J. Am. Chem. Soc. **1995**, *117*, 5824–5828

Reactive and Rigid Monolayers of Bisaroyl Azide Diamide Bolaamphiphiles on Polyacrylonitrile Surfaces

Peter Böhme,[†] **Hans-Georg Hicke,**[*,†] **Christoph Boettcher,**[‡] **and Jürgen-Hinrich Fuhrhop**[*,‡]

Contribution from the GKSS-Forschungszentrum Geesthacht GmbH, Institut für Chemie, Abteilung Membranforschung, Kantstrasse 55, D-14513 Teltow, Germany, and Institut für Organische Chemie der Freien Universität Berlin, Takustrasse 3, D-14195, Germany

Received December 2, 1994[⊗]

Abstract: Bolaamphiphiles with two *p*-amidobenzoyl azide head groups give erected monolayers on the air/water interface which have been transferred to polyacrylonitrile (PAN) surfaces. Gas phase reaction with amines converts only the outer azide group to amides, since the monolayer is crystalline. This is demonstrated by electron diffraction patterns as well as reflection-absorption infrared (RA-IR) spectroscopy of the monolayers on PAN. Subsequent UV-irradiation decomposes the remaining inner azide group to nitrenes and fixates it to the PAN subphase. It is thus possible to coat polymer surfaces quantitatively with crystalline and functional monolayers. Possible applications are shortly discussed.

Introduction

Bolaamphiphiles contain a head group on each end of a hydrophobic skeleton.[1] In surface monolayers at the air/water interface, they tend to lie flat on the water surface at low surface pressures. At higher pressures, they form either U-shaped monolayers, if the head group carries a charge,[2] or they lift one of the head groups out of the water.[3] Similar behavior has been observed on silver[4] and gold[5] surfaces. Bolaamphiphile monolayers on polymer surfaces have, to the best of our knowledge, not been reported so far. They offer the unique opportunity to bind the monolayers covalently to the polymer surface via one reactive head group and to modify the polymer surface properties *ad lib* by chemical reactions with reagents which cannot cross the monolayer lipid membrane.

We are particularly interested in the surface modification of polymers which can be applied to the fabrication of ultrafiltration membranes, e.g., polyacrylonitrile (PAN). Bolaamphiphile films may then be used to modify the surface and adsorption properties of the filter material. In order to simplify the syntheses of bolaamphiphiles and the defined monolayer transfer onto polymer surfaces we selected symmetric compounds with only one type of reactive head groups. The well-established aroyl azide group was chosen. It can be used (i) to attach the monolayer covalently to the polymer surface by UV irradiation[6,7] and (ii) to modify the surface properties by any nucleophilic reagent which can replace the azide leaving group[8] or (iii) by photochemical replacement reactions.[9] In this paper we establish experimental conditions under which the outer azide groups react quantitatively with various external reagents, whereas the inner azide groups remain untouched. They may then be fixed to the PAN subphase by UV-irradiation.

Experimental Section

Materials. Chemicals were used as received from Merck (Germany). PAN was a technical product (Buna-AG Schkopau, Germany; containing ca. 1% vinyl acetate; M_w = 135 000 g/mol; M_N = 35 000 g/mol). For LB experiments HPLC-grade chloroform (Merck, Germany) and Milli-Q water (Millipore reagent water system, Bedford, U.S.A.) were used.

Substrate Preparation. PAN films were deposited on gold covered glass slides (size about 20 × 10 × 3 mm, Spindler & Hoyer, Göttingen, Germany) using a spin coater (Convac, Wiernsheim, Germany). A 1% solution of PAN (0.1 mL) in dimethyl formamide was applied onto the support and spun at 5000 rpm for 60 s. Heating at 50 °C for 30 min *in vacuo* gave a solvent free film as proven by the absence of DMF infrared absorption bands. A thickness of 19.5 ± 0.5 nm was measured ellipsometrically.

Monolayer Preparation. Monolayers on water were formed in a microprocessor-controlled film balance (FW 2, Lauda, Königshofen, Germany). For **2** a chloroform and for **1a–d** a chloroform/methanol (8:2) solution of the compound (0.2 mg/mL) was spread on the water subphase at 20 °C. The monolayer was continuously compressed up to a surface pressure of 30 mN/m and then maintained for 10 min in order to stabilize it. The layer was then transferred by vertical withdrawal of the PAN film on the support from the subphase (dipping rate 1 mm/min). "Creep-tests" were performed maintaining the surface pressure constant at 30 mN/m and plotting the surface area vs time.

Infrared Measurement. Spectra were taken on a Nicolet Magma 550C FT-IR spectrometer with MCT/A detector and 4 cm^{-1} resolution. Typical number of scans were 2000 with new background spectra for every measurement. For the reflection-absorption spectra (RA-IR), a reflection attachment (Model VRA-1 with RMA, Harrick, Ossining, U.S.A.) equipped with a double diamond polarizer (PDD-J2R, Harrick) was used at an angle of incidence of 83°.

Contact Angle Measurement. Contact angles were measured by the captive bubble method. An air bubble was injected from a syringe with a stainless steel needle onto the sample surface under water. With the needle remaining inside the bubble, advancing and receding angle

---

[†] GKSS-Forschungszentrum Geesthacht GmbH.

[‡] Institut für Organische Chemie der Freien Universität Berlin.

[⊗] Abstract published in *Advance ACS Abstracts*, May 1, 1995.

(1) Fuhrhop, J. H.; Mathieu, J. *Angew. Chem.* **1984**, *96*, 124.

(2) Tsao, Y.; Tirell, M.; Davis, H. T.; Hessel, V.; Ringsdorf, H. *Langmuir* **1993**, *9*, 3461.

(3) Fuhrhop, J. H.; Krull, M.; Schulz, A.; Möbius, D. *Langmuir* **1990**, *6*, 497.

(4) Allara, D. L.; Atre, S. V.; Elliger, C. A.; Snyder, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 185.

(5) Colvin, V. L.; Goldstein, A. N.; Alivisatos, A. P. *J. Am. Chem. Soc.* **1992**, *114*, 5221.

(6) (a) McGarvey, C. E.; Holden, D. A. *Langmuir* **1990**, *6*, 1123. (b) Harmer, M. A. *Langmuir* **1991**, *7*, 2010. (c) Yan, M.; Cai, S. X.; Wybourne, M. N.; Keana, J. F. W. *J. Am. Chem. Soc.* **1993**, *115*, 814.

(7) Böhme, P.; Hicke, H. G.; Ulbricht, M.; Fuhrhop, J. H. *J. Appl. Polym. Sci.* **1995**, *55*, 1495.

(8) Berndt, D. C.; Faburada, A. L. *J. Org. Chem.* **1982**, *47*, 4167.

(9) Schuster, G. B.; Autrey, T. *J. Am. Chem. Soc.* **1987**, *109*, 5814.

0002-7863/95/1517-5824$09.00/0 © 1995 American Chemical Society

measurements were performed with a tilting stage goniometer (Carl Zeiss Jena, Germany) by stepwise changes of air pressure.

Transmission Electron Diffraction (TED). Electron diffraction was performed using PAN films (thickness 180 ± 2 nm as determined by ellipsometrie) made by spin-coating on a silicon wafer (4% PAN in DMF, 5000 rpm for 60 s). They were peeled off by water and then transferred onto the supporting wholly carbon coated microscope grids. For imaging a Philips CM12 transmission electron microscope equipped with a cryo specimen-holder (Gatan, U.S.A., Model 626) was used, maintaining the specimen temperature at −175 °C during measurements in order to reduce radiation damage. The accelerating voltage was 100 kV. Prealignment was performed by using the microscopes low dose kit, allowing a total irradiation dose of 0.5 e/Å^2 during 2 s of exposure time. Diffraction pattern were recorded on Kodak SO 162 film (Kodak, U.S.A.).

Ellipsometric Measurements. A Null ellipsometer AutoEL II (Rudolph, U.S.A.) in a PCSA arrangement and with He/Ne-laser (632.8 nm) was used. The angle of incidence was 70°. The estimation of film thickness was performed using identical probes as for RA-IR (on gold support) and TED (on a silicon wafer). Data were taken over three spots on every sample and averaged. The refractive index of PAN is known to be 1.52.[10a] A refractive index of 0.177 and 3.88 were used for gold and silicon, respectively.[10b]

Gas Phase Reaction. The gas phase reactions were performed in a desiccator which contained the liquid, volatile amine. The reactions were carried out by exposure the monolayer sample to the amine atmosphere for increasing reaction times from 10 s up to 30 min.

Solubility Measurements. The bolaamphiphiles **1a–d** were suspended in distilled water at room temperature. The suspensions were shaken for 6 h, left standing for 30 min and filtered off using a Millex-HV filter (Millipore, Bedford, U.S.A.; pore size 0.45 μm). UV-spectra of the filtrates were taken using a Lambda 15 spectrophotometer (Perkin-Elmer, Norwalk, U.S.A.). The extinction coefficient of **1d** in tetrahydrofurane solution was 3.8 × 10^3 m^2/mol at the absorption maximum of 300 nm.

Synthesis. The synthesis of mono aroyl azide amphiphile **2** (*p*-stearylamidobenzoic azide) was described elsewhere.[7]

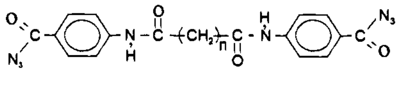
***N,N'*-Di-*p*-benzoic Acid Hexadecane Diacid Diamide.** Ethylchloroformiate (2.0 mL, 0.021 mol) was added dropwise to a solution of 2.86 g (0.01 mol) *n*-hexadecane-1,16-dioic acid (Fluka, Switzerland) and 7.6 mL (0.055 mol) of triethylamine in 100 mL of tetrahydrofurane (THF) at 5 °C and 4.11 g (0.03 mol) of *p*-aminobenzoic acid in 60 mL of THF was added slowly. After stirring for 2 h, the residue was filtered off and washed with water. The remaining white solid was suspended in hydrochloric acid (0.2 M) and stirred for 2 h. After filtration and drying the crude product (4.14 g, 79% yield) was obtained and used for further reaction without purification: ^{1}H NMR, (DMSO-d_6) δ 1.25 (CH$_2$), 1.58 (β-CH$_2$), 2.35 (α-CH$_2$), 7.74/7.90 (aromatic ring), 10.1 (amide), 12.7 (acid); IR (KBr pellet) ν(NH) = 3320 cm^{-1}, ν(C=O, amide + acid) = 1678 cm^{-1}. Anal. Calcd. for $C_{30}H_{40}N_2O_6$: C, 68.7; H, 7.7; N, 5.3. Found: C, 67.8; H, 8.1%; N, 4.8%.

***N,N'*-Di-*p*-benzoic Acid Azide Hexadecane Diacid Diamide (1a).** *N,N'*-Di-*p*-benzoic acid hexadecane diacid diamide (0.525 g, 1.0 mmol) and 0.55 mL (4 mmol) of triethylamine was dissolved in 120 mL of dimethyl formamide (DMF) and 0.65 mL (3.0 mmol) of diphenyl azido phosphate in 10 mL of DMF was added with stirring at room temperature. The stirring was continued for 4 h at 40 °C, and the solution was then poured into 500 mL of ice water. The white precipitate was filtered off and washed with water and methanol. The crude product (0.48 g, 84% yield) was recrystallized from nitromethane. For LB experiments the compound was purified freshly by chromatography (ethyl acetate/*n*-hexane 8:2) on silica: ^{1}H NMR, (DMSO-d_6) δ 1.26 (CH$_2$), 1.51 (β-CH$_2$), 2.33 (α-CH$_2$), 7.72/7.89 (aromatic ring), 10.31 (amide); IR (KBr pellet) ν(N$_3$)$_{as}$ = 2137 cm^{-1}, ν(C=O, Azid) = 1695 cm^{-1}, ν(N$_3$)$_{as}$ = 1255 cm^{-1}; MS (FAB$^+$, Xenon) *m/z* 574 (M + H)$^+$. Anal. Calcd for $C_{30}H_{38}N_8O_4$: C, 62.7; H, 6.7; N, 19.5. Found: C, 62.9; H, 6.9; N, 19.3.

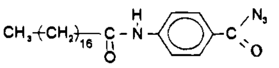
Results and Discussion

Monolayers at the Air/Water Interphase. The bolaamphiphiles **1a–d** were obtained from α,ω-dicarboxylic acids and *p*-aminobenzoic acid in dioxane–triethylamine mixtures. Azide was introduced with diphenyl azido phosphate[11] in dimethylformamide. The overall yields were 50–60%. The amphiphile **2** containing only one aroyl azide head group was described earlier.[7]

Solubilities in water were determined by UV-spectroscopy. Bolaamphiphiles **1a–d** were stirred for 6 h with water and then ultrafiltrated. The aqueous filtrate showed no UV-band at 300 nm indicating solubilities of <1 × 10^{-7} M. Elemental analyses of the residue gave the correct nitrogen value of the original azide (**1d**; N = 24.1%). Therefore no detectable hydrolysis had taken place at pH 7. Acidic or basic solutions were not studied, because only neutral subphases were applied in monolayer experiments.



n=14	n=10	n=8	n=6
1a	**1b**	**1c**	**1d**



2

The pressure/area isotherms of the bolaamphiphiles **1a–d** and of the amphiphile **2** are similar in shape for all compounds (Figure 1). The molecular area is about 0.25 nm^2 for **2** and somewhat larger for the bolaamphiphiles **1a–c** (0.28–0.33 nm^2). This is a typical value for amphiphiles with benzene derived head groups.[12,13] The bolaamphiphiles therefore occur in a stretched conformation and both the inner and outer surfaces should consist of benzoyl azide groups. The surface pressure reaches 60 mN/m in all cases. This is even true for the short-chain suberic acid derivative (**1d**). However, its experimental molecular surface area is too small for an amphiphile with a benzene-derived head group (≤0.20 nm^2/molecule, Figure 1). Although no water solubility was detectable by UV-spectroscopy for **1d**, we relate this observation to partial dissolution in the subphase.[14] Collapse took place only at relatively high surface pressures and a "creep test" [15] (insert in Figure 1) actually showed that some of the monolayer of **1d** dissolved within the first few minutes after it was formed from chloroform/methanol solutions. The longer chain amphiphiles **1a–c**, on the other hand, formed monolayers, which were perfectly stable for at least 80 min.

Langmuir–Blodgett Monolayers on Polyacrylonitrile (PAN). PAN films with a thickness of 20 nm as characterized by ellipsometry were produced by spin coating of gold-covered glass slides (see Experimental Section). They exhibited two intense infrared peaks at 2244 and 1475 cm^{-1}. Other peaks of the PAN spectrum appears only very weak in the reflection-absorption infrared spectra (RA-IR) of the coated films (Figure

---

[10] (a) Hall, C. *Polymer Materials*; John Wiley & Sons: New York, 1989; p 113. (b) Palik, E. D. *Handbook of Optical Constants of Solids*; Academic Press: New York, 1985.

[11] Shioiri, T.; Ninomiya, K.; Yamada, S. *J. Am. Chem. Soc.* **1972**, *94*, 6203.

[12] (a) Furlong, D. N.; Scoberg, D.; Davy, J.; Prager, R. H. *Langmuir* **1993**, *9*, 766. (b) Holden, D. A.; Ringsdorf, H.; Haubs, M. *J. Am. Chem. Soc.* **1984**, *106*, 4531.

[13] Tillman, N.; Ulman, A.; Schildkraut, J. S.; Penner, T. L. *J. Am. Chem. Soc.* **1988**, *110*, 6136.

[14] Gericke, A.; Simon-Kutscher, J.; Hühnerfuss, H. *Langmuir* **1993**, *9*, 2119.

[15] Berg, J. M.; Eriksson, L. G. T.; Claesson, P. M.; Borve, K. G. N. *Langmuir* **1994**, *10*, 1225.

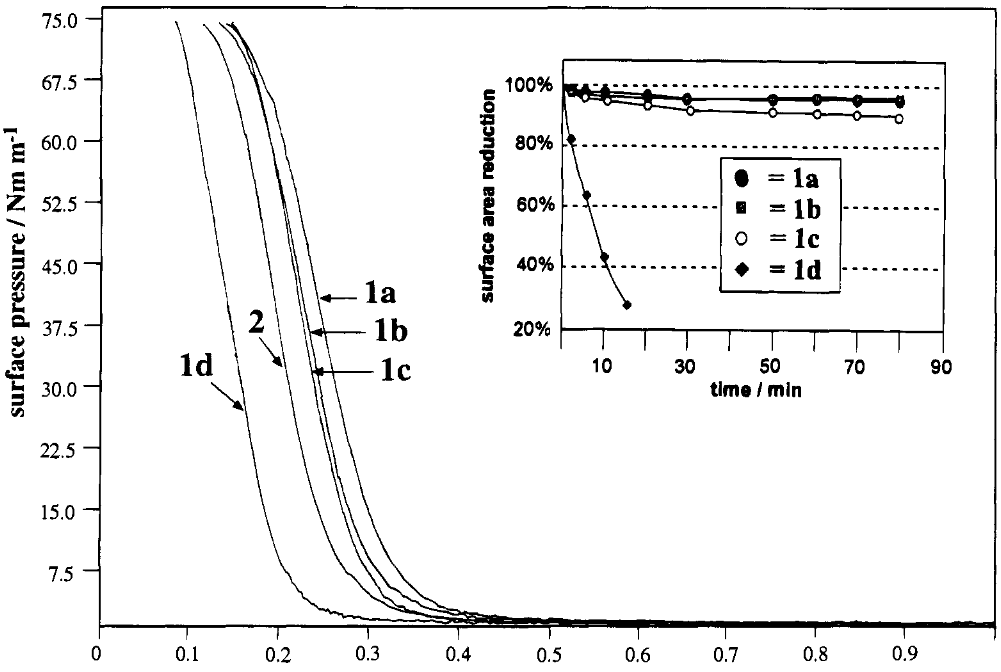


Figure 1. Surface area pressure isotherm of **1a–d** and **2** on water. The insert indicates the long-time stability of the monolayers of **1a–c** ($n \geq 8$), whereas **1d** ($n = 6$) dissolves within a few minutes.

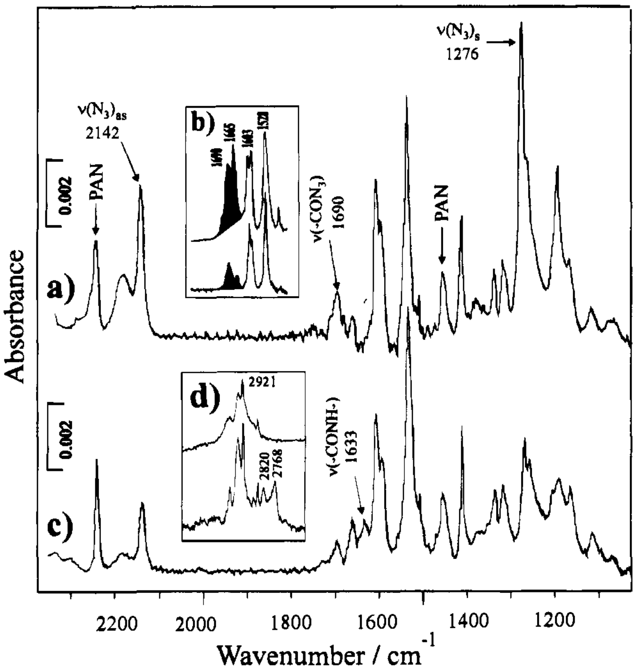


Figure 2. Infrared spectra of bolaamphiphile **1b**. (a) Crystalline monolayer on PAN. (c) Monolayer on PAN after reaction with hexyl amine. Insert: (b) Comparison of carbonyl vibration region of monolayer (bottom) and KBr-pellet (top) spectrum of **1b**. (d) Comparison of CH vibration region before and after reaction with DMEDA.

2). Monolayers of **1a–c** were transferred at room temperature. The short-lived monolayer of **1d** could neither be transferred at 20 nor 5 °C. RA-IR spectra (Figure 2a) showed only weak absorptions for the amide and azide carbonyl groups at 1690 and 1665 cm^{-1}, whereas the same bands are very strong in isotropic KBr pellets (see Figure 2b). This loss of absorption intensity points to a parallel orientation of the carbonyl groups in the surface monolayer in respect to the gold surface.[16] In dehydrated monolayers of bolaamphiphiles with identical α- and ω-head groups, the distance between the monomers is fixed by the head groups, since they have a slightly larger cross-sectional area than the oligomethylene chains connecting them. One therefore expects more mobility of these chains as compared to surface monolayers of single-headed amphiphiles, where area differences are adjusted by tilting. A shift of $\nu(CH_2)_{as}$ from 2918 cm^{-1} in the monolayer of **2**[7] to 2921 cm^{-1} in the double-headed monolayer of **1b** is in agreement with this prediction. Furthermore, the azide vibration frequencies at 2142 and 1276 cm^{-1} are shifted to higher wavenumbers as compared to the KBr spectra (2137 and 1258 cm^{-1}). A general small shift to higher wavenumbers were reported in many cases using RA-IR technique.[17] In the system described here, the shift was, however, only observed for the azide group. Comparable effects

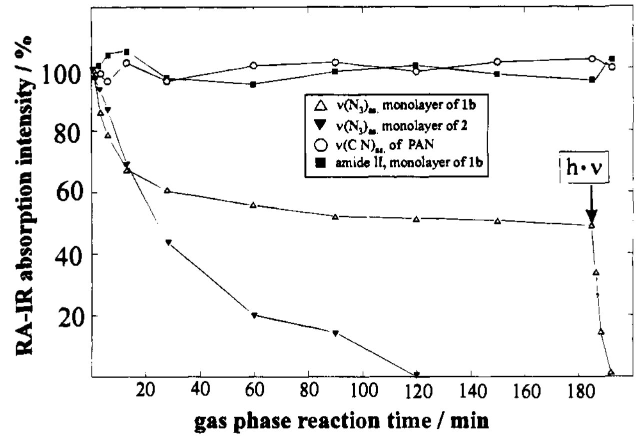


Figure 3. Time course of the benzoyl azide decomposition in monolayers of **1b** and **2** as indicated by the decrease of the 2142 cm^{-1} band. For a comparison absorption, intensities of two bands not involved in the reaction are given.

---

(16) (a) Snyder, R. G.; Strauss, H. L.; Elliger, C. A. *J. Phys. Chem.* **1982**, *86*, 5145. (b) Naselli, C.; Rabe, J. P.; Rabolt, J. F.; Swalen, J. D. *Thin Solid Films* **1985**, *134*, 173.

(17) (a) Allara, D. L.; Baca, A.; Pryde, C. A. *Macromolecules* **1978**, *11*, 1215. (b) Umemura, J.; Kamata, T.; Kawai, T.; Takenaka, T. *J. Phys. Chem.* **1990**, *94*, 62. (c) Kaito, A.; Nakayama, K. *Macromolecules* **1992**, *25*, 4882. (d) Ihs, A.; Uvdal, K.; Liedberg, B. *Langmuir* **1993**, *9*, 733.

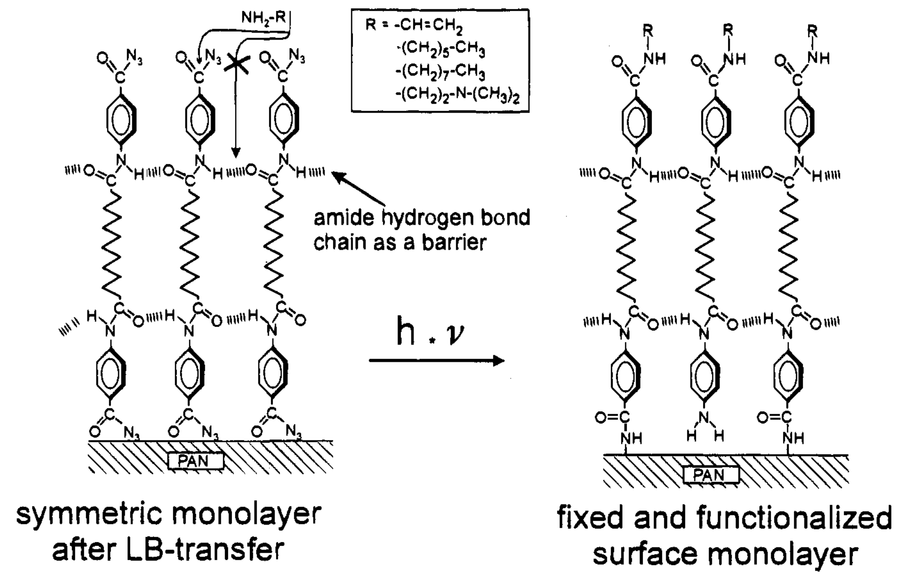


Figure 4. Model of a section of the crystalline monolayer of **1b** before the surface reaction with amine and after amination and photolinking to PAN surface.

have only been reported for carbon monoxide and formaldehyde at metal surfaces.[18] We assign the high-frequency shift of the azide vibration tentatively to a dipole–dipole coupling effect as observed for alkylcarboxylic acids adsorbed onto aluminum oxide.[19]

In order to establish the distinction of inner and outer benzoyl azide head groups of the monolayer, we chose a gas phase reaction with volatile amines, which was recently applied to surface modification of self-assembled monolayers on gold.[20] The PAN coated gold slides with the dibenzoyl azide bolaamphiphile monolayer were placed in a desiccator and reacted with various amines in the gas phase. RA-IR spectra measurements were used to characterize the amidation reactions. The decrease of the intensity of the azide band at 2142 cm^{-1} is nearly 50%, and a new, weak amide band at 1633 cm^{-1} appeared (Figure 2a,c). Hexylamine produced only this new detectable absorption band, whereas the reaction product with *N,N*-dimethyl ethylene diamine (DMEDA) also gave new absorptions at 2768 and 2820 cm^{-1} (Figure 2d), which are typical for the dimethylamine unit.[21] Figure 3 shows the time dependent absorption of three characteristic RA-IR bands. In the case of hexylamine 40% of the intensity of the azide absorption peak disappeared within 20 min indicating rapid reaction of the azide groups. Fifty percent of the original absorption remained unchanged for 180 min, which is in agreement with the previous assumption that the bolaamphiphile lies perpendicular to the PAN surface and has a stretched conformation: one head group lies on the outer surface; the other is in contact with the support. Only the outer azide groups of the bolaamphiphilic membrane are thus accessible to gaseous amines (Figure 4). The crystallinity of the membranes prevents their diffusion through the monolayer and to the polymer surface. The inner, unreacted benzoyl azide group could then be used to fixate the monolayer covalently to the polymer surface by a short UV irradiation (Figures 3 and 4).

PAN films for electron microscopy had to be thicker than in the infrared experiments, because 20 nm films were not transferable. We used 180 nm films and characterized them again by ellipsometry. Transmission electron microscopical diffraction (TED) proved the crystallinity of the bolaamphiphilic surface monolayer.[22] The diffraction pattern of the supporting PAN as measured without the monolayer coating showed only a broad ring pattern (including $d_{020} = 0.53$ nm, $d_{110} = 0.51$ nm)[23] in some cases. The pattern observed after LB transfer of a monolayer of **1b** is, however, typical for a face centered orthorhombic unit cell (Figure 5). The corresponding *d*-spacings are $d_{11} = 0.480$, $d_{20} = 0.435$, and $d_{02} = 0.289$ nm. The parameters of the unit cell were $a = 0.848$ and $b = 0.563$ nm, corresponding to an area per molecule of 0.24 nm^2 which is about 20% less than that observed on water. It falls in the usual range of phenyl rings.[13] We occasionally also observed patterns which pointed to parallel shift along the [10] lattice planes (not shown).

Furthermore, an undisturbed crystalline arrangement of the bolaamphiphilic monolayer of **1b** also after the reaction with *n*-hexylamine was indicated by unchanged electron diffraction patterns. Contact angle measurements indicated that the surface of the terminal benzoyl azide groups are modestly hydrophilic. The values around 75° are comparable to methyl amide or methyl ester moieties[24] (Table 1). Drastic changes occurred after the surface reaction with amines. For *n*-octylamine the water advancing angle rises to 97°. After reaction with DMEDA, on the other hand, a cationic trialkyl ammonium surface was produced by short contact of the probe with dilute aqueous citric acid solution. The water contact angles obtained in this case are typical for hydrophilic surfaces[25] (Table 1). Gaseous surface reaction with other amines were also possible. Contact angles for the modified monolayer surfaces are in good agreement with recently published results.[24,25] The monolayer made of amphiphile **2** behaved differently. Reaction with gaseous *n*-hexylamine occurred quickly and quantitatively with the benzoyl azide groups located at the polymer surface (Figure

---

(18) Bradshaw, A. M.; Schweizer, E. Infrared Reflection-Absorption Spectroscopy of Adsorbed Molecules. In *Spectroscopy of Surfaces*; Clark, R. J. H., Hester, R. E., Eds.; John Wiley & Sons: New York, 1988; p 413.

(19) Touwslager, F. J.; Sondag, A. H. M. *Langmuir* **1994**, *10*, 1028.

(20) (a) Duevel, R. V.; Corn, R. M. *Anal. Chem.* **1992**, *64*, 337. (b) Sun, L.; Crooks, R. M.; Ricco, A. J. *Langmuir* **1993**, *9*, 1775.

(21) Hill, R. D.; Meakins, G. D. *J. Chem. Soc.* **1958**, 760.

(22) (a) Bonnerot, A.; Chollet, P. A.; Frisby, H.; Hoclet, M. *Chem. Phys.* **1985**, *97*, 365. (b) Garoff, S.; Deckman, H. W.; Dunsmuir, J. H.; Alvarez, M. S.; Bloch, J. M. *J. Physique* **1986**, *47*, 701. (c) Engel, M.; Merle, H. J.; Peterson, I. R.; Riegler, H.; Steitz, R. *Ber. Bunsenges. Phys. Chem.* **1991**, *95*, 1514.

(23) Hobson, R. J.; Windle, A. H. *Macromolecules* **1993**, *26*, 6903.

(24) Laibinis, P. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1992**, *114*, 1990.

(25) Balachander, D.; Sukenik, C. M. *Langmuir* **1990**, *6*, 1621.

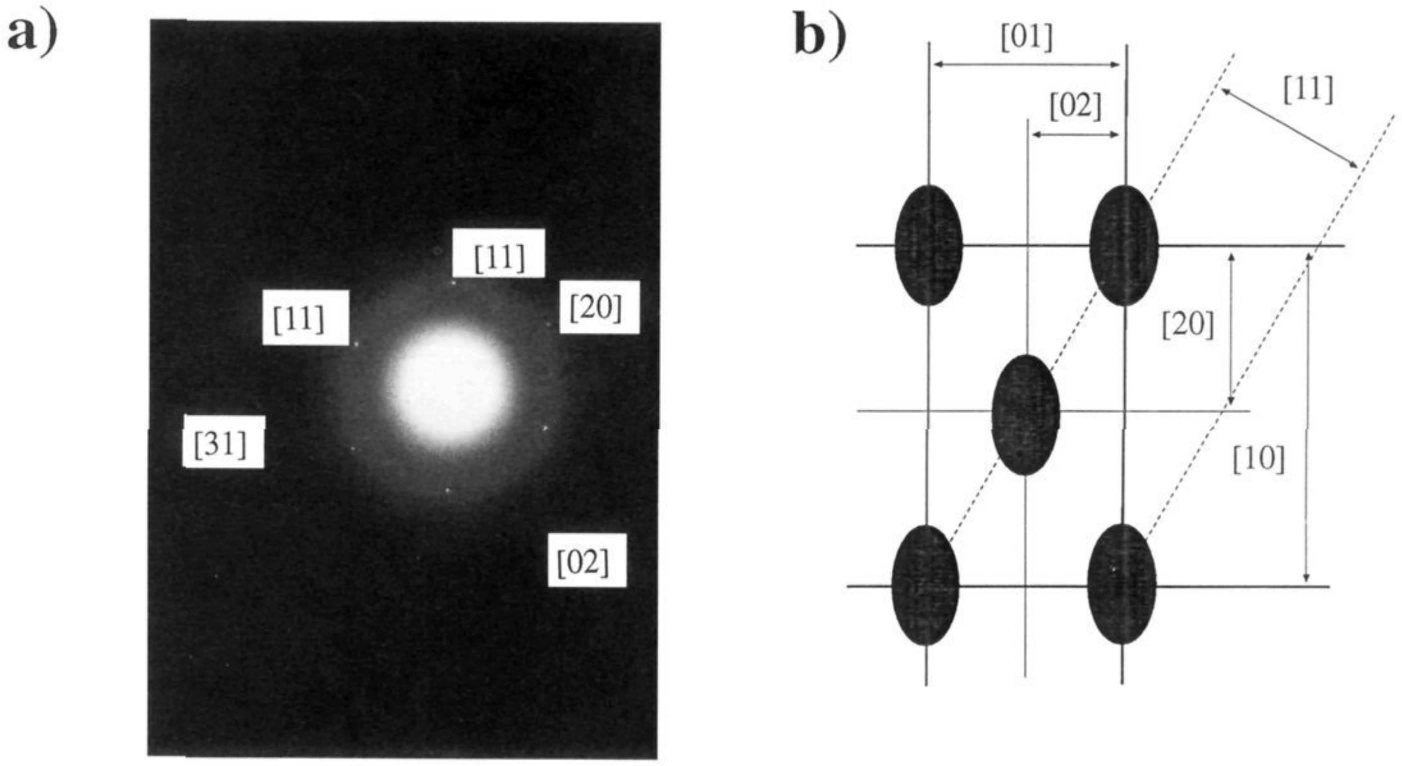


Figure 5. Typical electron diffraction pattern of the bolaamphiphilic monolayer of **1b** on PAN and structural assignments. The [02] and [31] diffraction spots are very weak.

Table 1. Contact Angles of LB Monolayer on PAN Surfaces

surface	advancing angle θ_{adv} (deg)	receding angle θ_{rec} (deg)	hysteresis $\Delta\theta$ (deg)
PAN spin-coating (sc) film	59 ± 1	40 ± 1	19
LB monolayer of **2** on PAN sc film	93 ± 1	84 ± 1	9
LB monolayer of **1b** on PAN sc film	74 ± 2	58 ± 2	16
LB monolayer of **1b** after gas phase reaction with:			
allylamine	83 ± 1	47 ± 2	36
hexylamine	89 ± 2	71 ± 2	18
octylamine	97 ± 2	75 ± 3	22
dimethyl ethylene diamine (DMEDA)	60 ± 1	17 ± 3	43
citric acid salt of DMEDA derivative	45 ± 2	0	

3). The original crystallinity of the monolayer was thereby completely destroyed. The hydrogen bond chain of a single amide group close to the inner surface is obviously not sufficient to protect the inner azide group against attack by alkylamine reagents. Cooperative effects of two amide hydrogen bond chains are needed to render the monolayer impermeable (Figure 4).

Summary and Outlook

It was shown that a surface monolayer coat as thin as 0.2 nm can chemically isolate a polymer from its environment and change its reactivity pattern in any desired way. Surface benzoyl azide, methyl, and amino groups were given as examples. The sharp differentiation of outer and inner benzoylazide groups in respect to reactivity against external agents depends on two linear hydrogen bond chains which induce rigidity and crystallinity of the surface monolayer. The surface monolayers are so thin that they should not disturb the passage of molecules through ultrafiltration membranes. The reactive head groups should, however, bind various kinds of molecules, e.g., enzymes by nucleophilic substitution. The described surface modification is not restricted to PAN but should be applicable to several other polymers. In all cases, one would expect a partial covalent binding of the bolaamphiphiles to the polymer upon UV-irradiation and a closure of the surface coat by the hydrophobic effect and by cooperative amide hydrogen bonding.

Acknowledgment. We thank E. Götz for contact angle measurements, Dr. Fanter for ellipsometric measurements, and A. Schulz for LB experiments. This work was supported by the Deutsche Forschungsgemeinschaft (Project Hi 487/1-2), SFB 312 (Vectorial Membrane Processes), and by the Bundesministerium für Forschung und Technologie (Funktionale Supramolekulare Systeme).

Supplementary Material Available: Experimental detail for compounds **1b–d** (2 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA943903Z