilayer composed of fully extended amphiphiles. This “thinning” of monolayers after the adhesive jump must be a result of molecular rearrangement such as reorientation (tilting, folding, etc.), reorganization (desorption, aggregation, etc.), and interdigitation between the two opposing layers. To obtain an accurate account of a single monolayer thickness at the adhesive contact, we measured interactions between asymmetric surfaces of a mica piece and a monolayer. The corresponding thickness is 18 \AA , bigger than one-half of the opposing bilayer thickness at the adhesive contact (12.5 \AA), but smaller than an uncompressed DLVO-fitted layer thickness of 35 \AA . This implies that the opposing monolayers interdigitate to a certain degree at the adhesive contact and the DIPY08 monolayer is also compressible.

We argue that the reduced attraction in the force measurements between a bare mica surface and a monolayer-covered mica surface after the first approach is due to partial transfer of film-forming molecules between the two opposing mica surfaces. No hysteresis has been observed in the force measurements between two opposing

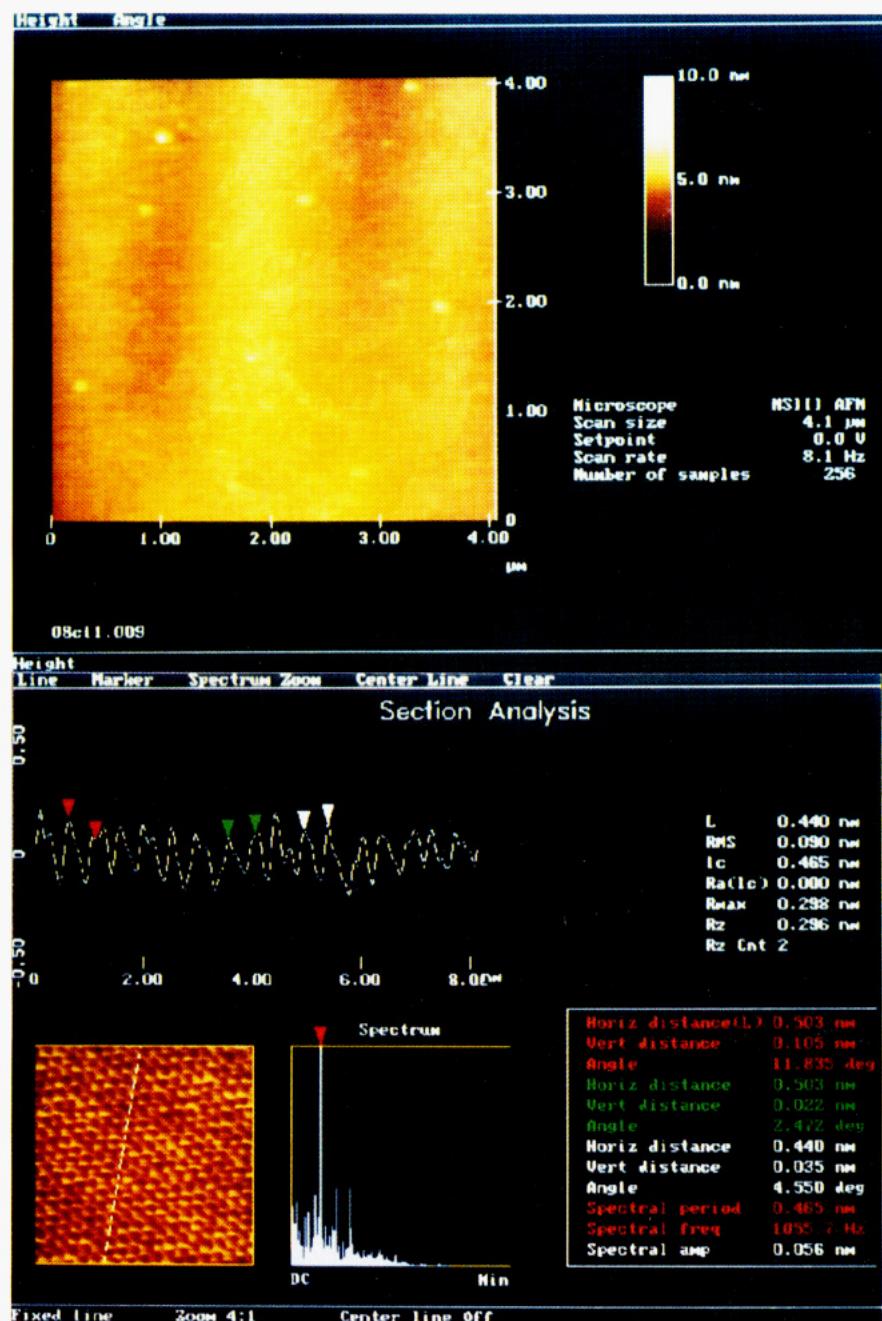


Figure 11. (a, top) AFM surface view of a monomeric amphiphile monolayer after immersing in chloroform for 5 min with a scan area of $4 \times 4 \mu\text{m}^2$. (b, bottom) AFM image with molecular resolution of the flat area, revealing the unit cell area of mica (24 \AA^2).

identical monolayers.²³ The bolaform amphiphile DIPY08 most likely assumes an end-on adsorption, exposing one of the head groups to the aqueous environment while it attaches the other one to the substrate. Bridging occurs when the bare mica surface is brought within the boundary of the exposed head group and the molecule attaches on both surfaces. Upon separation of the two surfaces some of the bolaform amphiphiles leave the original mica substrate and adsorb on the other mica surface. This will reduce the charge density of both surfaces and thus cause reduction in electrostatic attraction. The hysteresis in force measurements after UV irradiation is either due to the incompleteness of photopolymerization or related to the bond strength of electrostatic attraction between the substrate and the head group in physical adsorption. The presence of the attractive interaction in the consecutive approaches suggests that film-forming molecules were not evenly distributed between the two surfaces.

The effect of photopolymerization of the monolayer properties will be discussed in a following section.

Periodicity in Self-Assembled Multilayers. The regularity of film growth was first proved in the UV spectrometry study.²³ The absorbance of the self-assembled layers at 310 nm—proportional to the amount of the conjugated phenylenediacrylic acid groups in the film—is plotted against the number of dipping cycles of the substrate. The linear increase of the absorbance maximum at 310 nm with the number of the dipping cycles is a clear indication that with each deposition an equal amount of the amphiphile molecules was adsorbed onto the substrate.

In the SFA experiment, while the trend of film thickness growth with each amphiphile/polyelectrolyte deposition is unambiguous, the exact layer thickness is difficult to compute because of the complex nature of the interactions between multilayers. The shape of the force–distance profiles suggests that a combination of the DLVO-type electrostatic repulsion and steric force is primarily responsible for the observed interactions. At the initial stage of the interaction between the multilayers, the electrostatic

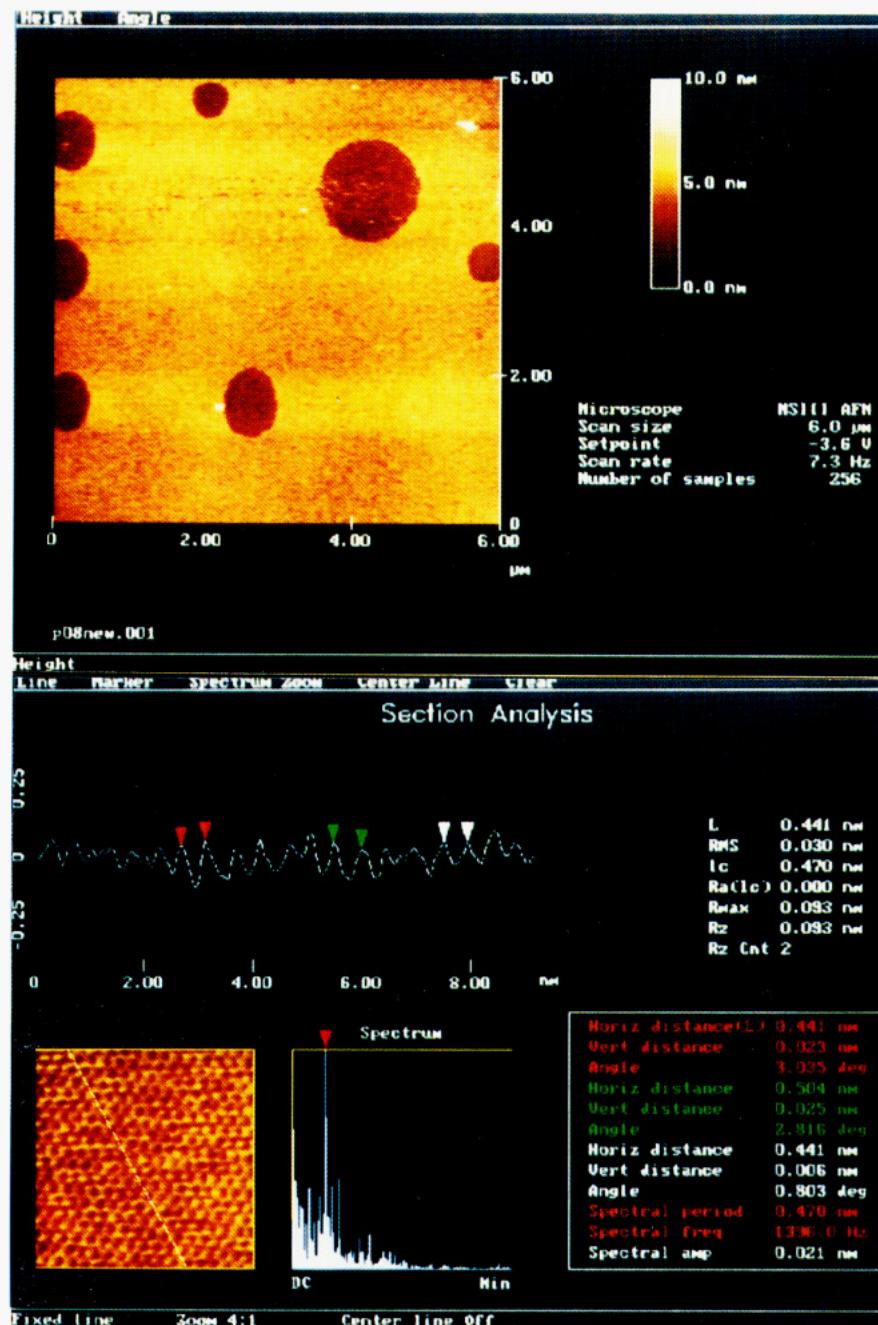


Figure 12. (a, top) AFM surface view of a photopolymerized amphiphile monolayer after immersing in chloroform for 2 h with a scan area of $6 \times 6 \mu\text{m}^2$. (b, bottom) AFM image with molecular resolution inside one of the holes, revealing the unit cell area of mica (24 \AA^2).

interaction is expected to dominate with little compression of the multilayers, since the electrostatic repulsion extends beyond the structural (steric) boundary of the layers. At the short distance end of the interaction, multilayers are strongly compressed against each other, therefore, the steric force rises above the electrostatic force. The transition between the two extremes, as indicated by the change in the slope of force versus distance, will be sharp if the layer and water interface is smooth and uniformly charged and the layer itself is rigid. In the case of a sharp multilayer/water interface, the distance where the slope changes abruptly gives a good estimation of the layer thickness. Otherwise, the transition will be gradual if the surface is rough with electrical charges distributed within a finite volume near the surface and the layer is fragile or flexible. In this case, it will be difficult to separate the electrostatic and the steric components of the interaction and the forces cannot be analyzed by the DLVO theory. The outer Helmholtz plane (OHP), defined

as the plane where the diffuse double layer originates, cannot be precisely located; therefore, it will be difficult to obtain a precise layer thickness.

We observed a transient stage in layer buildup from the first to the fourth DIPY08 amphiphile layers as the force profiles started to deviate from the DLVO force laws at longer surface separations. The structural force increases with the number of layers and stronger compression is required to bring surfaces into an adhesive contact. At the same time, the magnitude of the exponentially decayed electrostatic tails decreases with the number of layers. The slope of the electrostatic interaction part of the force curves, which is determined by the ionic strength of the solution, remains roughly constant for the different layers. The bulk ionic concentration calculated by fitting DLVO theory to experiment is about 4×10^{-5} mol/dm³. This concentration agrees with previous experiments and is consistent with that deduced from the electrical conductivity measurement of the distilled water

we used, which was saturated with the ambient atmosphere of CO₂. The surface potential decreases gradually during the multilayer deposition, from 106 mV for the first monomeric amphiphile layer to a small but finite value for amphiphile surface layers beyond the fourth layer. However, the exact value of the surface potential is difficult to calculate because of the uncertainty of the OHP. The low surface charge density for the multilayer suggests either an almost total neutralization of the surface as a result of multilayer buildup or a smearing of the electrostatic effect due to the roughness of the surface and the charge distribution within the layer.

We estimated an average amphiphile and polyelectrolyte double layer thickness by measuring the change in surface separation (D) for each double layer deposition, from the third (DIPY08(3)) to the sixth (DIPY08(6)) force curve of a photoirradiated surface layer, at a constant force F/R between 100 and 500 $\mu\text{N}/\text{m}$ in Figure 7. We chose the constant force between 100 and 500 $\mu\text{N}/\text{m}$ because we expected the onset of significant structural force to be in this range. We chose force curves of photoirradiated surface layers because the distinct periodicity they displayed. The average polyelectrolyte and bolaform amphiphile double layer thickness was estimated to be $149/2 = 74.5 \text{ \AA}$.

The surface roughness of six amphiphile and polyelectrolyte double layers is about 25 \AA , determined in the AFM measurement by the average peak to valley distance perpendicular to the plane of the substrate. This surface roughness is probably induced by the nonflat structure of the polyelectrolyte layers. The multilayer surface roughness of 25 \AA , though significantly bigger than the surface roughness of a mica piece and the first amphiphile monolayer (<1 \AA), is only 5.6% of the total layer thickness (450 \AA). It follows that despite the surface roughness and the low surface charge density, periodicity prevails in cationic amphiphile and anionic polyelectrolyte multilayer assembly.

In-Plane Ordering and Polymer Chain Conformation. Long-range molecular ordering was observed for the first bolaform amphiphile layer in air and in water with a unit cell area between 30 and 33 \AA^2 .^{23,26} However, the subsequent amphiphile multilayer surfaces in air were not molecularly smooth in the micron scale. Scanning of the multilayer surface in air in the range of $10 \times 10 \text{ nm}^2$ only displayed fuzzy images with no distinct surface features. This is probably due to the presence of mobile and nonflat underneath polyelectrolyte layers.

The multilayer system is highly photoreactive. The absorbance at 310 nm of a sample consisting of eight amphiphile and polyelectrolyte double layers is reduced to only 6.2% of its original value after 1 h of UV irradiation.²³ This implies that most of the C=C bonds in the monomers have reacted. Topochemical dimerization of phenylenediacrylic acid and cinnamic acid derivatives was only successful for highly ordered molecules since neighboring molecules have to be positioned uniquely with respect to each other to allow the conversion of two double bonds into a cyclobutane ring. The high photoreactivity of the multilayer system suggests that there is some ordering in the subsequent amphiphile layers. However, other techniques, such as spectroscopy methods, are needed to resolve the degree of in-plane ordering of the amphiphile multilayer films.

If the bolaform amphiphile DIPY08 packs closely with only one end attached to the surface in all subsequent layers and assumes the same layer thickness as the first anchoring (35 \AA) and there is no interdigitation between layers, the polyelectrolyte would have an average layer thickness of 39.5 \AA . A totally flat adsorption with the

polyelectrolyte chains oriented parallel to the surface would give a layer thickness of only 10 \AA or less.

It was commonly understood that an adsorbed isolated linear polymer chain consists of segments in trains (consecutive segments all in contact with the surface), loops (dangling in the solution bound by a train on each side), and tails (dangling in the solution with one end bound by a train).⁴⁸ It was shown both theoretically and experimentally that the adsorption of polyelectrolyte depends strongly on the substrate surface charge density, the fraction of charged monomers, the degree of charge dissociation of the polymer, the intrinsic chain flexibility, the ionic strength of the aqueous solution, and the polymer concentration.^{49–55} It was concluded from the studies, with a few exceptions, that a highly dissociated polyelectrolyte adsorbs flat, with the loop and tail formation suppressed, on a substrate with high charge density of the opposite sign in low salt solution.

The conformation of the PAMPSA polyelectrolyte adsorbed on a photopolymerized DIPY08 layer is not totally flat, as indicated by the estimated surface roughness (25 \AA) in air and thickness (39.5 \AA) of the layers in distilled water. PAMPSA is highly charged in distilled water. Every two hydrocarbons in the backbone is connected to one highly dissociated sulfonic acid group. The effective surface potential of the amphiphile layer is reduced after UV irradiation and further reduced after the deposition of more layers. The reduced electrostatic affinity might favors more loops than trains. Counterion condensation along the polyelectrolyte chain not only reduces the affinity between the polymer and the substrate but also results in a more coil-like conformation. Further adsorption after the surface saturation would also cause a transition from a flat conformation to a loopy conformation. Aggregates might be formed if there is a significant interchain association. However, the surface roughness does not grow with the multilayer deposition, which suggests that the amphiphile layers can bridge over the gap of the underneath layer and reverse the surface charge at the same time.

Film Stability and the Effect of Photoirradiation. Topochemical photopolymerization was only successful for highly ordered and closely packed molecular assemblies^{37–40} in which reactive double bonds of neighboring molecules could make close contact with each other to convert two double bonds into a cyclobutane ring. It was expected that the order in the self-assembled layers would be comparable to that of Langmuir–Blodgett mono- and multilayers. Thus, photopolymerization should be possible and lead to robust, yet flexible, multilayer films.

In a previous paper,²³ we have shown that photopolymerization of the bolaform amphiphile layer (1) increases the film resistance to external compression and disturbance; (2) maintains and maybe increases the film uniformity; and (3) lowers the surface charge of the monolayer by promoting counterion binding, which reduces the repulsion between head groups to accommodate the conversion of two adjacent double bonds to a cyclobutane ring. Also, photopolymerization of the first anchoring layer stabilizes the whole multilayer assembly.

(48) Jenkel, E.; Rumbach, B. *Z. Elektrochem.* **1951**, *55*, 612.

(49) Frisch, H. L.; Stillinger, F. H. *J. Phys. Chem.* **1962**, *66*, 823.

(50) Hesselink, F. Th. *J. Colloid Interface Sci.* **1977**, *60*, 448.

(51) Van der Schee, H. A.; Lyklema, J. *J. Phys. Chem.* **1984**, *88*, 6661.

(52) Cosgrove, T.; Obey, T. M.; Vincent, B. *J. Colloid Interface Sci.* **1986**, *111*, 409.

(53) Blaakmeer, J.; Böhmer, M. R.; Stuart, M. A. C.; Fleer, G. J. *Macromolecules* **1990**, *23*, 2301.

(54) Lukham, P. F.; Klein, J. *J. Chem. Soc., Faraday Trans. 1* **1984**, *80*, 865.

(55) Marra, J.; Hair, M. L. *J. Phys. Chem.* **1988**, *92*, 6044.

We were able to more clearly distinguish a photopolymerized film from a monomeric film by using an organic solvent such as chloroform. The much slower dissolution process of the UV-irradiated film proves that photopolymerization increases the film stability against chemical degradation. Statistically, desorption of a polymer chain is slower and more difficult than desorption of a monomer since all the segments in the polymer chain have to detach from the surface at the same time. But polymer desorption is possible when conditions are drastically changed from those prevailing during the adsorption experiment.

The dissolution of the photoirradiated film proceeds slowly enough to allow us observe the gradual development of solvent-etched regions. The circular shape of the holes suggests isotropic dissolution of film molecules. The continuous expansion of the holes we observed indicates that the monolayer film somehow allows the penetration of chloroform. We were not able to capture the initial stage of dissolution with AFM and can only speculate that the spots where holes originate are the defected spots which have not been revealed by simply incubating in water. These defected spots are most vulnerable to chloroform penetration. Once the solvent molecules seize the weakest points, they keep penetrating and enlarge the etched areas. But we do not know if these defects were created during film deposition or during the photopolymerization or came from contaminants in the environment.

In the surface measurement of bare mica and DIPY08 monolayer, surfaces were less attractive toward each other after the first approach for both the monomeric layer and polymeric layer even though the thickness at the adhesive contact remained the same. Photopolymerization in the monolayer might not be complete. We attribute the hysteresis to the exchange of amphiphile molecules between the original substrate and the bare mica surface. The fact that surface force before the adhesive contact was reached though reduced in magnitude is still pure attractive after the first approach means that film molecules were not evenly distributed between the two mica surfaces but preferred one surface to the other. This implies that a certain degree of integrity exists in the film.

Steric repulsive force between multilayers was almost always bigger when the surface layer was UV irradiated. The additional robustness contributed by photopolymerization of one layer was in most cases measurable by the surface force apparatus. Also, the better periodicity when the surface layer is photoirradiated is another indication of stabilization due to photoreaction. In fact, rapid deterioration of the multilayer assembly upon compression was observed when none of the layers were UV irradiated.

The difference in film stability and integrity as a result of UV irradiation has the potential of being applied to photolithography and patterning of surfaces.

Effect of Ionic Strength on Film Roughness. In salt-free water or at low ionic strengths, charge effects of the polyelectrolyte count most heavily. The polymer chain is extended and rigid due to mutual repulsion between the charged segments. At high ionic strengths, the charge effects are screened and the polymer chain becomes more flexible and coil-like, similar to a neutral polymer chain. An increase in salt concentration, on one hand, reduces the electrostatic attraction between the polymer and the substrate and, on the other hand, reduces the hydrodynamic volume of the polyelectrolyte coil and thus allows more polymers to adsorb on the substrate. Generally, the adsorbed amount increases with increasing salt concentration up to very high ionic strength.

In the AFM experiment, we find that the surface roughness of the multilayer is reduced from 30 Å to less than 10 Å if we adsorb the polyelectrolyte in the presence of 1 mol/dm³ salt. This better packing of the polyelectrolyte chains is due to the increased chain flexibility and reduced hydrodynamic coil size as a result of salt screening. In order to compare the adsorbed amount in the presence and in the absence of added salt, more surface force measurements have to be done.

Conclusions

We have measured interactions between two stacks of bolaform amphiphile and polyelectrolyte multilayers using the surface force apparatus. The multilayer is self-assembled via the electrostatic attraction between the cationic bolaform layer and the anionic polyelectrolyte layer. The bolaform amphiphiles in the multilayer are photopolymerizable when UV irradiated. The mechanical and surface electrical properties before and after UV irradiation have been explored and the effect of photopolymerization has been evaluated. Meanwhile, the multilayer surface topography has been studied by the atomic force microscopy. We have also started to study effects of the ionic strength and the organic solvent on film structural properties.

While a regular growth in film thickness with the number of layers has been observed, the molecular conformation and registration with respect to each other within a layer are difficult to probe using only the surface force apparatus and the atomic force microscope. The high photopolymerizability of the film is consistent with the model of closely packed bolaform amphiphile layers even though long-range order has never been observed in the multilayer system except for the first anchoring layer on a molecularly smooth mica surface. The lack of molecular order in the amphiphile layer under atomic force microscopy might be due to the underneath nonflat and possibly mobile polyelectrolyte layer. In some applications, a swollen and mobile layer eliminates the effect of a solid substrate and provides an appropriate support and flexibility for the functionality of subsequent layers. The bolaform amphiphile layer somehow can bridge over the gaps in the underneath layer and maintains a regular film growth and a surface roughness slightly less than a closely packed monolayer thickness.

We have tried photopolymerization in order to improve film stability against chemical, thermal, and mechanical degradation which is an essential issue in thin organic film applications. Chloroform etching proves to be a simple yet revealing method to study film chemical stability before and after UV irradiation. Photopolymerization increases the bolaform amphiphile film resistance to external pressure and chemical etching. But the multilayer film is still quite fragile, especially for the first few layers, as compared to chemically adsorbed layers, and defects have been identified in the monolayers. The photopolymerization process might be optimized by controlling the monolayer structure through selective variation of the amphiphile chemical structure.

Acknowledgment. This work was supported at the University of Minnesota by the Center for Interfacial Engineering, an NSF-supported Engineering Research Center. The authors thank Professor Michael D. Ward for the use of the CAChe computer drawing program.