

FT-IR Spectroscopic Investigations of Photochemical Grafting of Amphiphiles onto Polyacrylonitrile Surfaces

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SYNOPSIS

The photoreactive amphiphile *p*-(stearyl amido) benzoyl azide (SABAz) was synthesized and grafted onto surface of thin polyacrylonitrile (PAN) films by irradiation with UV light. Two different techniques were applied, namely, Langmuir–Blodgett (LB) deposition and casting from solution. A high degree of order and a hydrophobic surface were established by reflection-absorption FT-IR spectroscopy (RA-IR) and contact angle measurements. The stability against treatment with water, tetrahydrofuran, and chloroform was tested. A considerable amount of amphiphilic molecules remains on the surface also after treatment with chloroform. RA-IR spectra taken from photomodified PAN films prepared by both techniques are almost identical after chloroform treatment, indicating a similar coupling mechanism. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The generation of technologically useful surface properties is an important issue in materials science, because there is an increasing need for materials with tailor-made interfaces, e.g., for applications as biomaterials.¹ With synthetic polymers it is necessary to produce the desired surface characteristics without altering bulk chemistry and morphology. In particular, a heterogeneous modification of flat-sheet or hollow-fiber ultrafiltration membranes should not damage their porous structure. The adjustment of exclusively the outermost surface region of a solid material to the particular needs is desirable. A surface coat with a thickness in molecular dimensions represents the ideal surface modification.

Self-organization of amphiphilic molecules is a helpful process here.^{2–4} Planar, ordered, densely packed monolayer structures can be formed at the water–air interface and can be transferred onto suited substrates using the Langmuir–Blodgett (LB)

technique.⁵ While the LB technique yields two-dimensional structures, crystallization of the same amphiphiles from solutions produces a three-dimensional crystallinity.⁶

Several studies have appeared that explore the alteration of surface characteristics after adsorption of surfactants on polymers⁷ or the transfer of monolayers onto the polymeric surface.^{8,9} A first surface modification of polymers with amphiphilic reagents on polyethylene powders using azides was reported by Holden et al.^{10,11} Among all covalent coupling methods, photochemical grafting possesses some advantages. By the choice of the substitution in a photoreactive compound nearly every functional group can be introduced; spatial and sequential resolution of the modification steps are possible. Numerous applications of azide photochemistry also exist in photolithography or photolabeling of biomolecules.¹² A few studies also deal with the application of azides to heterogeneous surface modifications, namely of polystyrene and poly(3-octylthiophene),¹³ and polyethylene, polyimide, and poly(tetrafluoroethylene),¹⁴ respectively.

In the course of our studies on the photomodification of polyacrylonitrile (PAN) ultrafiltration membranes,^{15,16} we investigated the possibility to

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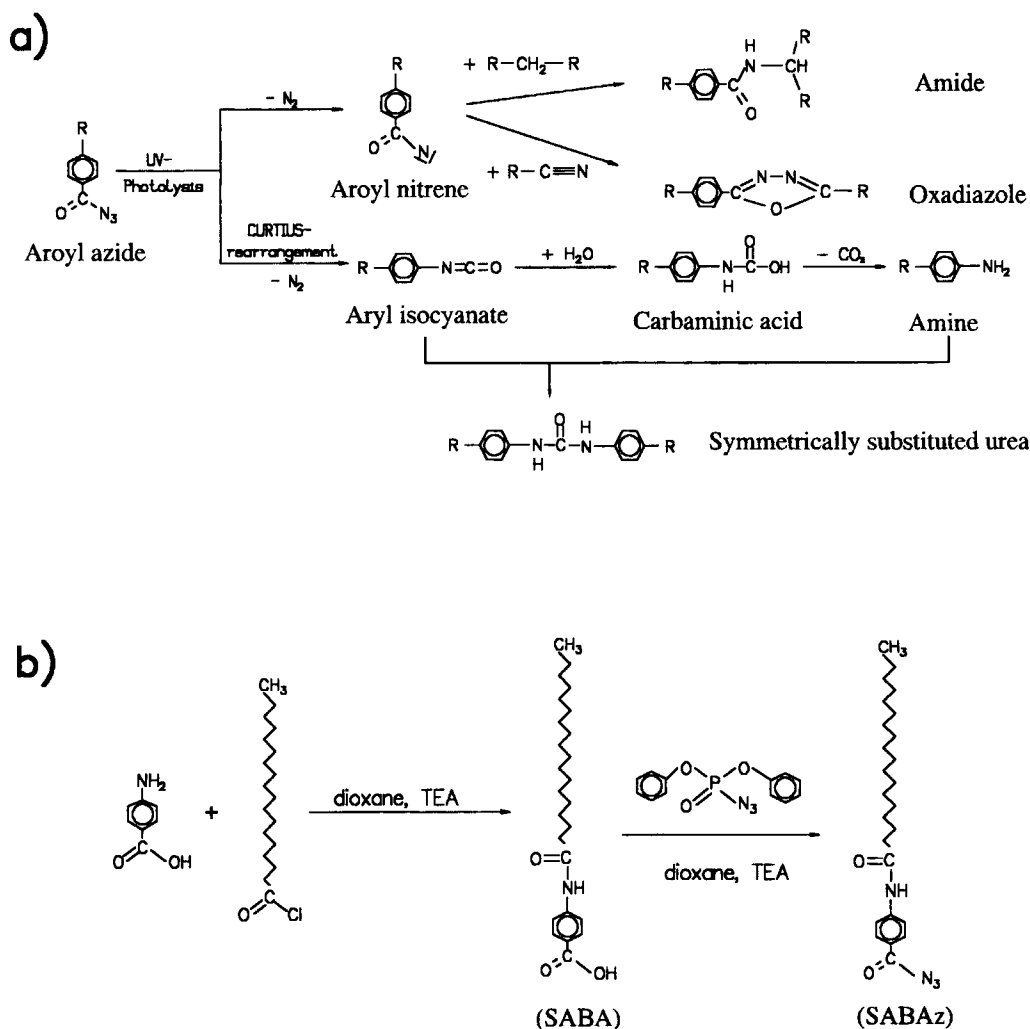


Figure 1 (a) Typical reactions of aroyl azides. (b) Synthesis of *p*-(stearyl amido) benzoyl azide (SABAz).

bind amphiphiles covalently onto surfaces via photolysis of aroyl azides. These compounds produce after ultraviolet (UV) irradiation and nitrogen extrusion aroyl nitrenes and aryl isocyanates [Fig. 1(a)]. Isocyanates can be trapped with nucleophiles, e.g., with water yielding carbaminic acids which easily decarboxylate to amines. Reactive aroyl nitrenes can undergo a variety of insertion reactions—even into C—H bonds; in this case amides are formed. With nitrile compounds the formation of oxadiazoles via cycloaddition may be possible, too. We therefore synthesized the amphiphile *p*-(stearyl amido) benzoyl azide (SABAz) derived from stearic acid [Fig. 1(b)]. It contains an aroyl azide group with sufficient thermal stability. We used 15-nm-thick PAN films, prepared by spin coating on a reflecting gold support. The film surface was shown to be smooth and continuous. The modification process

can be monitored spectroscopically, e.g., with reflection-absorption FT-IR (RA-IR) spectroscopy. Using polarized light gives additional information about structure and orientation of amphiphile molecules on the surface.^{17,18} For the application of thin layers of SABAz on PAN we used two different techniques, LB deposition and casting from solution. In order to evaluate the orientation on the surface, coupling efficiency, surface hydrophobicity, and solvent stability, RA-IR spectroscopy and contact angle measurements were applied.

EXPERIMENTAL

Materials

PAN was a technical product (Buna AG Schkopau, Germany; containing ca. 1% vinyl acetate; M_w

= 135,000 g/mol; M_n = 32,000 g/mol). All other chemicals and solvents were purchased from Merck (Germany) and used without purification. For LB experiments HPLC-grade chloroform (Merck, Germany) and Milli-Q water (Millipore reagent water system, Bedford, USA) were used.

Syntheses

p-(Stearyl Amido) Benzoic Acid (SABA)

12.1 g (0.04 mol) stearoyl chloride was added to 5.38 g (0.04 mol) *p*-aminobenzoic acid and 12 mL (0.25 mol) triethyl amine in 300 mL dioxane. The solution was stirred for 3 h at 50°C. The solvent was evaporated under reduced pressure. The residue was washed with 0.5M hydrochloric acid, methanol, and recrystallized from dioxane, leaving 13.8 g of pure product (yield 86%).

CHN: Calcd: $C_{25}H_{41}NO_3$, $M = 403.31$ g/mol: C, 74.4%; H, 10.2%; N, 3.5%.

Found: C, 74.1%; H, 10.1%; N, 3.4%

IR: (KBr-pellet) $\nu(NH) = 3330$ cm^{-1} , $\nu(C=O, \text{ acid} + \text{amide}) = 1668$ cm^{-1} .

1H -NMR: (DMSO- d_6) δ : 0.82 (CH_3), 1.24 (CH_2), 1.58 (β - CH_2), 2.34 (α - CH_2), 7.74/7.90 (aromatic ring), 10.32 (amide), 12.65 (acid).

p-(Stearyl Amido) Benzoyl Azide (SABAz)

1.0 g (2.47 mmol) SABA was dissolved in 100 mL of tetrahydrofuran (THF); 0.7 mL (5 mmol) triethyl amine and 0.83 g (3 mmol) diphenyl azido phosphate were added and the solution was stirred for 8 h at 35°C. After solvent evaporation the solid was washed with methanol and redissolved in chloroform. The residue was filtered off, evaporation of the solvent left a white solid. Recrystallization from diethylether at -50°C gave 0.76 g of white crystals (yield 72%).

CHN: Calcd: $C_{25}H_{40}N_4O_2$, $M = 428.32$ g/mol: C, 70.0%; H, 9.4%; N, 13.1%.

Found: C, 69.9%; H, 9.5%; N, 12.9%.

IR: See Table II.

1H -NMR: (DMSO- d_6) δ : 0.86 (CH_3), 1.26 (CH_2), 1.61 (β - CH_2), 2.35 (α - CH_2), 7.72/7.89 (aromatic ring), 10.50 (amide).

Preparation of PAN Spin-Coating Films

The 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): 0.1 mL of a 1% solution of PAN in dimethyl formamide was applied onto the

support and spun at 5000 rpm for 60 s. Heating at 50°C for 30 min in vacuum gave a solvent-free film.

Atomic Force Microscopy (AFM) Measurements

A Nanoscope III AFM (Digital Instruments, Santa Barbara, USA) with microfabricated silicon nitride cantilever (spring constant 0.12 N/m) was used in the constant deflection mode. Imaging was done in air with a 200- μ m scanner.

Contact Angle Measurements

The contact angles were measured using the captive bubble method. An air bubble was injected from a syringe with stainless steel needle onto the sample surface under water. The needle remaining inside the bubble, advancing and receding angle measurements were made with a goniometer fitted with a tilting stage (Carl Zeiss Jena, Germany) by stepwise adding and withdrawing of air.

Infrared Measurements

All measurements were made using a Nicolet Magna 550C FT-IR spectrometer with MCT/A detector and 4 cm^{-1} resolution. Typical number of scans was 2000 with new background spectra for every measurement.

For the reflection-absorption spectra, a reflection attachment (Model VRA-1 with RMA, Harrick, Ossining, USA) equipped with a double diamond polarizer (PDD-J2R, Harrick) was used at an angle of incidence of 83°.

Monolayer Preparation and Transfer

For monolayer experiments a microprocessor-controlled film balance (FW 2, Lauda, Königshofen, Germany) was used. A chloroform solution (0.2 mg/mL) of SABAz was spread on the subphase of pure water at 20°C. The monolayer was continuously compressed up to surface pressure of 30 mN/m and then maintained for 10 min in order to stabilize the monolayer. The layer was transferred by vertical withdrawal of the PAN film on the support from the subphase (dipping rate 1 mm/min).

Casting of Amphiphilic Solution

Multilayer amphiphilic films were prepared by immersing the PAN film on the support in 10 mL of SABAz in chloroform (0.03, 0.1, and 0.8%) for 60 s, quickly vertically withdrawing from the solution and evaporation of the solvent in air.

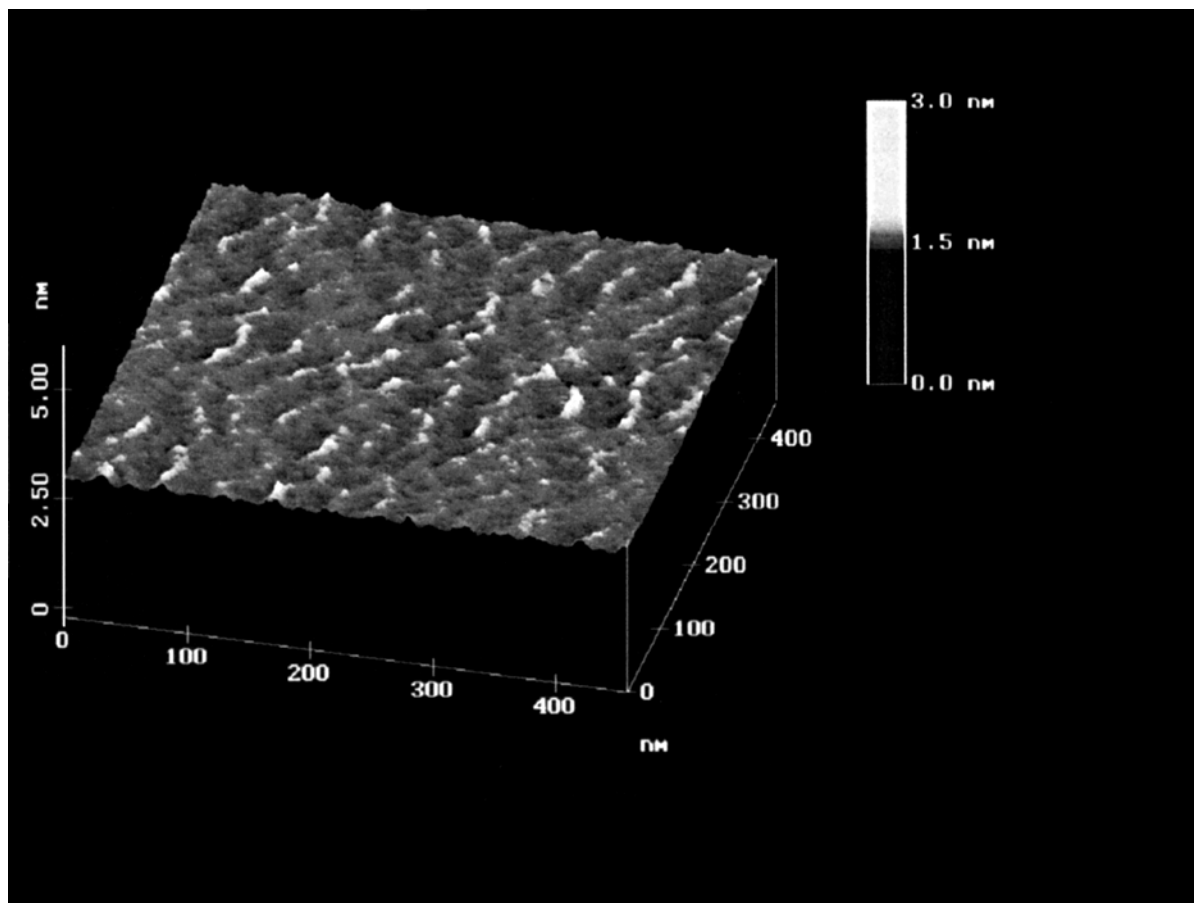


Figure 2 AFM image (3-D surface plot) of a PAN spin-coating film on gold-covered glass slide in air with a scan area of 450×450 nm.

Irradiation Experiments

Samples were irradiated under atmospheric conditions with a mercury lamp (HBO 50W/3, L.O.T.-Oriel, Darmstadt, Germany) equipped with a shutter for time-resolved photolysis and a water filter.

RESULTS AND DISCUSSION

SABAz Monolayers on PAN Films

Ultrathin PAN films were prepared by spin coating 1% polymer solutions in dimethylformamide (DMF)

Table I Contact Angles of Unmodified and SABAz Modified PAN Surfaces

Surface	Advancing Angle $\theta_{adv.}/(^{\circ})$	Receding Angle $\theta_{rec.}/(^{\circ})$	Hysteresis $\Delta\theta/(^{\circ})$
PAN spin-coating (sc) film	59 ± 1	40 ± 1	19
PAN sc film after LB transfer of SABAz monolayer	93 ± 1	84 ± 1	9
After UV irradiation and water storage for 24 h	89 ± 1	77 ± 1	12
After UV irradiation and chloroform treatment for 24 h	74 ± 2	44 ± 2	30
Parent PAN sc film after chloroform treatment	64 ± 2	36 ± 2	28
PAN sc film casted with SABAz solution			
$c = 0.8\%$	92 ± 4	48 ± 3	44
$c = 0.1\%$	76 ± 3	47 ± 3	29
$c = 0.03\%$	74 ± 3	47 ± 3	27
$c = 0.8\%$, after UV irradiation and chloroform treatment for 24 h	78 ± 2	45 ± 2	33

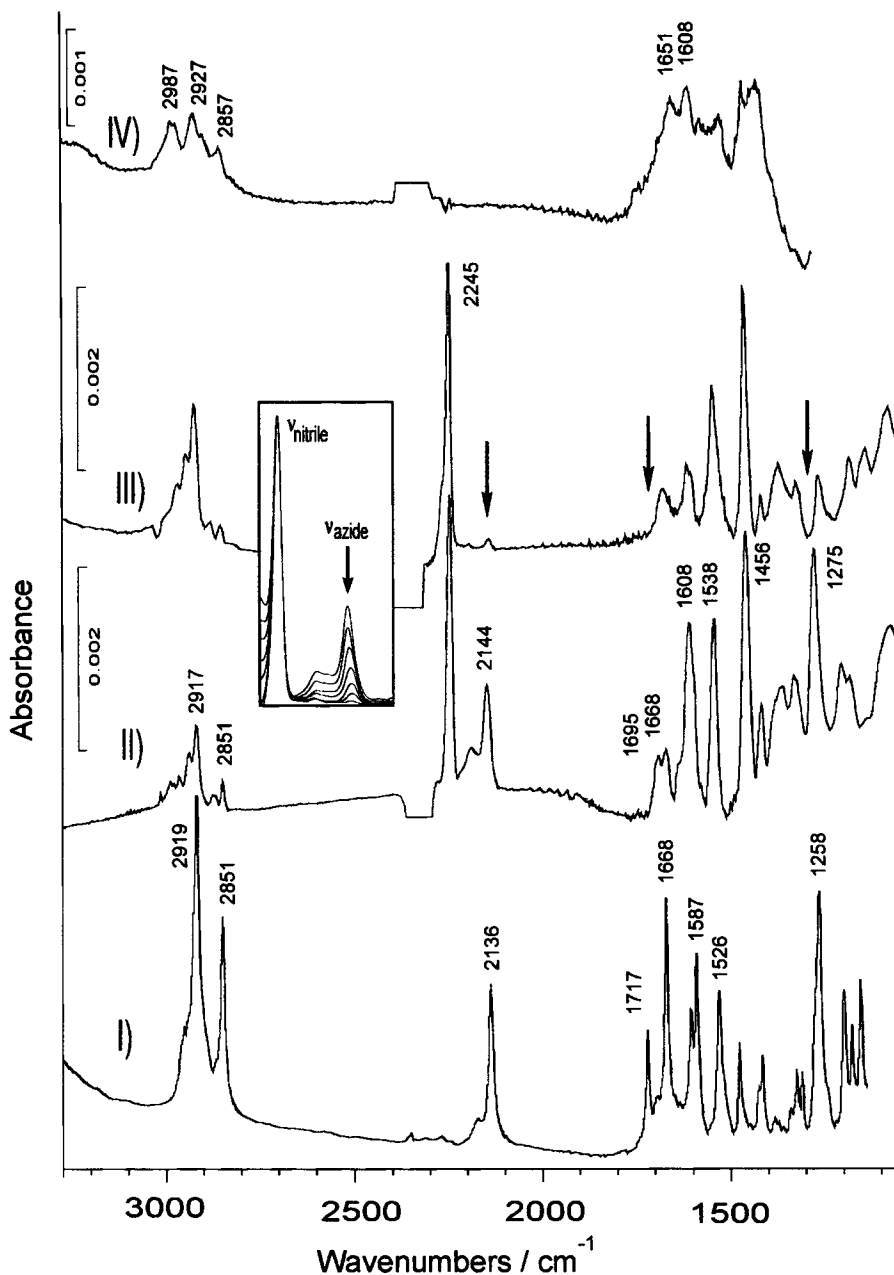


Figure 3 Transmission-IR spectra of (I) SABAz/KBr pellet and RA-IR spectra (*p*-polarized) of (II) SABAz monolayer on PAN spin-coating film after LB transfer, (III) the same sample after photolysis for 40 s, and (IV) after treatment with hot chloroform. Note that spectrum IV was obtained by subtraction of the spectra of an unmodified PAN spin-coating film. The insert spectrum shows the photochemical azide degradation.

on gold-sputtered glass slides. A final PAN film thickness of about 15 nm was measured by ellipsometry. The surface appears homogeneous and smooth in AFM images (Fig. 2). Defects or discontinuities could not be detected, the maximum height differences in the surface profiles are a few angstroms only. This smoothness of the surface is pre-

sumably also responsible for the low contact angle hysteresis of 19° (Table I). The corresponding value for PAN ultrafiltration membranes is about 30° . The measured advancing and receding contact angles indicate a moderately hydrophilic surface.

We have tested the monolayer behavior of SABAz on the Langmuir trough. The surface pressure versus

area curve for SABAz indicates a condensed region up to a surface pressure of 40 mN/m and an area per molecule of 0.25 nm² in the solidlike state of the monolayer. This is in agreement with values in the literature, reported for similar amphiphiles having an aromatic ring incorporated.^{19–21}

A monolayer of SABAz was then transferred at a constant pressure of 30 mN/m to the ultrathin PAN film on gold support by vertical lifting. Figure 3 shows the RA-IR spectrum of an about 15-nm thick PAN spin-coating (sc) film with one LB monolayer of SABAz, and the spectrum of pure SABAz dispersed in a KBr pellet for comparison. The characteristic PAN peaks (ν_{CN} at 2245 cm⁻¹ and δ_{CH} at 1456 cm⁻¹) appear in the spectrum. Other peak position and mode assignments are listed in Table II.

The comparison of spectra provides important information about the structure of the monolayer.^{17,18,22,23} The absorption bands for $\nu_{(\text{CH}_2)\text{symm.}}$ at 2851 cm⁻¹ and $\nu_{(\text{CH}_2)\text{asymm.}}$ at 2919 and 2917 cm⁻¹, respectively, in both the KBr pellet and in the monolayer of SABAz, indicate an all-trans configuration of the methylene chains.^{22,23} The peak-height ratio of asymmetric CH₂ stretch at 2917 cm⁻¹ and asymmetric CH₃ stretch at 2975 cm⁻¹, however, is only 2.3 in the monolayer as compared with 9.6 in the bulk transmission spectrum (KBr). This finding suggests that carbon chains in the monolayer are oriented almost perpendicular with respect to the surface and the transition dipole moment of the CH vibration almost parallel to the surface.^{22,23} The carbonyl vibration intensities are also reduced in the RA-IR spectra. Consequently, the dipole moments

of these groups are expected to be also parallel to the plane of incident of the IR beam, caused by their defined orientation in the monolayer on the PAN film.

In conclusion, the highly ordered state of the SABAz monolayer at the air–water interface was maintained after the transfer on the PAN film surface. More evidence for the good transfer quality is provided by the large contact angle of $\theta_{\text{adv.}} = 93^\circ$ caused by the SABAz monolayer (Table I). The low contact angle hysteresis of 9° also indicates high chemical and morphological uniformity.²⁴ The overall transfer behavior makes it very likely that the polar photoreactive group of the amphiphile is located close to the PAN surface. UV irradiation of these monolayers should therefore provide a high-yield modification of the PAN surface.

Photofunctionalization of PAN Films with SABAz from Monolayers

SABAz in THF solution shows a single UV absorption band at 302 nm. SABAz monolayers on 15-nm-thick PAN films have therefore been irradiated with UV light of a high-pressure mercury lamp. The only change in the RA-IR spectra of SABAz monolayers on PAN films observed after UV irradiation was the decrease of the azide bands at 2144, 1695, and 1275 cm⁻¹ (arrows in Fig. 3, Table II). Photolysis was monitored in intervals of 5 s (insert spectra, Fig. 3) and found to be complete within 40 s. Irradiation of the PAN film alone, with the same UV doses, did not produce any changes in the RA-IR spectra.

Table II Comparison of Mode Assignments and Peak Positions for SABAz

Vibrational Mode	RA-IR of LB Monolayer on PAN SC Film (See Fig. 2)	RA-IR of Multilayers on PAN SC Film (See Fig. 4)	Transmission Spectra of Chloroform Solution
$\nu_{(\text{NH,amide})\text{as}}$	—	3339	3431
$\nu_{(\text{CH}_2)\text{as}}$	2917	2917	2928
$\nu_{(\text{CH}_2)\text{s}}$	2851	2850	2855
$\nu_{(\text{azide})\text{as}}$	2144	2143	2136
$\nu_{(\text{C=O,azide})}$	1695 ^a	1694	1690 ^c
$\nu_{(\text{C=O,amide})}$	1668 ^a	1668	1690 ^c
$\nu_{(\text{C=C,aromatic})}$	1608/1597 ^b	1608/1597 ^b	1604
$\nu_{(\text{amide II})}$	1538	1538	1515
$\delta_{(\text{CH}_2)}$	1415	1412	—
$\nu_{(\text{azide})\text{s}}$	1274	1275	1253

^a Very weak intensity.

^b Peak splitting.

^c Only one peak.

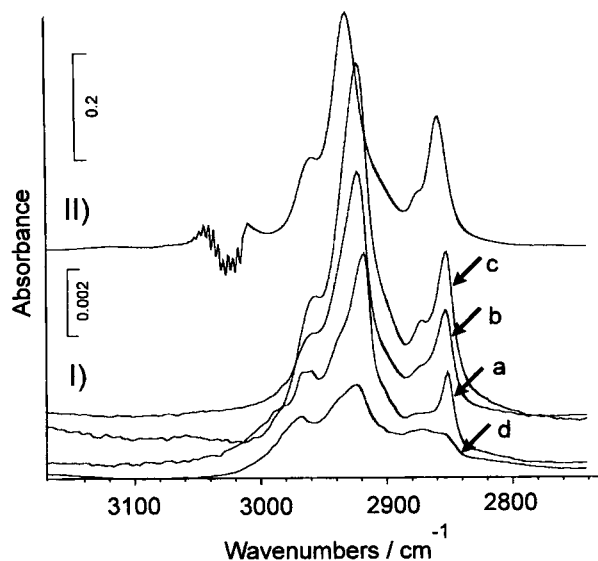


Figure 4 Comparison of CH vibration region: (I) RA-IR spectra of SABAz monolayer on PAN spin-coating film after (a) LB transfer, (b) after UV and treatment with water for 30 min, (c) with water for 72 h, and (d) with hot chloroform and (II) of a SABAz solution in chloroform.

Addition of water to surface monolayers should only change the degree of order in monolayers, characterized by the all-trans conformation of methylene groups, since SABAz is insoluble in water. The reason for shifts and broadening of the corresponding CH_2 bands is the increased gauche conformation content in the methylene chains, which is caused by penetration of water molecules into the monolayer and formation of defect areas.^{24,25} The observed shifts and broadening, as well as the enhanced intensity of CH_2 stretching bands after contact with water are an indication of decreasing crystallinity (Fig. 4, spectra b, c). Reduced chain density and/or defects change the orientation of the polymethylene chains relative to the surface. The methylene dipole moment comes to an increasing extent into an IR active orientation. This effect explains that the absorption intensity grows. Chloroform on the other hand should dissolve all of the noncovalently bound molecules from the surface. Indeed, the treatment yields a further band shift. The gauche/trans ratio for the SABAz in solution is, however, not reached (Table III). These spectroscopic results can be interpreted with domains of covalently bound molecules, preserving a relatively high degree of order. A similar phenomenon has been observed recently for the adsorption of surfactants onto silicon.²⁶ For low surface coverage, micellelike surfactant aggregates are discussed. Their IR absorption

maxima are very similar to the data obtained by us for PAN surface-bound amphiphiles (cf. Table III).

The contact angles of the photomodified films also changed upon solvent treatment. Extended exposure to chloroform caused a decrease of advancing and receding contact angles, along with a significantly enhanced hysteresis (Table I). However, the final values, especially the value of $\theta_{\text{adv.}} = 74^\circ$ (compared with $\theta_{\text{adv.}} = 59^\circ$ for the untreated PAN), show that the PAN films have been hydrophobized permanently.

Figure 5 summarizes the changes of the SABAz monolayers on PAN after UV irradiation due to treatment with solvents. With the analytical techniques used, it is impossible to distinguish between two possible mechanisms for the observed alterations, rearrangement under water ("overturning" hypothesis^{27,28}), or decrease in molecular order only by diffusion of water molecules into the monolayer.^{24,25} Nevertheless, all observations indicate, that the structure obtained by LB deposition and subsequent photolysis is not completely stable to solvents. The maximum yield of photofunctionalization, expected from the ordered state before irradiation, is obviously not reached. This may be caused by side reactions, e.g., the Curtius rearrangement [cf. Fig. 1(a)].²⁹ The acyl nitrene may also react with water molecules adsorbed between polymer and monolayer or with neighbor molecules yielding dimers or oligomers.

An unirradiated SABAz monolayer on PAN undergoes fast changes in morphology. Both contact angle and RA-IR spectra indicate the complete loss of the monolayer after treatment with cold chloro-

Table III Peak Positions of the CH_2 Stretching Vibrations of SABAz in Different Systems

Sample	$\nu_{(\text{CH}_2)_{\text{asymm.}}}$ (cm^{-1})	$\nu_{(\text{CH}_2)_{\text{symm.}}}$ (cm^{-1})	Remarks
Crystal	2919	2851	KBr pellet
Micelle	2923	2853	Ref. 28
Solution	2928	2857	Chloroform
	2933	2861	Ref. 28
Monolayer 0	2917	2851	On PAN sc film
Monolayer 1	2920	2851	After UV and 30 min water
Monolayer 2	2921	2853	After UV and 72 h water
Monolayer 3	2927	2857	After UV and 60 min Chloroform (60°C)

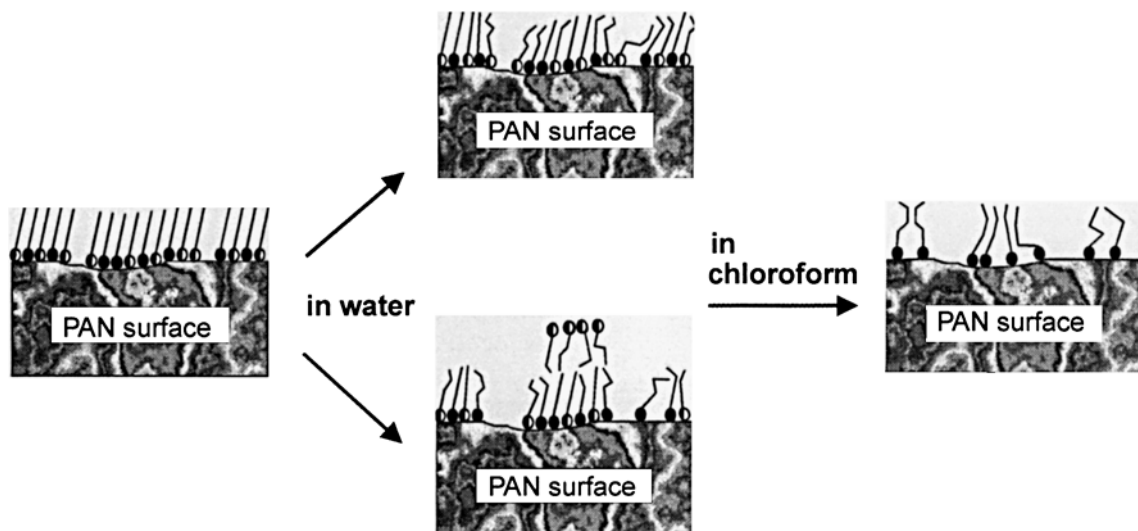


Figure 5 Schematic illustration of molecular rearrangement in the monolayer on PAN surfaces after the treatment with water and chloroform. The molecules with a black head group are covalently linked to the surface, half-filled circles represent other photolysis products.

form. Only a small increase in contact angle hysteresis is measured, caused by an increase in surface roughness by contact with chloroform observed with the parent PAN film, too (see Table I).

Photofunctionalization of PAN with SABAz Multilayers Casted from Solution

The use of the LB technique has practical limitations in modifications of large polymer surfaces or of porous materials such as flatsheet or hollow-fiber membranes. Simple casting of amphiphiles from solution is known to produce ordered multilayer films.^{6,30-32} Since chloroform does not dissolve or swell the polymer PAN, it can be used for casting procedure.

Figure 6 summarizes the procedure with help of RA-IR spectra of thin PAN films: (I) after coating with a SABAz solution in chloroform (0.8%) and solvent evaporation, (II) after UV irradiation for 2 min, (III) after storage at 60°C for 10 min, and (IV) after treatment with hot chloroform. SABAz on the PAN film was detected easily by RA-IR spectroscopy (Fig. 6, spectrum I). Complete UV-induced azide decomposition was observed within 120 s. One expected product, aryl isocyanate [cf. Fig. 1(a)], was indicated by its characteristic band at 2275 cm^{-1} . Isocyanate degraded completely within 10 min at 60°C. A new strong band appeared at 1565 cm^{-1} (Fig. 6, spectrum III). These bands could be assigned to two possible isocyanate products. Hydrolysis of

isocyanate produces arylamine via thermal decarboxylation of carbamic acids. The formation of symmetrically substituted urea by amine addition to isocyanate is known to be effective and may be favored by the simultaneous presence of both in the multilayer film [cf. Fig. 1(a)].

Water at room temperature and at 50°C induced no changes. Exposure to THF lead to a decrease of all bands except the PAN bands. Finally, chloroform at 50°C caused a further decrease in peak intensities. However, a difference spectrum (Fig. 6, spectrum IV) still shows bands in the methylene and carbonyl regions (at 1642 and 1606 cm^{-1}) but not the peak at 1565 cm^{-1} .

These results are interpreted as follows. Application of the amphiphile by solvent evaporation from a chloroform solution leads to a multilayered structure on the exposed polymer surface (Fig. 7). The interactions of the aromatic rings and the possible formation of an extended chain of amide hydrogen bonds should promote the SABAz layer formation.^{3,4,6} Stabilizing hydrophobic interactions between methylene groups are also possible in such a structure. Evidence for ordered multilayers comes from the RA-IR spectra: the positions of the CH_2 valence bond absorptions (2850 and 2917 cm^{-1}) indicate chains within crystalline phases. However, the intensity of the carbonyl bands (1694 and 1662 cm^{-1}) depends on the concentration of SABAz solution. The insert spectrum in Figure 6 shows the carbonyl region at three concentrations. Both, the

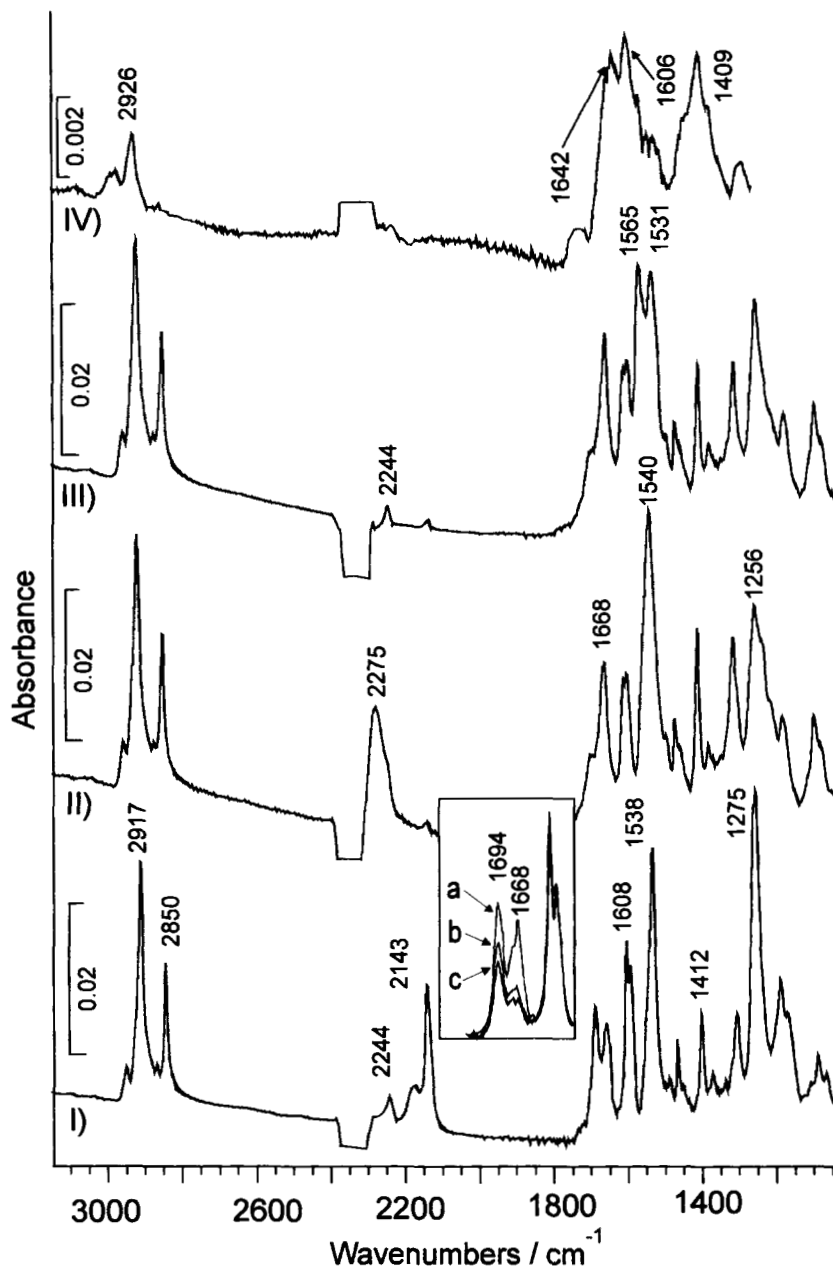


Figure 6 RA-IR spectra of amphiphilic multilayers on PAN spin-coating film (I) after solvent evaporation, (II) after photolysis for 2 min, (III) after heating at 60°C for 10 min, and (IV) after treatment with hot chloroform. The insert spectrum shows the carbonyl band region of spectrum I for different SABAz concentrations ($a = 0.8\%$, $b = 0.1\%$, $c = 0.03\%$). Note that spectrum IV was obtained by subtraction of the spectra of an unmodified PAN spin-coating film.

intensities of azide carbonyl and amide carbonyl bands increase with increasing concentration less than for other bands. Therefore, it seems likely that well-ordered multilayers with defined orientation (carbonyl vibration parallel to the surface) were built up from low concentrated amphiphilic solution. At

larger concentration less oriented structures were obtained. This may be explained with the rapid formation of a multilayered microcrystallites situated randomly on the polymer surface. The contact angle measurements showed a hydrophobic surface for all samples (Table I), but large hystereses and poor re-

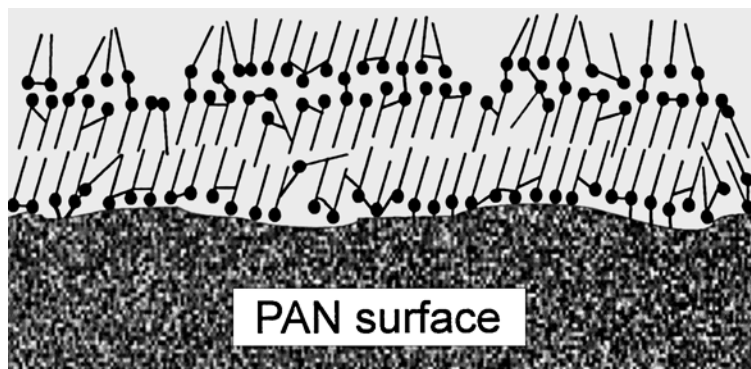


Figure 7 Schematic illustration of multilayered crystal structure covalently linked to PAN surface and crosslinked by UV irradiation resulting in a hydrophobic surface.

producibilities were characteristics of surface coatings obtained with highly concentrated solutions. Presumably, the hydrophobic parts of the SABAz molecules are again aligned at the crystal–air interface, but the microroughness of the crystal-coated surface seems to be responsible for hysteresis and low reproducibility. UV irradiation of such multilayers should a priori provide the possibility of chemical crosslinking within the crystals.

The effect of solvents was also studied for the multilayer crystallites. No effect of water was detectable. Treatment with THF, relatively good solvent for unirradiated SABAz, results in some loss of material, but most remained on the polymer surface. Nonirradiated SABAz was under the same conditions completely removed. These observations may be a result of typical isocyanate reactions, such as formation of an urea with two long-chain alkyl substituents, probably not soluble in polar solvents. However, hot chloroform removes this product too, but not the covalently bound molecules. Consequently, RA-IR spectra and contact angle measurements confirm a significant and permanent hydrophobization of the PAN film comparable with the effect of LB modification.

It is most remarkable that the difference spectra, obtained after both the LB monolayer and the solution casting procedures are very similar (cf. Fig. 3, spectrum IV and Fig. 6, spectrum IV). This leads to the conclusion that irrespective the constellation before photoreaction, the binding step, the formation of a covalent bond to the polymer will be similar. With respect to the photoproducts, absorptions around 1650 and 1610 cm^{-1} can be attributed to the CH-insertion reaction product (secondary or tertiary amide). Additionally, it should be mentioned that both the amide and aromatic bands of SABAz are located in this region. Their broad shape is probably

due to the superposition of all these vibration bands. A theoretically possible PAN-specific functionalization product having oxadiazole structure (formed via cycloaddition of acyl nitrene and nitrile³³) was not detected. This may be due to a lack of specific IR absorption bands.

CONCLUSIONS

The aroyl azide head group of SABAz provides sufficient hydrophilicity and stability toward hydrolysis to form stable monolayers. The aryl amide linkage does not disturb formation of a dense packing.

Spin-coated thin PAN films are excellent supports for SABAz LB films because of their smooth surface and moderate hydrophilicity. Application of such PAN films on gold allows the detailed characterization of amphiphile structure on the polymer surface by RA-IR spectroscopy.

The results prove a high degree of monolayer crystallinity and orientation. Casting of SABAz solution onto PAN leads at first to a much less ordered surface.

Quantitative photoconversion of SABAz on PAN induced by UV irradiation occurs within minutes. Permanent surface modification, causing a significant PAN hydrophobization, is always obtained.

For practical purposes the solution casting procedure is probably the method of choice because it yields a higher degree of water-stable surface hydrophobization than the LB method. Nevertheless, the LB photografting approach is also promising in applications with aqueous solutions.

Polymer surfaces with intrinsic reactivity toward nitrene and isocyanate reactions (e.g., cellulose) may be functionalized even more efficiently than PAN. In general the mild modification conditions avoid polymer degradation during functionalization.

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