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Self-Assembly of Photopolymerizable Bolaform Amphiphile Mono- and Multilayers

Guangzhao Mao, Yihua 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, 55099 Mainz, Germany

Mono- and multilayers of photopolymerizable bolaform amphiphiles and polyelectrolytes self-assembled onto mica from aqueous solution were studied by surface force measurement and atomic force microscopy. Multiple layers of positively charged amphiphiles self-assemble if a negatively charged polyelectrolyte is inserted between them. The layers can be photopolymerized with a high-pressure UV lamp. The atomic force microscopy images indicate that the photopolymerized amphiphile monolayer has a higher degree of order than the unpolymerized monolayer, although the latter possesses some long-range order. Mechanical properties of the system measured by the surface force apparatus indicate that a photopolymerized layer is more robust and demonstrate that the rigidity and integrity of the first anchoring layer greatly influence the stability of the multilayer. The interaction between polyelectrolyte layers in water can be either attractive or repulsive depending on the coverage of the polyelectrolyte on the amphiphile layer. The mica separation of a pair of opposed monolayers in contact in the presence of water is surprisingly small (25 Å) compared to the thickness (78 Å) of a bilayer composed of fully extended amphiphiles.

Introduction

Ultrathin organic films gained increasing interest during the last decade due to their possible applications in modern surface technology, e.g., in optical, sensor, and coating techniques.[1,2] Several thin film preparation methods have been studied: the Langmuir–Blodgett (LB) technique,[3,4] spin coating,[5] and chemisorption[6–8] techniques. The preparation method can influence the properties of the films by affecting the structure and degree of order in the films.

Films containing both polymers and surfactants offer many interesting possibilities for manipulating their structure and properties. Self-assembly via physical adsorption is a particularly simple means of creating such films. It needs neither preformation of oriented films nor special equipment. Electrostatically attractive interaction of the hydrophilic headgroups and appropriate substrates, such as negatively charged mica, forces molecules to pack closely on the substrate. Short-range van der Waals forces between amphiphile molecules become important. Thus, organic molecules can spontaneously form highly ordered and oriented layers. The present work examines structures created by self-assembly of alternating amphiphile/polymer multilayers.

Self-assembly by physical adsorption of cationic surfactants onto mica has been used by Tsao and Evans in

some of their recent work.[9] A similar concept was described recently for the self-adsorption of dipolar cationic/anionic amphiphiles[10] and cationic/anionic polymers[11] and mixed systems of both dipolar amphiphiles and polymers[12] by Decher et al. Regular multilayers were thus prepared on a chemically modified quartz surface by a simple dipping technique from solutions of the amphiphiles or polymers. By alternate adsorption of anionic and cationic molecules, more than 70 layers were built up.

This paper describes the alternating self-assembly of a photoreactive bolaform phenylenediacrylic acid amphiphile with two pyridinium headgroups in the α and ω positions (DIPY08) and an anionic poly(sulfonic acid) (PAMPSA) (Figure 1) on mica surfaces with the goal to study the surface properties by surface force measurements and atomic force microscopy (AFM).

Topochemical photopolymerization of phenylenediacrylic acid and cinnamic acid derivatives has already been reported, but was only successful for highly ordered molecules, e.g., in the crystalline state and in monolayers.[13–15] It was expected that the order in the self-assembled layers would be comparable to that of LB mono- and multilayers. Thus, photopolymerization should be possible and might increase the rigidity of self-assembled layers and lead to robust, yet flexible, self-assembled multilayers.

In the work reported here surface force and AFM techniques have been used to study the buildup of DIPY08/PAMPSA multilayers and the effects of photopolymer-

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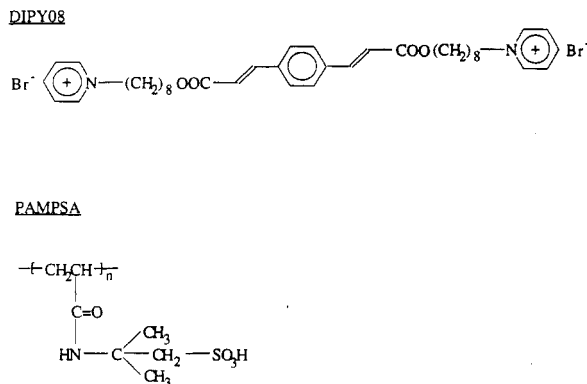
DIPY08

PAMPSA

Figure 1. Structure of the bolaform phenylenediacrylic acid derivative (DIPY08) and poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPSA).
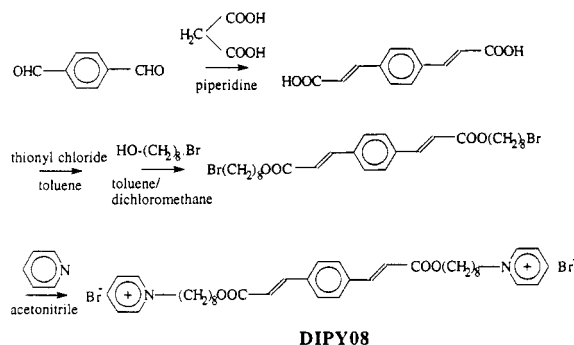

DIPY08

Figure 2. Synthesis of the bolaform phenylenediacrylic acid derivative amphiphile (DIPY08).

ization on the structure and properties of the layers. Because of the high water solubility of the bolaform amphiphile DIPY08 and its strong adsorption onto negative surfaces, dipping mica sheets in aqueous solutions affords a convenient way to prepare samples for the surface force and AFM measurements.

The amphiphile was designed for the purpose of constructing physically adsorbed multilayers to contain central phenylenediacrylic acid groups as a rigid core, connected to cationic pyridine end groups via flexible alkyl chains of eight carbons each. The surface charge of mica is reversed by adsorbing bolaform cationic amphiphiles. An end-on adsorption maintains a maximum charge density and thus is desirable. The length of the flexible part of the amphiphile is chosen to be not too short or too long to increase an end-on adsorption of the bolaform amphiphile and to minimize flat and looplike adsorption.[10] In addition, this end-on adsorption will be stabilized via mesogenic interaction of the phenylenediacrylic acid groups as already shown for the biphenylene units by Decher et al.[10]

Materials and Methods

Materials. The bolaform phenylenediacrylic acid amphiphile was synthesized in three steps (see Figure 2). First, a Knoevenagel condensation of terephthaldialdehyde and malonic acid (E. Merck, West Germany) in pyridine leads to the *p*-phenylenediacrylic acid. The diacid was converted to its diacid dichloride by reaction in boiling toluene and SOCl₂. Second, the diacid dichloride was esterified with 8-bromo-1-octanol in a mixture of toluene and dichloromethane. Third, the diester was quaternized with pyridine in acetonitrile.

***p*-Phenylenediacrylic Acid.** The reaction was carried out according to the literature.[16] Yield: 84.7%. Melting point: 360 °C dec. Anal. Calcd: C, 65.9; H, 4.5. Found: C, 66.0; H, 4.5.

(16) Ruggli, P.; Theilheimer, W. *Helv. Chim. Acta* **1941,** *24,* 899.

^{1}H NMR (DMSO-d_6, 200 MHz, ppm): of 6.60 (d, –CH=CHCOOH, 2H); 7.60 (d, –CH=CHCOOH); 7.78 (s, phenyl ring, 4H); 12.48 (s, –COOH, 2H). IR (FT-IR, KBr, cm⁻¹): 982 (=CH, δ) 1224 (C—O, ν), 1624 (C=C, ν), 1693 (C=O, ν), 3061 (=CH, ν), 3400 (CO—OH, ν).

***p*-Phenylenediacrylic Acid Dichloride.** *p*-Phenylene diacrylic acid (15 g, 69 mmol) and thionyl chloride (45 g, 378 mmol) in 200 mL toluene were refluxed for 4 h. Five drops of the catalyst DMF were added. When the mixture was cooled, the diacid dichloride precipitated as yellow needles. The mixture was filtered carefully (excess thionyl chloride!). The crude product was recrystallized in toluene. Yield: 77.0%. Melting point: 170 °C. IR (FT-IR, KBr, cm⁻¹): 978 (=CH, δ), 1224 (C—O, ν), 1623 (C=C, ν), 1739 (C=O, ν), 3035 (=CH, ν$_s$), 3064 (+CH, ν$_{as}$).

8-Bromo-1-octanol. 8-Bromo-1-octanol was synthesized by a standard procedure.[17] Yield: 66.2%. n^{20}_D: 1.4762. Boiling point: 89–90 °C (0.03 mbar). ^{1}H NMR (CHCl₃, 200 MHz, ppm): δ 1.27 (m, –(CH₂)₄(CH₂)₂Br, 16H); 1.53 (t, –CH₂CH₂Br, 4H); 1.85 (t, HOCH₂CH₂–, 4H); 3.35 (t, –CH₂Br, 4H); 3.59 (t, HOCH₂–, 4H).

***p*-Phenylenediacrylic Acid Bis(11-bromoundecyl ester).** Diacrylic acid (8 g, 31.4 mmol) was dissolved in 50 mL of hot toluene and added dropwise to a stirred solution of 14.0 g (66.8 mmol) of 8-bromo-1-octanol and 6.7 g (66.8 mmol) of triethylamine in 70 mL of dichloromethane. The solution was refluxed for 2 h and stirred at room temperature overnight. After evaporation of the solvent the crude residue was dissolved in ether. The precipitated triethylamine–hydrochloride was filtered. The filtrate was shaken with 0.1 N HCl, saturated aqueous NaHCO₃ solution, and water. After drying over MgSO₄ the solvent was evaporated. The crude product was purified via flash chromatography. Dichloromethane was used as the solvent. Yield: 11.2%. Melting point: 92–93 °C. Anal. Calcd: C, 56.0; H, 6.7; Br, 26.7. Found: C, 56.5; H, 6.7; Br, 25.8. ^{1}H NMR (MeOH-d_4, 200 MHz, ppm): δ 1.30 (m, –(CH₂)₄(CH₂)₂Br, 16H); 1.68 (t, –CH₂CH₂Br, 4H); 1.82 (t, –COOCH₂CH₂–, 4H); 3.39 (t, –CH₂Br, 4H); 4.19 (t, –COOCH₂–, 4H); 6.43 (d, –CH=CHCOO–, 2H); 7.50 (s, phenyl ring, 4H); 7.62 (d, –CH=CHCOO–, 2H).

***p*-Phenylenediacrylic Acid Bis(11-pyridinium-*N*-yl undecyl ester) Dibromide (DIPY08).** Diester (2.1 g, 3.65 mmol) and pyridine (5.8 g, 73 mmol) were stirred in 50 mL of acetonitrile at 70 °C for 2 weeks (under an argon atmosphere). The mixture was added dropwise to 500 mL of dry ether, which was stirred. A white solid precipitated. After a night in the refrigerator the ether suspension was filtered. The pure white solid was dissolved in millipore water and freeze dried. Yield: 90.5%. Melting point: 177 °C. Anal. Calcd: C, 60.2; H, 6.6; N, 3.7; Br, 21.1. Found: C, 59.2; H, 6.7; N, 4.0; Br, 19.8. ^{1}H NMR (MeOH, 200 MHz, ppm): δ 1.26 (m, –(CH₂)₄(CH₂)₂Br, 16H); 1.61 (t, –CH₂CH₂Br, 4H); 1.90 (t, –COOCH₂CH₂–, 4H); 4.15 (t, –COOCH₂–, 4H); 4.63 (t, –CH₂N=, 4H); 6.71 (d, –CH=CHCOO–, 2H); 7.64 (d, –CH=CHCOO–, 2H); 7.79 (s, phenyl ring, 4H); 8.17 (t, –N=CHCH=CH–, 4H); 8.62 (t, –N=CHCH=CH–, 4H); 9.17 (d, –N=CHCH=CH–, 2H).

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 used in surface force experiments was certified ACS sodium bromide crystal, received from Fisher Scientific, used without further purification.

Surface Preparation. Grade 2, muscovite ruby mica purchased from United Mineral and Chemical in New York was hand-cleaved and used as the main substrate. Mica surfaces are negatively charged (1 per 0.48 nm²) in water because of the dissociation of potassium counterions from mica lattice sites. Water was filtered through a Millipore purification system and was processed with a Water Prodigy polishing unit from Labconco Corp. The bolaform amphiphile DIPY08 as already described was stored in the solid state as prepared and kept away from light as much as possible. Freshly cleaved mica sheets were used for multilayer deposition by a procedure similar to that used by Decher et al.[10] A clean mica sheet was first placed in DIPY08 aqueous solution in a small nitric acid-cleaned flask. The DIPY08

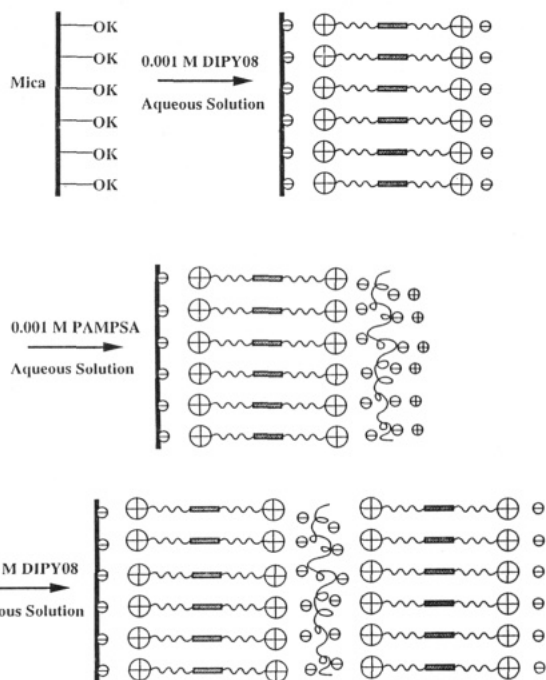(17) Kang, Y.; Kim, W. S.; Moon, B. H. *Communications* **1985,** 1161.

Figure 3. Schematic of cationic bolaform amphiphile (DIPY08) and anionic polyelectrolyte (PAMPSA) multilayer self-assembly on mica.

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 for DIPY08) to avoid the possibility that micelles instead of isotropically dissolved monomers might adsorb on mica. After 30 min of immersion the mica sheet was lifted from the solution with a tweezer holding an edge of the mica and was rinsed by pouring 500 cm³ of water slowly onto the sheet. We then placed the mica in 0.001 mol of monomer units/dm³ PAMPSA aqueous solution and let the adsorption proceed for 30 min. The mica was again lifted from the solution and rinsed with 500 cm³ of water by pouring water slowly onto the mica. The above procedures of depositing DIPY08/PAMPSA layers were repeated to allow multilayers self-assembled on mica (Figure 3). The mica surface bearing the adsorbed layers was dried in a laminar hood at room temperature before characterization measurements were carried out.

The above procedures of surface preparation followed in the UV and AFM studies were adapted in the surface force measurements and will be mentioned in the part where this technique is described.

Photopolymerization. Photopolymerization of the mica-mounted mono- and multilayers was carried out in a laminar hood at room temperature by UV irradiation for up to 30 min with a 200-W Hg/Xe ozone-free lamp purchased from Oriel Corp.

UV Molecular Absorption Spectrophotometry (UV Spectrometry). The UV spectra were taken using the HP 8452A diode array spectrphotometer from Hewlett-Packard. The HP 8452A diode array spectrometer is a single-beam, microprocssor-controlled, UV–vis spectrometer with collimating optics and measures wavelengths from 190 to 820 nm with a wavelength accuracy of ±2 nm and photometric accuracy of ±0.005 AU. The bare mica was used as the reference (or blank) and was cleaved as uniformly thin as possible in order to obtain a good baseline spectrum. Mica absorbs strongly at wavelengths below 285 nm and has a flat baseline spectrum above 285 nm. The spectrum of a mica piece bearing adsorbed layers was measured several times at different areas and was plotted when there was no noticeable difference between each run. The reported intensities are the peak intensities at 310 nm minus intensities at 400 nm where neither the sample nor mica absorbs to reduce the effect of baseline fluctuation.

Atomic Force Microscopy (AFM). The self-assembled layers on mica were visualized by atomic force microscopy using a Digital Instruments Nanoscope II in air at room temperature. In the AFM experiments, mica bearing adsorbed layers was glued
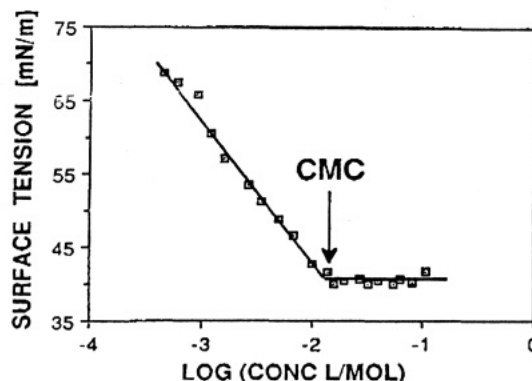

Figure 4. Surface tension measurement of the bolaform amphiphile DIPY08.

onto a stainless steel disk. The AFM apparatus was operated at a minimum force on all surfaces studied. Si_3N_4 probes from Digital Instruments were used. The spring constant of the cantilever was 0.58 N/m. A 0.7- or a 12-μm scanner was used. Both were calibrated with highly oriented pyrolytic graphite (HOPG; Union Carbide Corp.) and muscovite mica (Union Mica Corp.).

Surface Force Apparatus (SFA). The forces between mica-mounted bolaform amphiphile/polyelectrolyte layers were measured using the method developed by Israelachvili et al.[18] with a modified measurement and control system replacing the translator-mounted eyepiece with a slow scan, liquid-cooled videacamera (Model Star I, Series 300, Photometrics Ltd., Arizona).[19] A computer analyzes the digitized videocamera signal. This new measurement system simplifies instrument operation and improves measurement consistency and resolution. The 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 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 semilog or linear plots of F/R versus D, where F is the measured force and R is the measured mean radius of curvature of the mica surfaces in the region where they are interacting. The distance D reported here is relative to the measured water contact position of the bare mica surfaces. The quantity F/R is equal to 2π times the free energy per unit area of interaction between two flat surfaces[20] and is used as a way of normalizing the data. The cleanliness of mica surfaces is checked by bringing the two surfaces into contact in both air and water. Drops (~0.4 cm³) of DIPY08 0.001 mol/dm³ stock solution were injected through a millipore filter (0.22 μm) in between the two mica surfaces (because of the limiting amount of amphiphiles we have). After 30 min of adsorption, the force measurement chamber was rinsed thoroughly with distilled water and filled with distilled water. Salt solution or PAMPSA solution was added to the aqueous phase in the apparatus with a needled syringe. After at least 4 h of mixing and adsorption, the measuring chamber was rinsed thoroughly with distilled water. Force profiles presented here were obtained in distilled water, with or without added salt. The temperature was controlled at 298.5 K.

Results and Discussion

Surface Tension Measurement. The critical micelle concentration (cmc) of the bolaform amphiphile DIPY08 was determined by surface tension measurement using the ring method (Figure 4). Several stock solutions of the amphiphile with different concentrations were prepared

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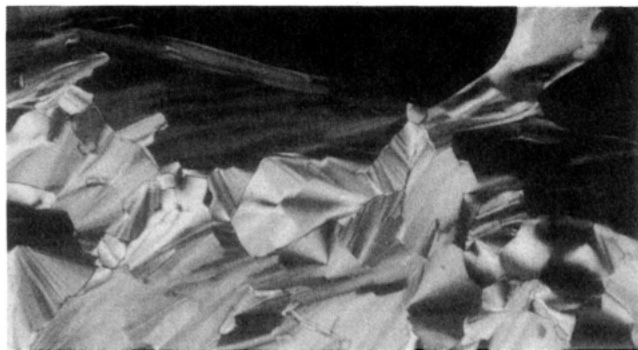
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Figure 5. Polarization microscopy measurement. The DIPY08 sample (50.5 mass %) in water forms a lyotropic mesophase at 35.5 °C.

Monomer: 320 nm   Polymer: 286 nm

Figure 6. Idealized schematic structure of stepwise [2 + 2]-cycloaddition of the multipolar amphiphiles.

Figure 7. UV absorption measurement of amphiphile/polyelectrolyte multilayers. Absorbance at 310 nm in the sample spectrum is plotted against the number of treatments of the substrate with amphiphile and polyelectrolyte solutions. A straight line is drawn through the data points to indicate a linear relation between absorbance and number of treatments.

and measured. To get more data points, some of these stock solutions were diluted after the first measurement. The measured cmc of DIPY08 is 1.5×10^{-2} mol/dm³, a value quite reasonable for an amphiphile with about eight to ten hydrophobic CH_2 groups per headgroup. The surface tension is 41 mN/m at the cmc, a rather low value compared to the surface tensions observed previously for similar bolaform amphiphiles.[21,22] These similar bolaform amphiphiles usually yield a surface tension of about 50 mN/m at the cmc. The area occupied by the amphiphile DIPY08 at the interface can be calculated from the slope of the surface tension versus logarithm of concentration plot (Gibbs adsorption isotherm).[21,22] The average area occupied by an adsorbed molecule at the water–air interface calculated from the slope in Figure 4 is 151 Å², a value consistent with a looplike conformation with both cationic pyridine headgroups located at the water–air interface and the hydrophobic part lifted clear.

Polarization Microscopy Measurement. A 50.5 mass % sample of DIPY08 in water was a biphasic mixture (isotropic/crystalline) at room temperature. Upon heating, the mixture became biphasic isotropic/lyotropic at 48 °C. At 59 °C the sample was only isotropic and showed no birefringence anymore between crossed polarizers. Figure 5 shows a lyotropic mesophase at 35.5 °C, which was heated to the isotropic region first and cooled. The lyotropic mesophase does not show the typical mosaic texture, which is usually typical for a lamellar mesophase. An exact structure analysis can only be made by X-ray measurements.

The surface tension measurement demonstrates the ability of the bolaform cationic amphiphile DIPY08 to form micellar aggregates at low concentrations, while the polarization microscopy measurement shows that lyotropic mesophases are built up at high concentrations. This strong tendency toward aggregation should assist the formation of multilayers on solid supports.

UV Spectrometry Study. The sequential adsorption of bolaform amphiphile/polyelectrolyte layers on mica and the photopolymerization process of the adsorbed layers were monitored by UV molecular absorption spectrophotometry. DIPY08 belonging to the category of photopolymerizable rigid conjugated diolefins absorbs UV light at 320 nm in dilute aqueous solution and shifts its absorbance slightly to 310 nm when absorbed on mica. The UV absorption peak appears at 286 nm following the four-center photopolymerization process forming 1,3-*trans*-cyclobutane rings in the polymer main chain with the
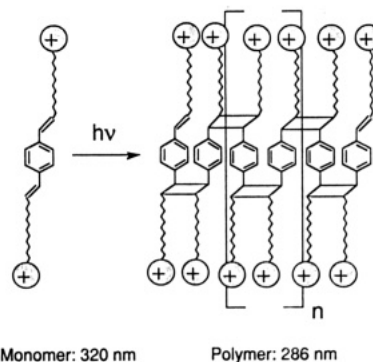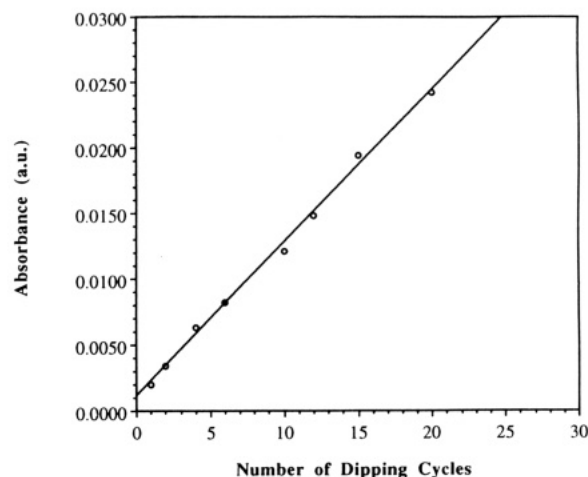
disappearance of aliphatic >C=C< bonds (Figure 6). In Figure 7, the absorbance of the self-assembled layers at 310 nm—proportional to the amount of the conjugated diolefin groups in the monomer film—is plotted against the number of dipping cycles of the substrate. Here each dipping cycle includes dipping a substrate in the bolaform amphiphile solution, rinsing it with distilled water, dipping it in the polyelectrolyte solution, rinsing it with water, and drying it in air before the next measurement. The linear increase of the absorbance maximum at 310 nm with the number of dipping cycles is a clear indication that with each treatment an equal amount of amphiphile molecules was adsorbed onto the substrate.

DIPY08 amphiphile molecules containing conjugated *p*-phenylenediacrylic groups were photopolymerized in the adsorbed state with a high-pressure Hg/Xe lamp followed by the diminishing of the absorbance peak at 310 nm in the UV spectrum. The photopolymerization of the conjugated diolefins is a four-center topochemical [2 + 2]-photocyclodimerization reaction.[14,23,24] Figure 8 shows plots of the absorbance versus wavelength at various times for a sample consisting of eight amphiphile/polyelectrolyte layers on mica. From the rapid reduction of the peak at 310 nm after 5 min of UV irradiation, it can be concluded that most of the C=C bonds of the DIPY08 monomers have reacted. After 1 h of UV irradiation the absorbance

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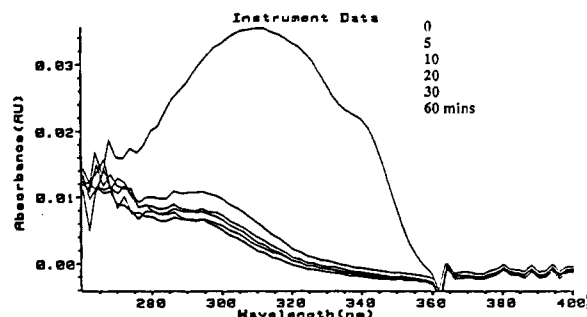(24) Ramamurthy, V.; Venkatesan, K. *Chem. Rev.* **1987**, *87*, 433.

Figure 8. UV spectra or eight DIPY08/PAMPSA layers self-assembled on mice UV irradiated at different times.

at 310 nm remains the same. Thus, the photoreaction can be considered to be finished.

Surface Force Measurements. The surface force apparatus has traditionally been used to study colloidal interactions between various surfaces.[25] An understanding of the interaction between charged and uncharged amphiphilic layers in aqueous solutions is essential to an understanding of the properties of membranes and membrane mimetic systems, soap films, emulsions and microemulsions, and surfactant solutions. Force measurements between deposited amphiphilic mono- and bilayers prepared by either the Langumuir–Blodgett dip-coating or self-assembly method have been reported over the past several years.[26-30] DLVO force laws, named after its originators, Derjaguin, Landau, Verwey, and Overbeek,[31] including van der Waals force and electrostatic force do not always account for the surface force profiles measured experimentally. Other more subtle interactions, such as hydration forces, hydrophobic forces, undulation forces, and protrusion forces, have been identified as observations on smaller distance scales and at greater precision have been accomplished. Interactions between surface-bound neutral and charged polymeric amphiphiles in aqueous solutions have also been studied by the surface force apparatus.[32-35] These studies revealed a more complex nature of polymer-mediated interactions including steric forces, osmotic forces, and bridging effects, and sometimes these force measurements are coupled with hysteresis. Here we present a model system with alternating cationic photopolymerizable bolaform amphiphiles and anionic preformed polyelectrolyte layers in order to study the combined effects of forces of various origins as briefly mentioned above when encountered in our system. In addition, the effect of photopolymerization of deposited films on the film properties was investigated for the first time with the surface force apparatus.

Monolayers of the Monomeric and Polymeric Phenylene Diacrylic Amphiphile DIPY08 (DIPY08 Monolayers). Contact positions between bare mica surfaces
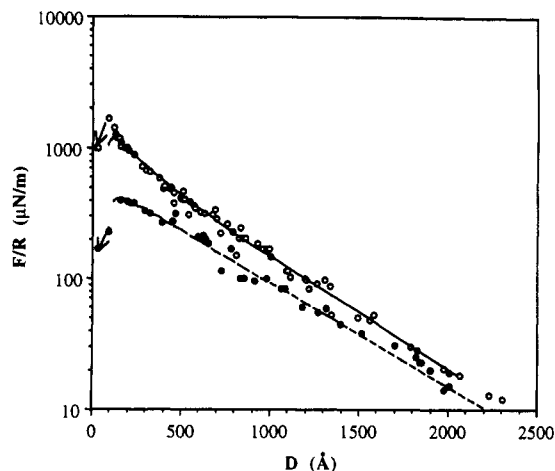
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Figure 9. Surface force profiles (F/R vs D) between DIPY08 monolayers before and after UV irradiation on mica in distilled water at 298.5 K. The open and shaded circles are experimental data for monomeric and polymeric amphiphile layers, respectively. Inward arrows represent inward jumps. The lines represent DLVO "best fits" assuming constant surface potential, a 1:1 electrolyte, and a nonretarded van der Waals interaction with an estimated Hamaker constant of 1.0×10^{-20} J. The solid line fits the measured force between monomeric DIPY08 layers assuming a surface potential of 106 mV, a bulk ionic concentration of 3.89×10^{-5} mol/dm³, and a shift of the location of the charged surface groups and water interface about 34 Å presumably due to the existence of the adsorbed layers deduced from the distance where the measured force starts to deviate from the DLVO prediction ($D = 68$ Å = 2×34 Å). The dashed line fits the measured force between polymeric DIPY08 layers assuming a surface potential of 71 mV, a bulk ionic concentration of 3.40×10^{-5} mol/dm³, and a shift of the location of the charged surface groups and water interface of 35.5 Å by matching the distances of the measured force maximum and the DLVO predicted force maximum ($D = 71$ Å = 2×35.5 Å) (force-maxima-matching method).

were measured in air and in distilled water before any amphiphile samples were introduced into the system in order to check the cleanliness and to define a reference position. Figure 9 displays surface force profiles between two identical DIPY08 monolayers on mica in distilled water before and after 30 min of UV irradiation *in situ* and the mean-field DLVO theoretical fits. The theoretical DLVO curves were calculated using an exact numerical solution[36] to the Poisson–Boltzmann equation assuming constant surface potential and a nonretarded van der Waals interaction using a Hamaker constant of 1.0×10^{-20} J, which should be about that expected for a hydrocarbon layer on mica. We observed long-range repulsive double-layer interactions beyond a surface separation of about 150 Å between both unpolymerized and photopolymerized amphiphile monolayers.

Upon further compression, the two surfaces jump into a strongly adhesive contact position of 25 ± 5 Å indicated by flattened fringe tips due to the deformation of the glue between the mica and the lens on which it is mounted. The jump between polymeric DIPY08 layers was rather sluggish ($\sim$5 min) compared to jumps between bare micas and between monomeric DIPY08 layers (<1 min). The surfaces coated with polymeric DIPY08 layers were pulled toward each other slowly and spontaneously, and at least one data point in each run could be recorded in the time interval of 5 min at an intermediate separation between the force maximum and adhesive contact.

The slope of the logarithm of the double-layer part of the force curves remains the same before and after UV

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irradiation. The ionic concentration calculated by fitting DLVO theory to experiment is $(3.65 \pm 0.25) \times 10^{-5}$ mol/dm³ corresponding to a Debye length of about 505 Å in both cases. This concentration is consistent with that deduced from the electrical conductivity measurement of our distilled water, which is saturated with the ambient atmosphere of CO_2. From DLVO fits to data, it follows that photopolymerization reduces the surface potential of the amphiphile layers. The surface potential between monomeric layers lies between 121 and 106 mV, the uncertainty being in the location of the charged groups and the water interface. A surface potential of 106 mV is obtained if the position of the charge interface is placed where the repulsive force begins to rise above the DLVO curve. The surface potential of the polymeric DIPY08 layer was determined in two steps: the first was to fit the slope of the experimentally measured double-layer interaction curve with a DLVO curve by varying the surface potential and Debye length; then the DLVO curve was shifted along the D axis so that the two force maxima obtained by experiment and theory also overlapped each other. The "force-maxima-matching" method should give a relatively accurate estimate of the magnitudes and positions of force barriers because we used a relatively soft spring with a spring constant of 1.166×10^2 N/m in our experiments, so the jumps into contact at the force maximum occur very close to where the force actually peaks. The unperturbed DIPY08 monolayer thickness (defined as the layer thickness before strong adhesion occurs) obtained in this way is 35 ± 5 Å which is comparable to a layer thickness of 38.3 Å estimated with a model assuming that only one end of the amphiphile is adsorbed and that it is in a fully stretched molecular configuration. At this point we have no other experimental data on the layer thickness of DIPY08 adsorbed on mica in water to verify the value obtained by our DLVO fit of the surface force measurement.

Surface force profiles between DIPY08 monolayers self-assembled on mica before and after UV irradiation were also obtained in an aqueous solution of 10^{-4} mol/dm³ NaBr. The results are shown in Figure 10. NaBr stock solution was injected through a filter into the force measuring chamber up to a final NaBr concentration around 10^{-4} mol/dm³. A detectable repulsive force arises at about 1500 Å and increases exponentially with decreasing D until a force maximum is reached at about 107 Å. Surfaces jump into an adhesive contact very much the same as in distilled water. As expected we observed a Debye length estimated from DLVO theory of 300 ± 5 Å corresponding to an ionic concentration of $(1.03 \pm 0.03) \times 10^{-4}$ mol/dm³. Again we observed a surface potential drop from 105 to 73 mV after photopolymerization. The unperturbed layer thickness estimated by the force-maxima-matching method is about the same as that of distilled water. However, in the presence of the NaBr, the small deviation of the repulsive force from the DLVO theory is not observed. A sluggish jump was also observed between polymeric DIPY08 layers in the presence of added salt.

These force profiles we have observed agree remarkably well with the DLVO theory between charged surfaces in 1:1 electrolyte solutions at all but small surface separations where structural effects are no longer negligible. The range of double-layer interaction decreases significantly with the slight increase in bulk ionic concentration from 3.6×10^{-5} to 10^{-4} mol/dm³ whereas the surface potential is less sensitive to ionic concentration. The difference between monomeric DIPY08 layers in pure water and in 10^{-4} mol/dm³ NaBr solution at the short range is very subtle in that
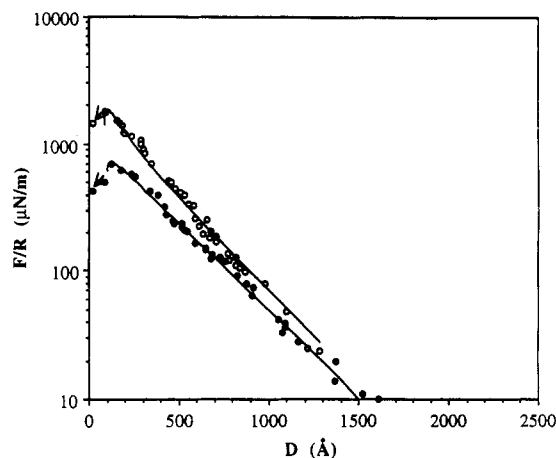

Figure 10. Surface force profiles of DIPY08 monolayers before and after UV irradiation on mica in 1×10^{-4} mol/dm³ NaBr aqueous solution at 298.5 K. The open and shaded circles are experimental data for monomeric and polymeric amphiphile layers, respectively. Inward arrows represent inward jumps. The lines represent DLVO best fits assuming constant surface potential, a 1:1 electrolyte, and a nonretarded van der Waals interaction with an estimated Hamaker constant of 1.0×10^{-20} J. The solid line fits the measured force between monomeric DIPY08 layers assuming a surface potential of 105 mV, a bulk ionic concentration of 1.06×10^{-4} mol/dm³, and a shift of the location of the charged surface groups and water interface about 35 Å determined by the same force-maxima-matching method. The dashed line fits the measured force between polymeric DIPY08 layers assuming a surface potential of 73 mV, a bulk ionic concentration of 0.995×10^{-4} mol/dm³, and a shift of the location of the charged surface groups and water interface of 36 Å using the force-maxima-matching method.

the magnitudes of interaction and the jump positions are about the same in the absence and in the presence of added salts. The hydration-like small bump in the force profile observed in distilled water becomes undetectable in the presence of a small amount of added salt, perhaps a result of reduced contrast due to the slope increase. The inward jump between the surfaces presumably is due to van der Waals interaction since the only other likely attractive force, the hydrophobic force, can be ruled out because of the strongly hydrophilic nature of DIPY08 layers, which is proved by its high water solubility.

Photopolymerization reduces the magnitude of the repulsion peak reflected by an apparent surface potential drop, implying that either the attraction component is stronger or the repulsion component is weaker or both between the two surfaces. The difference in the Hamaker constant between monomeric and polymeric amphiphile layers does not alter the magnitude or the position of the repulsion peak much and thus is neglected in our consideration. It is reasonable to consider mainly the effect of electrostatic interaction because of the good agreement with the DLVO theory. The reduction in surface potential and surface charge density after photopolymerization implies that the polymeric layer surface associates more with counterions than the monomeric layer surface; in other words, the photopolymerization process promotes ion-binding to the hydrophilic surface groups. Topochemical photopolymerization was only successful for highly ordered and closely packed molecular assemblies[13-15] in which reactive double bonds of neighboring molecules could make close contact with each other to convert two double bonds into a cyclobutane ring. However, the average spacing between neighboring DIPY08 molecules determined from the AFM measurements which will be discussed in the following section is bigger than a carbon–carbon bond distance. It has been suggested[2] that if the

self-assembly of organic molecules to the underlying substrate is to enforce a lattice spacing larger than 4.24 Å (optimum van der Waals contact distance), the molecules would be expected to "tip" away from the normal in such a way as to establish again optimum van der Waals contacts. Close-packing of molecules containing rigid, bulky groups embedded in semiflexible alkyl chains, such as in the case for DIPY08, results in a larger free volume for the alkyl chains as compared to molecules without the bulky groups. Distortion of molecules by the reorientation of the bulky groups in addition to tilting of the alkyl chains might minimize the total free energy depending on the competition between the elastic energy associated with the internal degrees of freedom and the van der Waals interactions responsible for the close-packing. Similarly it can be argued that the tilting of alkyl chains and/or reorientation of the photoreactive phenylenediacrylic acid groups in the self-assembled DIPY08 monolayers help bring neighboring reactive double bonds to the contact distance required by photopolymerization while maintaining the average translational distance between molecules. At this point, we cannot see experimentally molecular tilting or other molecular reorientations resulting from photopolymerization in DIPY08 monolayers. In any case, our observed surface potential suggests that photopolymerization adds more hydrophobicity into DIPY08 monolayers, perhaps a result of molecular reorientations in the monolayer, which dehydrates the surface groups, hinders the dissociation of counterions, and promotes ion-binding with the consequent reduction of the surface potential.

Another piece of evidence of the photopolymerization-induced ion-binding in the system comes from the electrical conductivity measurement made by Wibbing[37] on the micellar solution of amphiphile DIPY11. DIPY11 has a structure similar to that of DIPY08 except it contains eleven carbons in each alkyl chain instead of eight. The variation of electrical conductivity of DIPY11 aqueous solutions with DIPY11 concentrations reveals a cmc and a C_t (C_t is defined as the transition concentration of the surfactant microstructure). At the C_t, the microstructure of the amphiphiles changes, probably from a spherical to a lamellar structure. Then a concentrated solution of DIPY11 is irradiated with UV light in order to photopolymerize the micellar aggregates. Again, the electrical conductivity is measured for the polymeric solution. Now only a cmc = C_t is found. The amount of dissociated counterions α can be calculated from the slope of the conductivity after the cmc versus the slope of the conductivity before the cmc. α is 0.60 for the monomer, but is 0.30 for the polymer. Thus, the amount of dissociated counterions is significantly higher for the monomer than for the polymer. The stronger binding of the counterions to the polymer is a direct consequence of the reduced distance between the headgroups because of covalent linkage.

The other peculiar feature in force profiles at a short interaction range is the sluggish jump when bringing two photopolymerized DIPY08 monolayers toward each other. We did not observe such slow movements of surfaces pulled toward each other with the unpolymerized DIPY08 monolayers. The reduced mobility of photopolymerized DIPY08 layers perhaps results from the covalent bonding induced between neighboring molecules. This strong interconnectedness will rquire collective and thus slower rearrangements as the surfaces are drawn together by adhesion.
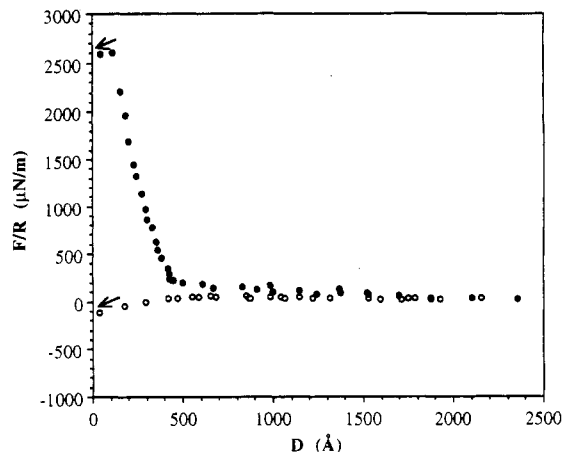
(37) Wibbing, M. Unpublished results.

Figure 11. Surface forces profiles of PAMPSA adsorbed on photopolymerized DIPY08 layers on mica in distilled water at 298.5 K (linear plot of F/R vs D). The open and shaded circles are experimental data at two solution concentrations of PAMPSA: 3.384×10^{-5} g/dm^3 (or 1.633×10^{-7} mol of monomer units/dm^3) and 2.211×10^{-1} g/dm^3 (or 1.067×10^{-3} mol of monomer units/dm^3), respectively. Inward arrows represent inward jumps.

The final separation of the surfaces corresponds to a puzzlingly small monolayer thickness of about 12 Å, implying a rather flat molecular configuration and reduced adsorbed amount at the contact spots. There is thus some sort of "thinning" of monolayers after the adhesive jump. This must be a result from molecular rearrangement and reorganization at the interface. We imagine somehow in the adhesive contact process some DIPY08 molecules are pushed down into a relatively flat position while other molecules may be squeezed out of the contact surface areas, possibly to accumulate at the edges just outside the contact areas. However, permanent desorption of DIPY08 is unlikely to occur since no hysteresis in the force measurement was observed when we repeatedly separated and rejoined the two surfaces 4 h after the first measurement. This indicates that molecules are able to relax back into the original monolayer configuration when the adhesive force is taken away. Unfortunately, we cannot give a more convincing explanation of what is going on at this point in time.

Layers of the Anionic Polyelectrolyte PAMPSA Adsorbed on Layers of the Bolaform Amphiphile DIPY08 (DIPY08/PAMPSA Layers). The next step in our multilayer construction is to adsorb negatively charged polyelectrolyte PAMPSA onto positively charged DIPY08 monolayer surfaces. The polyelectrolyte concentration was varied by successive injection of PAMPSA stock solution into the aqueous phase in the surface force apparatus. Surface forces were measured in PAMPSA-free distilled water after each injection of the stock solution. Figure 11 displays surface force profiles between PAMPSA layers adsorbed at two concentrations on photopolymerized DIPY08 monolayers in distilled water at 298.5 K. In the case of a lower polymer concentration (1.633×10^{-7} mol of monomer units/dm^3), two surfaces were largely neutralized and hardly any forces were observed until around 450 Å where the interactions become detectably attractive. The magnitude of the attractive force continued to increase as the surfaces were brought closer. The surfaces were pulled toward each other slowly and spontaneously until reaching a final separation of 39 ± 5 Å which was indicated by flattened fringe tips. Next a stock solution of PAMPSA was added to the apparatus to obtain a polymer concentration of 1.067×10^{-3} mol of monomer units/dm^3. After equilibration and replacement

of the solution by distilled water the surface force was measured again. The surface forces in this case were small and repulsive and increased exponentially with surface separation from 2500 to 450 Å. Analysis of this region with DLVO theory yields a Debye length similar to that of distilled water. At around 450 Å the slope of the force profile takes a sharp turn upward, indicating an onset of structural forces. Surface forces continued to increase with further compression until 110 ± 5 Å where a force barrier was hit and a jump to final surface separation of 44 ± 5 Å occurred indicated by flattened fringe tips. The force measurements discussed here were reproducible over a number of approaches.

Interactions between two surfaces bearing physisorbed polymer layers are highly dynamic and their magnitude largely depends on the molecular weight of the polymer, the quality of the solvent for the adsorbed polymer, and the coverage of the surfaces by the polymer.[32,38,39] PAMP-SA adsorbs onto DIPY08 monolayers because of its high electrostatic affinity for the monolayer surface even though water is a good solvent for PAMPSA. PAMPSA does not adsorb on a surface such as mica in water because the charge on mica is negative. Forces between polyelectrolyte layers in a good solvent can be attractive when the surface coverage is low, or they can be repulsive because of the osmotic, steric, and electrostatic effects. The attractive force observed between two PAMPSA layers at a low polymer concentration is likely to be due to the bridging. Generally a lower temperature and lower adsorbed amount promote attraction. Situations which favor a strong bridging attraction are those where the polymer is attracted to both surfaces, but where the coverage is not too low or too high. In the case of a low polymer concentration DIPY08 layers are not fully saturated with PAMPSA. At a surface separation of around 450 Å, negatively charged PAMPSA chains are able to span over the gap and adsorb on both positively charged DIPY08 monolayer surfaces. Higher surface coverage makes it more difficult for polymer chains to form bridges because of fewer adsorption sites and denser layer barriers. Osmotic force and steric force together with electrostatic force become dominant when two densely covered polyelectrolyte surfaces are brought close to each other. Bridges might be formed only when two layers are strongly pressed toward each other and a polymer chain slowly penetrates through the adsorbed polyelectrolyte layer and finds the few empty sites in the DIPY08 layer on the other surface. The jump at high compression in the higher adsorption concentration case may well represent bridging at both high surface coverage and high compression. We also cannot rule out the possibility of molecular rearrangement and molecular reorganization at the surface upon compression.

Layers of the Bolaform Amphiphile DIPY08 Adsorbed on Layers of the Anionic Polyelectrolyte PAMPSA (DIPY08/PAMPSA/DIPY08 and P-DIPY08/PAMPSA/DIPY08 Layers). A second layer of DIPY08 was self-assembled using the "drop" method onto PAMPSA fully-covered (assembled at the high polymer concentration), photopolymerized DIPY08 monolayers (P-DIPY08/PAMPSA/DIPY08). Interactions between such layers in distilled water at 298.5 K are displayed in Figure 12 together with DLVO fits assuming a constant surface potential and a nonretarded van der Waals interaction with an estimated Hamaker constant of 1.0×10^{-20} J. A long-range repulsive interaction increases

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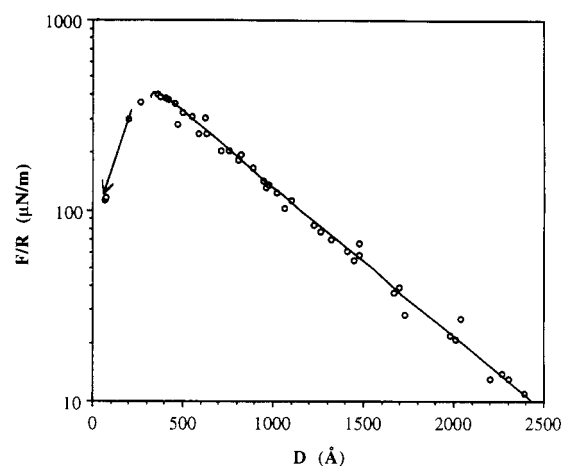(39) Granick, S.; Patel, S.; Tirrell, M. *J. Chem. Phys.* **1986**, *85*, 5370.

Figure 12. Surface force profiles of P-DIPY08/PAMPSA/DIPY08 on mica in distilled water at 298.5 K. The open circles are experimental data of a monomeric second DIPY08 layer adsorbed on a PAMPSA fully-covered polymeric DIPY08 anchoring layer. The inward arrow represents an inward jump. The solid line represents DLVO best fits assuming a 1:1 electrolyte, a nonretarded van der Waals interaction with an estimated Hamaker constant of 1.0×10^{-20} J, a constant potential of 72 mV, a bulk ionic concentration of 3.37×10^{-5} mol/L, and a shift of the location of the charged surface groups and water interface of 135 Å using the force-maxima-matching method.

Table I. List of the Magnitudes of F/R Primary Minima between Mica and Bolaform Amphiphile and Polyelectrolyte Layers Measured by the Surface Force Apparatus

surface material (in distilled water unless specified)	primary minima of F/R (μN/m)
mica (air)	-8.31×10^5
mica	-1.06×10^4
DIPY08	-1.56×10^5
P-DIPY08	-1.71×10^5
P-DIPY08/PAMPSA (3×10^{-5} g/L)	-1.33×10^5
P-DIPY08/PAMPSA (2×10^{-1} g/L)	-1.20×10^5
P-DIPY08/PAMPSA (2×10^{-1} g/L)/DIPY08	-1.18×10^5

exponentially with decreasing surface separation and reaches its maximum at a surface separation of 361 ± 5 Å. Further compression results in a sluggish jump similar to that observed between polymeric DIPY08 monolayers. A strong adhesive contact was reached at $D = 68 \pm 5$ Å indicated by flattened fringe tips. At separation below the adhesive contact point the repulsive force rises very sharply (not shown in the figure). A Debye length (524 Å) is obtained from the DLVO fits and is in reasonable agreement with the value obtained in our monolayer force measurements. A DLVO force curve with surface potential equal to 72 mV overlaps the experimental force curve using the force-maxima-matching method assuming the charged surface groups and water interface are 135 Å away from the original mica/water interface. Interactions between P-DIPY08/PAMPSA/DIPY08 layers apparently not only agree with the DLVO theory beyond the force barrier but also bear surprisingly close resemblance to those measured between photopolymerized DIPY08 monolayers except for a change in the distance of the surface charge from the mica surface: 35.5 Å for P-DIPY08 and 135 Å for P-DIPY08/PAMPSA/DIPY08. This seems to imply that a second bolaform amphiphile layer retains the surface properties of the first bolaform amphiphile layer despite the obvious differences that the first bolaform layer is polymeric and sits on a smooth rigid substrate while the top second layer is monomeric and sits on a mobile polymeric network. However, the validity of such a comparison should be checked upon further assessment
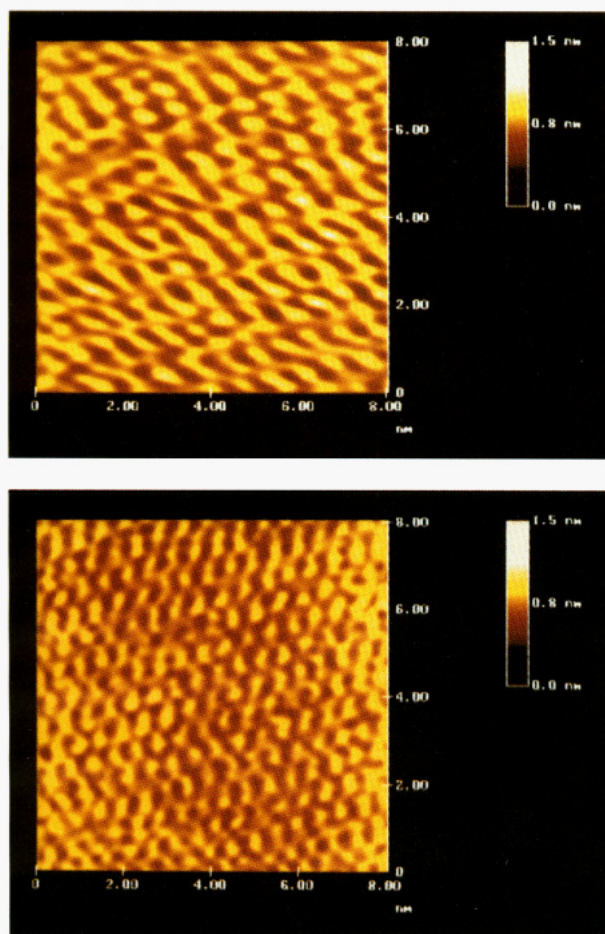
Figure 13. AFM surface views of monomeric and polymeric DIPY08 monolayers on mica in air with a scan area of 8×8 nm^2: (a) monomeric DIPY08; (b) polymeric DIPY08.

Figure 14. AFM surface views of DIPY08 multilayers on mica in air with a scan area of 4×4 μm^2: (a) DIPY08/PAMPSA/DIPY08; (b) P-DIPY08/PAMPSA/DIPY08.

of colloidal interactions between surfaces that cannot be accurately described by the DLVO theory. The unperturbed layer thickness of 135 Å in the presence of the second DIPY08 layer is smaller than the layer thickness of 225 Å (450/2 Å) in the absence of the top DIPY08 layer which indicates a more compact film in the presence of the second amphiphile layer. This compaction is probably due to partial neutralization of the PAMPSA layer by addition of the second DIPY08 layer. The force profile reported in Figure 11 is reproducible over several approaches at the same spot in contrast to interactions measured between DIPY08/PAMPSA/DIPY08 layers (not shown here). In this latter case, interactions become monotonically repulsive in the successive approaches after the jump into contact in the first approach, which is a trend suggesting deterioration of the multilayer structure. The observed differences in SFA-measured mechanical strength between DIPY08/PAMPSA/DIPY08 and P-DIPY08/PAMPSA/DIPY08 lead us to speculate that photopolymerization of the DIPY08 anchoring layer not only stabilizes the layer itself but also indirectly influences a second layer of DIPY08 self-assembled on top of the polyelectrolyte layer. Our data argue (1) that films of amphiphilic polymers are mechanically more stable than those of simple molecules and (2) that the robustness of the anchoring layer largely determines the stability of the successively assembled multilayer.

The magnitudes of the primary force minima, not shown in the force profiles we have displayed, were estimated by counting the number of steps taken by the upper motor to separate the two surfaces brought into strong adhesive contact. These data are not well understood at the moment
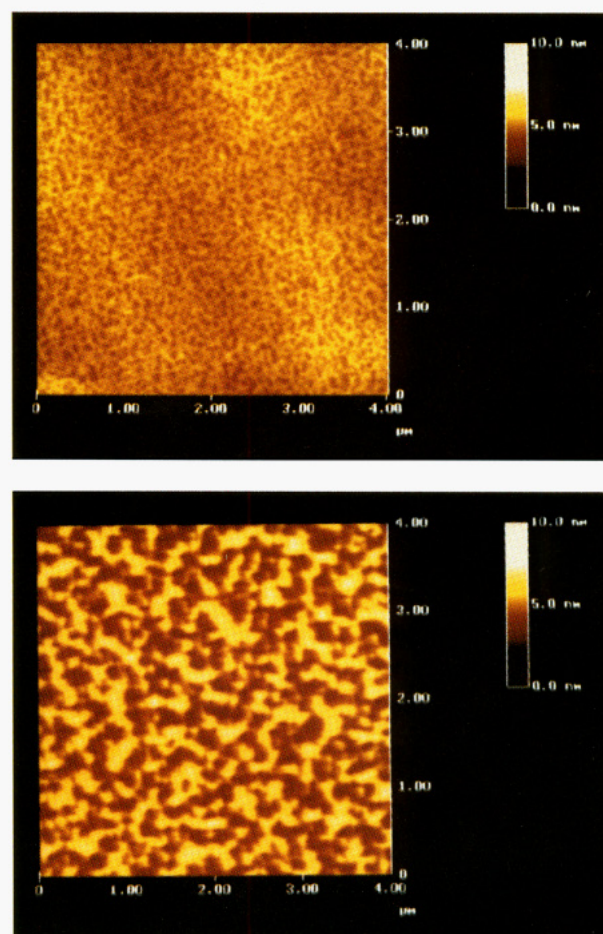
and for future references are listed in Table I for all the systems we studied.

AFM Measurements with Molecular Resolution. For further investigation of the molecular arrangement of DIPY08/PAMPSA layers on mica and the effects of photopolymerization, surfaces bearing adsorbed layers were imaged with molecular resolution using AFM. In Figure 13 we compare AFM images of monomeric and polymeric DIPY08 monolayers on mica in air at room temperature. The self-assembled monolayers are continuous and uniform over tens of micrometers. The Fourier transform of the photopolymerized DIPY08 monolayer (not shown) reveals a pronounced hexagonal lattice structure. Measurements of the cross-sectional profiles allow us to calculate the unit cell area of 32.0 Å^2. The image of the unpolymerized monolayer of DIPY08 appears less ordered. Its Fourier transform (not shown) reveals four bright dots instead of six, a result that is consistent with a less ordered lattice structure. The unit cell area is calculated to be 32.9 Å^2, quite close to the value of the photopolymerized DIPY08 layer. We cannot rule out that one reason we see less order in the unpolymerized DIPY08 layer may be that it is perturbed more by the AFM measuring tip than is the photopolymerized DIPY08 layer.

In Figure 14 we compare AFM images of two DIPY08 layers with one PAMPSA layer in between self-assembled on mica measured in air at room temperature. The only difference between the two surfaces is in one image the first anchoring DIPY08 layer is photopolymerized before more layers are assembled on top of it while in the other image neither of the DIPY08 layers are photopolymerized.

The scan area of the two images is 4×4 μm^2. High-magnification AFM images of the surfaces are not possible. Both films exhibit high durability. The same image was obtained from the same spot after several scans. The film in which neither of the DIPY08 layers is photopolymerized has smaller aggregates than the film in which the underneath DIPY08 layer is photopolymerized. However, readers should bear in mind that these AFM images were obtained in air and therefore might not reflect the surface structures in aqueous solutions.

Conclusions

We have studied a self-assembled multilayer system composed of a novel photoreactive cationic bolaform amphiphile with pyridinium headgroups and polyelectrolytes of the opposite charge. This multilayer system has proved suitable for the surface force and atomic force microscopy measurements. The two methods have the potential to relate the configuration and mechanical properties of the multilayers to the multilayer composition and solution conditions during fabrication and measurement and should help us to gain more understanding of the role of molecular forces in multilayer formation. The experimental results in return should enable us to make thin organic films with desirable functions. The experimental results reported here can be summarized as follows: (1) Multilayers of the photoreactive bolaform amphiphiles self-assemble if polyelectrolyte layers of the opposite charge are inserted in between amphiphile layers. (2) Photopolymerization of the bolaform amphiphile layers changes the apparent electrostatic properties of the layer interface and undoubtedly increases the lateral strength of the film while maintaining and maybe increasing its uniformity. (3) The nature of the first surfactant layer assembled on the substrate is a major factor controlling the stability of successive layers. Such a well-character-ized, cationic bolaform amphiphile monolyer can thus serve as a potential substrate for immobilization of polyelectrolyes, proteins, DNA, and anionic molecules which cannot readily adsorb on negatively charged substrates such as mica. (4) The polyelectrolyte neutralizes the amphiphile layer at low solution concentrations. The interaction between the polyelectrolyte layers can be either attractive or repulsive depending on the coverage of the polyelectrolyte on the amphiphile layer.

Ordered thin organic multilayer films show considerable technological promise in fields such as nonlinear optical devices, sensors, and protective coatings. Most of these applications require the preparation of well-defined films in which molecules with desirable properties are positioned uniquely with respect to each other and to the substrate. Self-assembly through physical adsorption has advantages over chemisorption in that it does not require 100% reaction at each stage. Moreover, the film molecules are free to adjust their positions to improve the overall packing since they are not covalently bound to the substrate. Self-assembly through physical adsorption also has advantages over the classical Langmuir–Blodgett technique in that a solution process is independent of the substrate size and topology and that the process is suitable for automation and large-scale application. The scientific issues we address in this study, such as the film's mechanical strength, its integrity, the size of its molecular clusters, and the orientational and positional order in these clusters, will hopefully help those trying to make practical films and add to our understanding of thin organic films.