Synthesis and Langmuir–Blodgett Multilayer-Forming Properties of Photo-Cross-Linkable Polyglutamate Derivatives

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ABSTRACT: The synthesis of polyglutamate derivatives containing methyl, octadecyl, and 11-cinnamoylundecyl side chains is described. The influence of the different side-chain ratios on the spreading behavior and the compressibility of the monolayers is discussed. Stable monolayers were obtained that could be transferred onto hydrophobic substrates to build up multilayers, showing an orientation of the α-helical rods parallel to the dipping direction. Multilayers were cross-linked by exposure to UV light. The cinnamoyl groups show a fast cis/trans isomerization due to the large free volume available in the layers. The change of the internal structure of the films during irradiation, annealing, and after rinsing with solvent were probed with X-ray reflectometry. It is shown that the photo-cross-linkable polyglutamates provide a negative-type photoresist without the disadvantage of swelling.

Introduction

A general problem hindering the practical application of conventional Langmuir–Blodgett (LB) films[1] is the domain structure of the polycrystalline layers of most of these materials. The electrical, optical, and transport properties of these films are mainly determined by grain boundaries. Many attempts have been reported to diminish the defect density of this kind in LB films of amphiphilic compounds and polymers.[2] Additional problems arise from the fact that the hydrophilic part of conventional LB layer-forming systems may introduce considerable amounts of water into the multilayer assembly. Drying procedures subsequent to the assembly process will then lead to structural reorganizations.[3]

Recently, a new type of molecular design, based on rigid rodlike polymers decorated with hydrophobic flexible side chains (hairy rods), suitable for the formation of Langmuir–Blodgett films was introduced.[4,7] Rodlike polymers such as polypeptides in their α-helical conformation are well-known as surface-active materials which produce stable monolayers at the air/water interface.[8] Generally, however, these monolayers are not suitable for the LB process and thick multilayers cannot be assembled.[9] The attachment of flexible hydrocarbon side chains, typically C_{12}–C_{22} chains, to this kind of polymers has been shown to lead to monolayers that are transferable onto hydrophobic substrates during down- and upstroke.[6] Since side-chain crystallization was found to be adverse to the LB transfer behavior of these polymers, ordering phenomena in the side-chain region are generally suppressed by the synthesis of copolymers in which short and long side chains are randomly mixed. This design allows for the transfer of these monolayers and gives the multilayer assemblies the character of molecularly reinforced liquids.[10] Thick films of up to 1000 individual layers have been prepared and investigated. Characterization of multilayers of copolyglutamate as waveguides demonstrates the high quality of these films.[11,12] The film-forming principle involved is totally different from that of classical LB films and is due to the anisotropic interactions between the rigid rods. It is worth mentioning that polymers of similar kind form thermotropic cholesteric liquid crystalline phases.[13]

The side-chain elements of the copolyglutamates can act as a host matrix for small oleophilic molecules within the layered assembly.[7] It should therefore be possible to introduce covalently fixed photoreactive "guest molecules" into the side-chain moieties of these polymers, thus obtaining photo-cross-linkable LB multilayers to be used in the lithographic fabrication of patterns. Since the cross-linking should take place in the disordered part of the assemblies, it should not lead to reorganizational processes or substantial changes in the dimensions of the assemblies. In practice, there exists a considerable demand for ultrathin films, photoresists, and membranes to be applied in advanced technologies.[14]

The cinnamoyl group is a well-known photoactive residue for cross-linking of polymers.[15] In the following, the investigation of ternary copolyglutamates containing methyl, octadecyl, and 11-cinnamoylundecyl side chains is described with regard to the influence of the functional groups on the monolayer behavior at the air/water interface, the formation of multilayers, and their structural characterization before and after cross-linking with UV light.

Experimental Section

Materials. *trans*-Cinnamoyl chloride (98%) was received from the Aldrich Chemical Co. and was used as received. γ-Methyl-L-glutamate (>99%), L-glutamic acid (>99%), trichloromethyl chloroformate (97%) and 11-bromoundecanol (97%) were obtained from the Fluka Chemical Corp. Tetrahydrofuran (HPLC grade) was destilled over sodium, dichloromethane (HPLC grade) over P_4O_{10}, and *n*-hexane (HPLC grade) over $LiAlH_4$.

Synthesis and Characterization. γ-Methyl-L-glutamate *N*-carboxyanhydride was prepared by the treatment of γ-methyl-L-glutamate with trichloromethyl chloroformate (diphosgen).[16] γ-*n*-Octadecyl-L-glutamate *N*-carboxyanhydride was prepared according to ref 17.

11-Bromoundecyl Cinnamate (1) was prepared by the slow addition of a dichloromethane (50 mL) solution of cinnamoyl chloride (7.33 g) to a water-cooled mixture of 11-bromoundecanol (10.04 g, 40 mmol), pyridine (6 mL), and

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dichloromethane (80 mL). After being stirred for 1 h at room temperature, the reaction mixture was filtered over silica gel and the solvent evaporated to give 15 g (98%) of **1**: mp 30 °C; IR (KBr) 3050, 2925, 2850, 1712, 1635, 1450, 1310, 1170, 980, 770, 710, 685 cm^{-1}. ^{1}H-NMR and ^{13}C-NMR spectra fit the structure exactly. Anal. Calcd for $C_{20}H_{29}BrO_2$: C, 63.00; H, 7.66. Found: C, 63.20; H, 7.80.

***γ*-(11-Cinnamoylundecyl)-L-glutamate (2)** was prepared according to ref 18 by the addition of 35 g (92 mmol) of 11-bromoundecyl cinnamate to a solution of the tetramethylguanidinium salt of the copper complex of L-glutamic acid (prepared by the slow addition of 10.9 mL of *N,N,N′,N′*-tetramethylguanidine to a stirred mixture of 10.65 g of Cu (Cu-(Glu)$_2$, 6.46 g of L-glutamic acid, 39 mL of DMF, and 6.2 mL of H_2O, which was diluted with 31 mL of DMF after all solids had been dissolved). The reaction mixture was stirred at 40 °C for 2 days and further treated as described in ref 18. The crude amino acid was recrystallized from 2-propanol/water (2:1) to give 14.4 g (35%) of **2**: mp 165 °C; TLC (acetic acid/*n*-butanol/water 100:10:3; ninhydrin) $R_F = 0.68$; IR (KBr) 3440, 2920, 2845, 1730, 1710, 1630, 1615, 1580, 1500, 1410, 1180 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$/TFA-d_1) δ 7.75 (d, $J = 16$ Hz, 1H), 7.54 (m, 2H, Ph), 7.41 (m, 3H, Ph), 6.48 (d, $J = 16$ Hz, 1H), 4.41 (brs, 1H), 4.27 (t, $J = 6.7$ Hz, 2H, CH_2O), 4.16 (t, $J = 6.7$ Hz, 2H, CH_2O), 2.82 (t, $J = 6$ Hz, 2H), 2.42 (m, 2H), 1.72 (m, 4H), 1.32 (m, 14 H); ^{13}C NMR (75.5 MHz, TFA) δ 179.5, 175.1, 174.7, 150.7, 136.3, 133.6, 131.4, 130.7, 118.5, 70.4, 69.6, 56.4, 33.0, 31.7, 31.4, 30.7, 30.5, 28.1, 27.9, 27.2. Anal. Calcd for $C_{25}H_{37}NO_6$: C, 67.09; H, 8.33; N, 3.13. Found: C, 66.85; H, 8.54; N, 3.52.

***γ*-(11-Cinnamoylundecyl)-*N*-carboxy-L-glutamic anhydride (3)** was prepared following the method of Katakai and Iizuka[16] by the addition of trichloromethyl chloroformiate (0.4 mL, 3.35 mmol) to a mixture of *γ*-(11-cinnamoylundecyl)-L-glutamate (2 g, 4.47 mol), active charcoal (50 mg), and THF (50 mL). After being stirred for 30 min at 50 °C, the solution was filtered over Celite and evaporated, and the residue recrystallized from THF/*n*-hexane to give 1.47 g (70%) of **3**: mp 85 °C; IR (KBr) 3320, 2920, 2855, 1880, 1785, 1712, 1635, 1310, 1255, 1200, 1170, 1120, 940 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (d, $J = 16$ Hz, 1H), 7.51 (m, 2H, Ph), 7.35 (m, 3H, Ph), 6.83 (brs, 1H, NH), 6.42 (d, $J = 16$ Hz, 1H), 4.39 (t, $J = 6$ Hz, 1H), 4.06 (t, $J = 6.7$ Hz, 2H, OCH_2), 2.52 (t, $J = 6.8$ Hz, 2H, OCH_2), 2.25 (m, 1H), 2.10 (m, 1H), 1.65 (m, 4H), 1.32 (m, 14H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 172.6, 169.4 (C-1), 167.2, 151.5 (NHCOO), 144.64, 134.4, 130.2, 128.8, 128.0, 118.2, 65.4, 64.7, 57.0, 29.8, 29.4, 29.3, 29.14, 29.10, 28.7, 28.4, 27.0, 25.9, 25.8.

For the preparation of the copolymers, the freshly recrystallized *N*-carboxyanhydrides (NCAs) were dissolved at a concentration of 0.1 mol/L in dichloromethane/THF (4:1) and the polymerization was initiated by the addition of dry triethylamine (2 mol %). After being stirred for 2 days at room temperature, the reaction mixture was poured into a 4-fold volume of methanol to give a colorless, fibrous material: ^{1}H NMR (300 MHz, $CDCl_3$/TFA-d_1; Ci = cinnamoyl, Me = methyl, Oc = octadecyl) δ 7.73 (d, 1H-Ci, H-3″), 7.52 (m, 2H-Ci, arom), 7.39 (m, 3H-Ci, arom), 6.48 (d, 2H-Ci, H-2″), 4.60 (m, 1H, H-1), 4.25 (t, 2H-Ci, H-11′), 4.09 (m, 2H-Oc, 2H-Ci, H-1′), 3.70 (s, 3H-Me, OCH_3), 2.49 (m, 2H, H-4), 2.15 (m, 1H, H-3a), 1.98 (m, 2H-Oc, 2H-C, H-2′), 1.25 (m, 16H-Ci, 30H-Oc, CH_2), 0.86 (t, 3H-Oc, CH_3).

Sample Preparation. A solution of 0.3 mg of polymer/1 mL of $CHCl_3$ (Merck Uvasol) was spread on a pure water subphase (Milli-Q quality) contained in a commercial Lauda FW1 film balance. Surface pressure–area measurements were recorded at 20 °C subphase temperature with a rate of compression of 50 mm/min. Monolayer transfer was performed onto hydrophobic substrates with a Y-type deposition. Silicon wafers, quartz, and glass slides to be used as substrates were cleaned with $CHCl_3$ in an ultrasonic bath for 15 min, treated with a hot solution of NH_4OH (25%)/H_2O_2 (30%)/water (1:1:5) for 20 min, and rinsed with water. Hydrophobization was achieved by treatment with a solution of hexamethyldisilazane in $CHCl_3$ for 30 min at 50 °C.

Measurements. Infrared spectra were obtained on a Perkin-Elmer 1430 ratio recording infrared spectrophotometer (KBr pellet). NMR (^{1}H and ^{13}C) spectra were recorded on a Bruker AC 300 FT spectrometer. Copolymer compositions were determined with the integrated intensity of characteristic signals of each comonomer in the ^{1}H-NMR spectra of the polymers in $CDCl_3$/TFA mixtures.

X-ray reflection spectra of LB multilayers on float glass were recorded with the X-ray reflectometer (Rigaku rotating anode, Ni-filtered Cu Kα line) described in ref 19. The reflectivity of different LB films on float glass substrates was measured with a scintillation counter while the sample was rotated in steps of 0.008 deg and the detector in steps of 0.016 deg. The beam is collimated to 0.2 mm width, 1.0 cm height, and a divergence of 0.01 deg. The background is lower than 0.2 counts/s, and the flux on the sample amounts 10^6–10^7 counts/s. The experimental reflectivity is compared with simulations of different models of the LB multilayer system, calculated with the Fresnel matrix method[20] and the first Born approximation.[21]

UV spectra were recorded with a Perkin-Elmer Lambda 9 spectrometer. All measurements were done with quartz slides as substrates. The uncoated part of the slide was used as reference. FT-infrared measurements on LB multilayers were carried out with a Nicolet 69 SX FTIR spectrometer. Transmission spectra were recorded with a resolution of 4 cm^{-1} using silicon wafers as substrate (thickness 1 mm). Grazing incidence reflection spectra on the assemblies on gold substrates were measured as described previously.[22]

Results and Discussion

Synthesis of the Polymers. Terpolymers **II**–**IV** of *γ*-methyl-L-glutamate *N*-carboxyanhydride (**4**), *γ*-*n*-octadecyl-L-glutamate *N*-carboxyanhydride (**5**), and the photoreactive cinnamoyl group containing NCA **3** were synthesized by triethylamine-initiated polymerization following the well-known procedure of NCA polymerization.[23] The synthesis of monomers **4** and **5** was performed following refs 16 and 17; the synthesis of **3** is described in the Experimental Section. The copolymer **I** was synthesized as reported previously.[12]

A set of terpolymers of the general structure shown in Chart 1 was synthesized and characterized with regard to performance in the LB process. The conditions used here for the polymerization of NCAs commonly gives rise to polymers of high DP, typically of the order of 1000 < DP < 2000. We did not attempt to measure exact molecular weights of our samples since it was known from previous investigations that the chain length is not a crucial parameter in the LB process of this type of macromolecule.[24] The selection of the actual composition of the terpolymers was dictated by considerations already outlined above, namely, that side-chain crystallization had to be suppressed.

Behavior at the Air/Water Interface. Surface pressure–area isotherms of polymers **I**–**IV** are shown in Figure 1. Whereas the portion of octadecyl side chains is approximately 30% in all copolymers, the amount of cinnamoyl side chains is varied between 0 and 25%. The cinnamoyl groups in the copolymers have considerable influence on various parameters characterizing the surface activity. The area per monomer unit, the plateau surface pressure, and the compressibility ($C_s = A^{-1}(\delta A/\delta\pi)$) of the monolayers all depend on the concentration of cinnamoyl groups. These groups lead to an increase of the area per repeat unit of the α-helix. It is reasonable to assume that the ester groups at the end of the side chains interact in some way with the water surface in the expanded state of the monolayer. The shape of the isotherms is particularly interesting with regard to the compression mechanism of monolay-

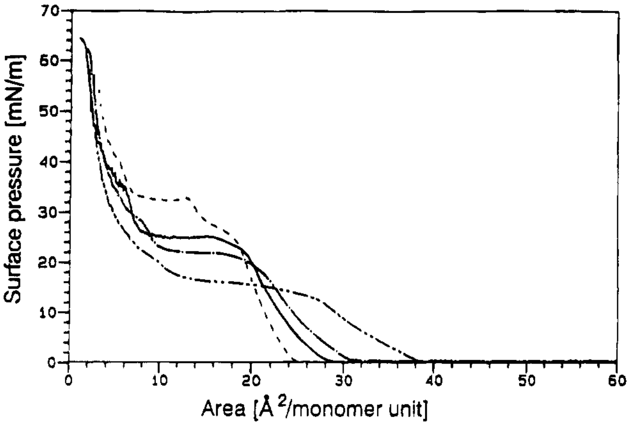


Figure 1. Surface pressure–area diagrams of copolyglutamates I (- - -), II (—), III (— • —), and IV (— - -) at 20 °C.

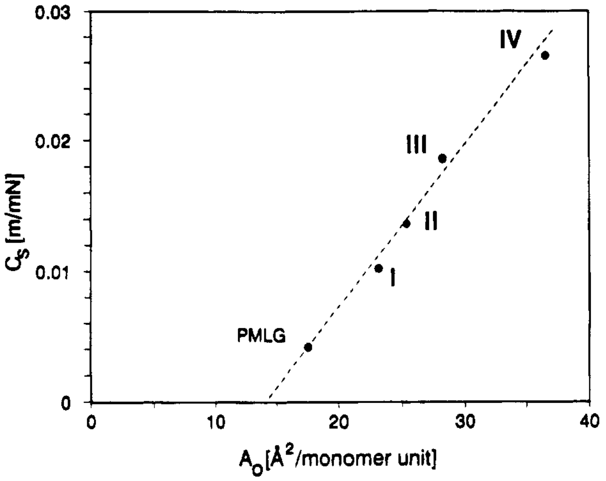
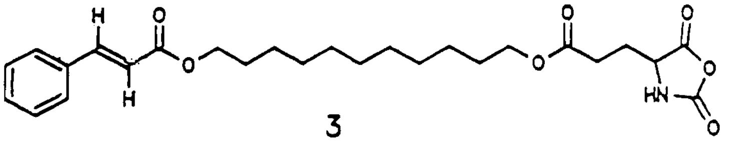


Figure 2. Monolayer compressibility C_s at the point of inflection in the surface pressure–area isotherms plotted against the extrapolated area per monomer unit A_0 at zero pressure. For identification of polymers I–IV, see Chart 1.

ers of hairy rods. In general, the compressibility decreases with decreasing area up to a point of inflection, after which a plateau in the π/A curves is observed. In the case of the polymers with additional cinnamoyl side chains, the onset of the surface pressure is at higher areas per repeat unit but the compressibilities are also considerably higher. This suggests that the cinnamoyl groups leave the interface during compression. When a polar group is attached to the side chain, the area per repeat unit is increased and additional energy (indicated by an increased area under the π/A isotherms) is required to remove the more polar side chains from the interface, but finally a similar compressed state is achieved. In Figure 2, the two-dimensional compressibilities C_s of polymers **I**–**IV** and poly(methyl-L-glutamate) (PMLG) at the point of inflection of the isotherms below the plateau are plotted against the area A_0, extrapolated to zero pressure. The points fit a straight line intersecting the abscissa at approximately 14 Å². This value can be regarded as the area related to the incompressible part of monolayers of substituted α-helical polypeptides. A monolayer of polyalanine, where only methyl groups are attached to the α-helical backbone, shows an area per repeat unit of 13.8 Å² at zero pressure.[8b] This shows that the incompressible part of the investigated monolayers is identical with the α-helical backbone with the smallest possible substituent. The observed proportionality between compressibility and area per repeat unit demonstrates that the compressibility of these hairy rod systems is mainly determined by the side-chain interactions with surfaces (here the water surface) and with each other. Work done on the monolayer during compression is balanced against osmotic pressure, which builds up with the concentration of the side chains in the remaining volume being increased. This reversible process may provide for the elasticity of these films, which is reflected in the excellent transfer behavior of these materials.

An interpretation of the plateau generally observed in the surface pressure–area isotherms of α-helical polypeptides was given by Malcolm.[25,26] He treated this

Chart 1



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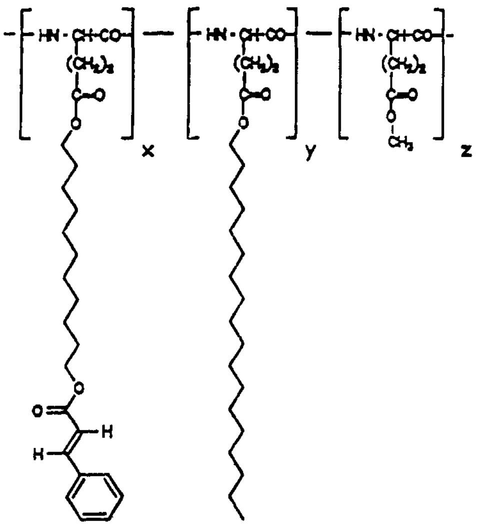


Sample	x	y	z
I	0	0.3	0.7
II	0.1	0.3	0.6
III	0.15	0.25	0.6
IV	0.26	0.26	0.48

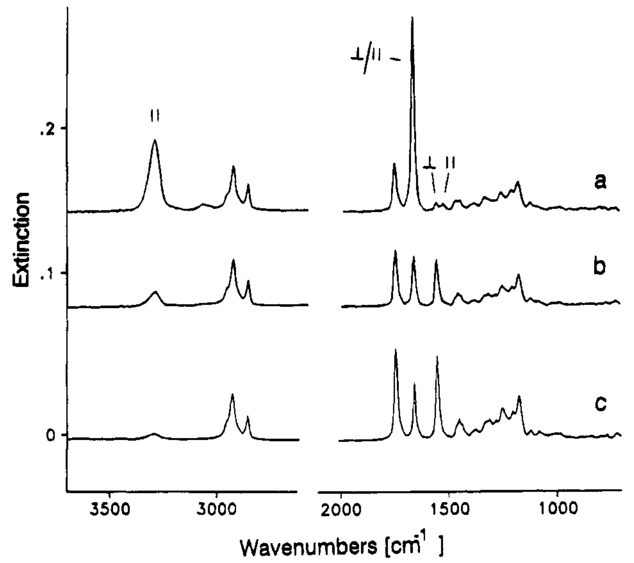


Figure 3. FTIR spectra of 40 layers of **II**. Transmission spectra with polarization of the electric field parallel (a) and perpendicular (b) to the dipping direction. The grazing incidence reflection spectrum (c) is depicted normalized to the transmission spectra for the C=O band at 1738 cm^{-1}.

plateau as a transition from a monolayer to a bilayer. However, it has been shown recently by ellipsometry on Langmuir films of these kinds of polymers that the plateau region corresponds to the formation of an undefined multilayer piling up in front of the barrier.[27] Nevertheless, the height of the plateau can be interpreted as a measure of the work required for this transition to be nucleated and it is therefore a function of the free energies of the water/air, water/polymer, and polymer/air interfaces.

α-Helical polypeptides show an increase of the plateau heights when decorated by increasing number of long side chains, which can be understood in this sense by a strengthening of the monolayer via the formation of a hydrocarbon-like film on top of the monolayer. This film reduces the free energy of the polymer/air interface and leads to an increase in the obtainable surface pressure of the monofilm. Transferred multilayers show a double-layer periodicity which is a direct consequence of the previously discussed nonsymmetric structure of the compressed monolayer at the air/water interface.

On this basis, we can qualitatively understand the influence of the content of cinnamoyl groups on the plateau height. According to our model, the cinnamoyl moieties affect mainly the free energy of the polymer/air interface in the compressed monolayer. The bulky cinnamoyl groups cause an increase of this energy and therefore should decrease the energy necessary for the bilayer formation. This is in agreement with our measurements (Figure 1).

Multilayers. In view of the investigation of photo-cross-linking of multilayers, polymer **II** was chosen, which can be transferred at a surface pressure of 20 mN/m (20 °C) and a dipping speed of 20–100 mm/min. The transfer ratio onto hydrophobic substrates was always 1 in down- and upstroke.

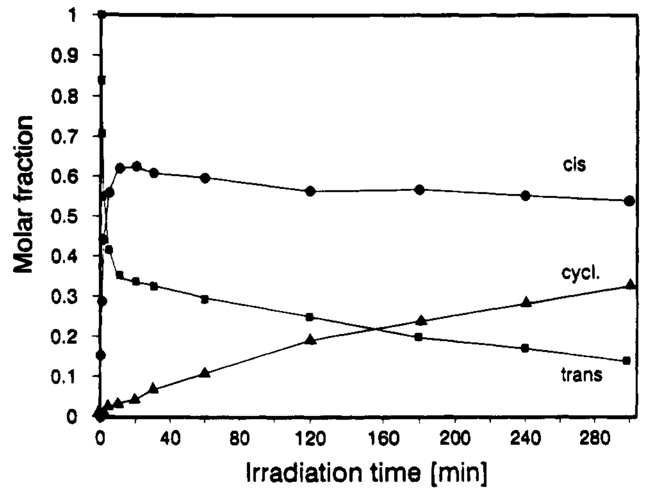
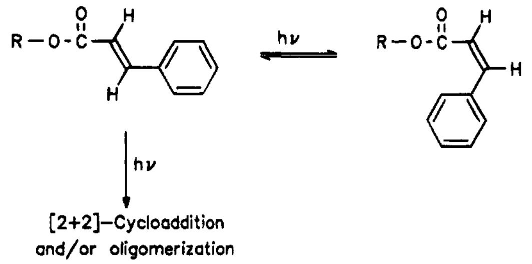


Figure 4. Progress of the cis/trans isomerization and cycloaddition reactions of the cinnamoyl groups in a multilayer of 120 layers **II** during irradiation with 254 nm UV light.

Scheme 1



FTIR Spectroscopy. FTIR spectra of multilayers of polymer **II** were taken in grazing incidence reflection (GIR) and in transmission geometry with polarized light and are depicted in Figure 3. The spectra show nearly the same pattern as has been reported for a similar copolymer without photoreactive groups.[6,22] The amide bands are designated by ∥ and ⊥ symbols, referring to the direction of the corresponding transition moment within the α-helix. The dichroism of the amide A band (∥; 3289 cm^{-1}) and of the amide II band (⊥; 1550 cm^{-1}) with respect to the dipping direction shows the existence of α-helices oriented parallel to this direction. From the observed linear dichroism of the amide II (⊥) band ($I_{\parallel}/I_{\perp} = 0.18$), a mean deviation between the α-helix axis and the dipping direction of 23 deg can be derived. The small intensities of the amide A and amide I (∥ and ⊥; 1658 cm^{-1}) bands and higher intensity of the amide II (⊥) band (1554 cm^{-1}) in the GIR spectra are a clear indication that the rods are arranged in the plane of the substrate.

UV Spectroscopy. Upon irradiation of cinnamate moieties, a cis/trans isomerization may compete with the expected cross-linking reactions. These are the [2 + 2] photocycloaddition and the formation of oligomer products (probably formed via a radical polymerization mechanism) (Scheme 1).

In very dilute solutions of, for example, ethyl cinnamate the isomerization is the only photoprocess. This is demonstrated by an isosbestic point at 250 nm which is observed in the UV spectra taken during irradiation.[28] At higher concentrations, photocycloaddition[29] competes with isomerization. In the bulk state, the rate of isomerization depends on the free volume available to the cinnamate moiety. In crystals of *trans*-cinnamic acid, dimerization is the only photoprocess.[30] In poly(vinyl cinnamate), the isomerization competes with cyclization to a small extent.[31] The progress of cyclization and isomerization can be estimated from the optical density at 250 nm as compared to that of the maximum at 275 nm, according to the method of Reiser et al.[31] The result of this evaluation for a multilayer assembly of 120 layers of **II** is depicted in Figure 4. The irradiation was carried out by reflecting the light of a

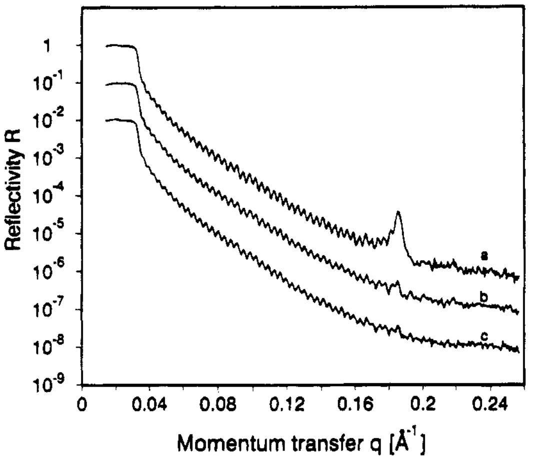


Figure 5. Reflectivity vs momentum transfer of 100 layers of **II**, annealed at 353 K for 0 (a), 30 (b), and 120 (c) min. Note the vanishing Bragg peak.

low-pressure mercury lamp from an aluminum mirror in order to cut out the 185 nm line. The striking feature is that for these multilayers the photostationary state (cis/trans = 1.85) is reached very quickly. This is a clear indication of the local fluidity of the matrix and the alkyl side chains. The intensity of the UV light as measured by a photometer was ca. 1 mW cm^{-2}. A quantum yield of $\phi = 0.005$ for the cross-linking reaction was estimated, which is a typical value found when dilute solutions of cinnamates are subjected to photodimerization.[32] For the sake of clarity it should be mentioned that the quantum yield relates in a strict sense to the disappearance of the double bonds as monitored from the UV spectrum. Thus, formation of cyclobutane rings and of oligomers via addition reactions to the double bonds cannot be differentiated.

X-ray Reflectometry. The structure of LB films of **II** was investigated by X-ray reflectometry in specular reflection geometry. This method probes the electron density of the layered assembly projected onto the substrate normal. In the present case, a resolution of about 1 nm was achieved.[19]

Effects due to annealing of the LB film prior to the cross-linking of the multilayers were investigated first. To this end a sample consisting of 100 monolayers was annealed at 353 K for 30 and 120 min and the angular dependent reflectivity was measured after each annealing step (Figure 5). The total thickness of $d = 168.0 \pm 1$ nm or 1.68 nm per layer was constant during the whole procedure, as seen from the constant spacing of the Kiessig fringes. The same was true for the surface and interface roughnesses. Fitting of the reflectivity vs scattering vector curve with the roughness of the layer/air interface and of the layer/substrate interface parameters[19] gave about 0.8 nm for the first and about 0.5 nm for the latter. Both values were typical for all the samples prepared.

The amplitude of the periodic modulation of the electron density in the film decreased as the annealing time was increased. Prior to any annealing, that is, in the layered assemblies as prepared, the electron density ϱ could be described by $\varrho(z) = (0.37 - 0.0032 \cos(2\pi z/p))$ e/Å^3 with a periodicity $p = 3.42 \pm 0.01$ nm. After 30 min of annealing, the Bragg peak had vanished and we obtained $\varrho(z) = 0.37$ e/Å^3. Additional annealing did not change the film any further.

The loss of modulation reflects a relaxation of the double-layer structure after the dipping process. Initially, two monolayers form one period of a superlattice, because the transferred layers remember the nonsymmetric structure of the monolayer at the air/water interface. The resulting LB architecture is not an equilibrium state since the films change with time into a more hexagonal structure. This model was confirmed by a detailed investigation of the final structure using neutron reflectometry on superlattices consisting of alternating monolayers of polyglutamate **I** with and without deuterated side chains.[33,34]

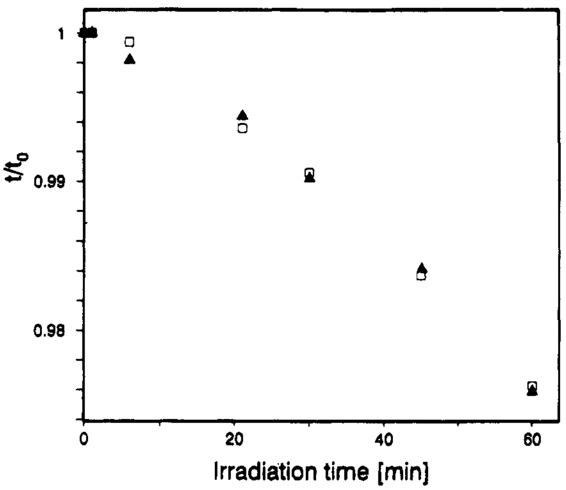


Figure 6. Change of the (normalized) thickness (squares) and periodicity (triangles) during illumination with 185 and 254 nm UV radiation (40 layers of **II**).

The UV irradiation necessary to cause the desired cross-linking may also lead to undesired side reactions such as photoablation. Therefore, the irradiation conditions had to be optimized. Side reactions were observed when a sample of 30 monolayers of **II** was irradiated with a low-pressure mercury lamp. The spectrum of this lamp contains two bands at $\lambda = 185$ and 254 nm, which cause cross-linking via the cinnamoyl groups but also lead to nonspecific breaks in the polymer chains. This effect is shown by the measurements shown in Figure 6: the total film thickness and the periodicity decrease simultaneously when irradiated. This means that an ablation of the film proceeds in the whole volume and not at the surface of the structure. Only the amplitude of the modulation also becomes smaller when the assembly is irradiated. In addition to a relaxation of the structure (annealing effect) other contributions may be important: the fragments of the polymers may move from their original positions and thereby reduce the contrast between the polyglutamate backbones and the side chains.

To avoid the destruction of the film, we used a high-pressure mercury lamp fitted with filters to cut off all intensity below 300 nm. A sample with 40 layers was irradiated (ca. 1 mW/cm^2) for different times up to 11.5 h and no change in thickness, periodicity, or amplitude of the electron density modulation was observed. Clearly, cross-linking does not alter the superstructure of the film. The relevant data are shown in Figure 7. A comparison of the experimental data of the unannealed sample with the best fit is shown in Figure 8 together with the obtained electron density profile. The same results were obtained by reflecting the light of a low-pressure mercury lamp on an aluminum mirror as described above.

In order to demonstrate the effectivity of the photo-cross-linking reaction, a sample consisting of 20 mono-

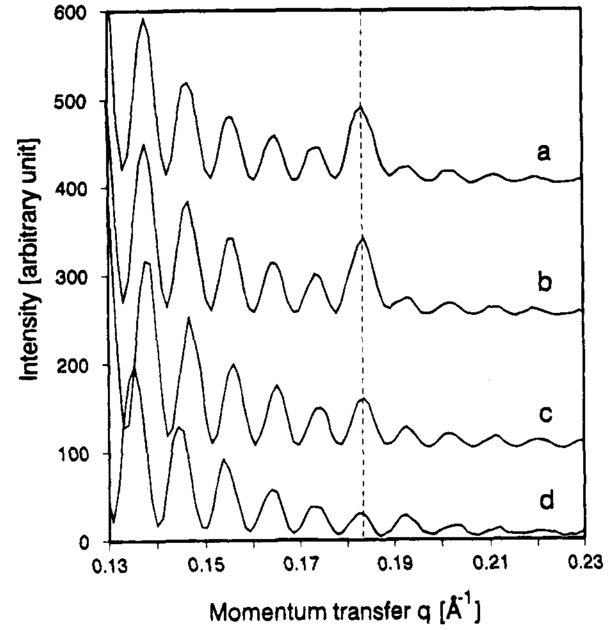


Figure 7. Intensity vs momentum transfer during irradiation with λ > 300 nm (40 layers of **II**). After 11.5 h (b) the intensity is the same as at the beginning (a). Annealing at 353 K for 30 min (c) has reduced the electron density modulation. The film became thinner after subsequent rinsing (d) with ethanol/chloroform (1:1).

layers of **II** was irradiated under the same conditions through a standard contact mask for characterization of photoresists and was developed by rinsing the substrate with a 1:1 mixture of ethanol and chloroform for 2 min. For contrast enhancement, 50 Å of Ag was evaporated on top of the structure.[35] A microscopic image of the pattern is shown in Figure 9.

An interesting point is that the photoinduced network is more stable to structural relaxations than the original LB film. This becomes clear when a cross-linked film was annealed at 353 K for 30 min (Figure 7c). Only the amplitude of the periodic modulation of the electron density is somewhat decreased. After 30 min of annealing time, the amplitude of the Bragg peak of the cross-linked sample changes by only about 35% (with constant periodicity of 3.50 nm) while in the un-cross-linked sample it is smeared out completely after the same time of annealing. Thus, cross-linking the LB layers improves their thermal and long-term stability considerably.

The influence of the conditions leading to pattern formation on the electron density was checked by rinsing the sample on the substrate as described above. After this procedure, the film—cross-linked at λ > 300 nm (Figure 7d)—was thinner by 5% and no periodicity was resolvable. An un-cross-linked film would dissolve rapidly and completely under the same conditions.

In this context, it is worth making a comparison between conventional photoresists and the material discussed here. A typical network of flexible polymers swells by absorption of the solvent, until the maximum swelling ratio is reached. The swelling ratio is conventionally linked to the theory of rubber elasticity via the Flory–Rehner equation in which the osmotic pressure of the solvent penetrating the network is balanced against the elastic deformation of the network due to volume increase.

In our case, the network is reinforced by the rigid rod polymer backbones in one dimension. A pictorial representation of the network structure is shown in Figure 10. Therefore, an affine deformation of the network is impossible and the conventional theory of rubber elasticity breaks down. This limits the swelling ratio considerably. Hence, pattern formation using a lithographic process is possible in cinnamoyl polyglutamate without swelling of the film. The edge profile is determined by the optical limits of the lithographic

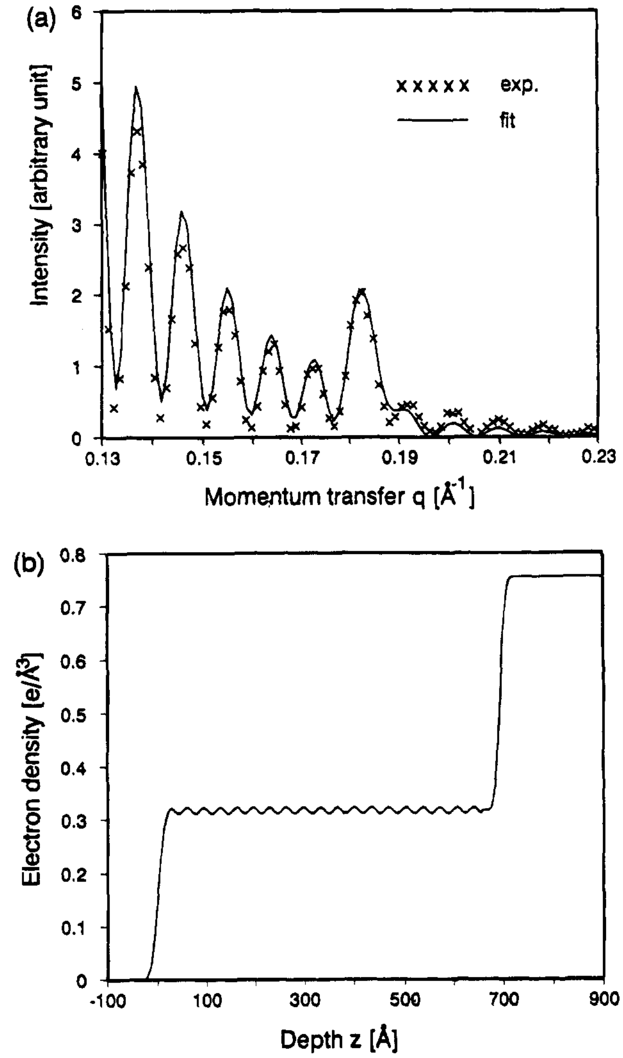


Figure 8. (a) Reflectivity vs momentum transfer of an unannealed film (40 layers of **II**). The best fit we obtained is shown (full line). (b) The electron density profile as obtained with the parameter from the best fit.

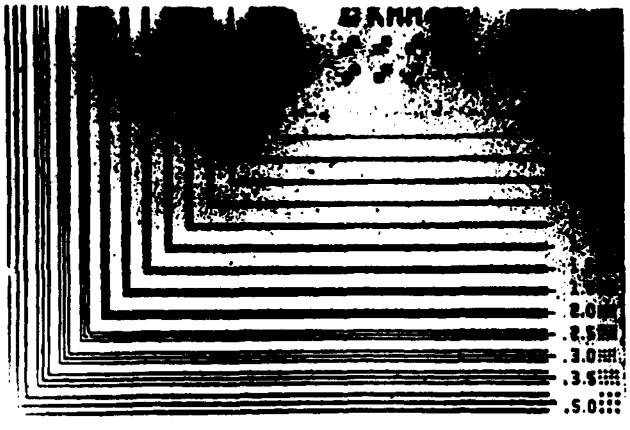


Figure 9. Optical micrograph (crossed polarizers) of a pattern of 20 layers of **II** (covered with 50 Å of Ag) obtained by contact irradiation through a mask. Dissolved parts of film appear dark.

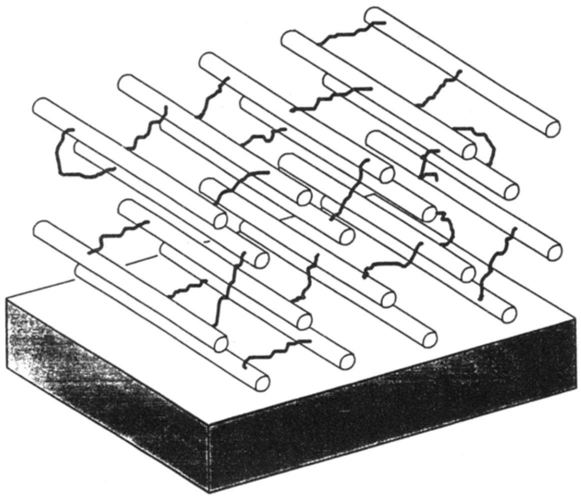


Figure 10. Schematic description of the molecular structure of photo-cross-linked copolyglutamate-layered assemblies. For the sake of clarity, only the side chains forming cross-links between adjacent rods or loops starting and ending at the same rod are shown. In the real sample, these network chains are embedded in a continuous matrix of the residual side chains.

system and not by the parameters of the subsequent development steps of the photoresist.

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