Fabrication of Alternating Multilayers of a Diacetylene Group Containing Amphiphilic Ligand and Acid, Using the Langmuir−Blodgett Technique

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The structure of alternating multilayers of two diacetylene group containing amphiphiles (an acid (A) and a pyridine ligand (B)), built up from a 5 mM CdBr$_2$ subphase, is examined. SAXR measurements revealed that these multilayers have a regular layer structure with a bilayer spacing of 55.2 Å. From this bilayer spacing in combination with FT-IR measurements, it can be concluded that the aliphatic tails of amphiphile A have a tilt angle (α) of about 34° with respect to the surface normal, while in the case of amphiphile B, α has a value of about 45°. In the all-trans aliphatic alkyl chains of both amphiphiles, the C−C−C plane has a preferred orientation such that the symmetric stretches of the methylene groups of the aliphatic chain must be close to being in a plane parallel to the substrate. These multilayers can be partly polymerized by means of UV irradiation, forming the red form ($\lambda_{max} = 540$ nm) of the polymer. Upon polymerization the regular layer structure is preserved and the bilayer spacing increases from 55.2 up to 57.9 Å. The preferred orientation of the C−C−C plane of the aliphatic tail chain around the chain director is lost during the polymerization process. Also, the all-trans alkyl chain is partly converted in a more irregular one containing gauche conformations.

Introduction

Already in 1935, Katherine Blodgett[1,2] had examined the stabilizing effect of metal ions (like Pb(II), Ca(II), Cd(II), etc.) dissolved in the subphase, on a fatty acid monolayer at the air−water interface, due to the cross-linking action of the metal ions. So, the interaction between metal ions and amphiphiles at the air−water interface has been well-known for many years. Nowdays there is a growing interest in functional Langmuir−Blodgett (LB) films in which the metal ions introduce special semiconducting, magnetic, or quantum physical properties into these ultrathin multilayer films.[3−6] For instance, using electron spin resonance, Pomerantz[7] demonstrated that, at temperatures near 2 K, LB films of fatty acids containing Mn(II) ions rapidly developed a large internal magnetic field. LB films which contain metal ions have potential applications as sensors, for chemical modification of electrodes, in catalytic systems, and in microelectronic devices.[4−6] However, a number of possible applications of LB films depend on the supramolecular structure of these films, and especially the alternate layer structures of two different amphiphiles (A and B) are of great interest, while by means of the alternating monolayer deposition technique, stable Y-type structures can be obtained without a plane of symmetry (noncentrosymmetric). These noncentrosymmetric multilayers are useful for or required for different applications like second-order NLO,[5,8,9] pyroelectric devices,[5,10] piezoelectric devices,[5] etc.

Chart 1
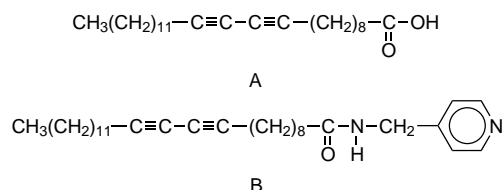
Metal ions (dissolved in the subphase) can be introduced into the monolayers at the air−water interface, first, by salt formation with acid groups as with fatty acids or, second, by complex formation with ligands which are incorporated into amphiphiles[11−16] (ligands as hydrophilic headgroups) or polymers.[17,18]

In a former publication[19] we already showed the possibility of incorporation of Cd(II) ions into multilayers of 4-[(10,12-pentacosadiynamido)methyl]pyridine. These multilayers were built up by means of Z-type transfer but "flip over" to form a Y-type structure, as was shown by small-angle X-ray reflection (SAXR) and FT-IR measurements. In this paper we describe the preparation of polymerizable, noncentrosymmetric Langmuir−Blodgett superlattices based on two diacetylene group containing amphiphiles (Chart 1) using the Langmuir−Blodgett technique. One amphiphile (A) contains an acid headgroup, and the other (B) contains a pyridine headgroup.

[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1997.

(1) Blodgett, K. *J. Am. Chem. Soc.* **1935**, *57*, 1007.

(2) Blodgett, K.; Langmuir, I. *Phys. Rev.* **1937**, *51*, 964.

(3) Miyashita, T. *Prog. Polym. Sci.* **1993**, *18*, 263.

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

(5) Roberts G., Ed. *Langmuir−Blodgett Films*; Plenum Press: New York and London, 1990.

(6) Ulman, U. *An introduction to ultrathin organic films: from Langmuir−Blodgett to self assembly*; Academic Press: San Diego and London, 1991.

(7) Pomerantz, M. *Phase transitions in surface films*; Plenum Press: New York, 1980.

(8) Teerenstra, M. N.; Vorenkamp, E. J.; Nolte, R. J. M.; Schouten, A. J. S. *Thin Solid Films* **1991**, *196*, 153.

(9) Schoondorp, M. A.; Schouten, A. J.; Hulshof, J. B. E.; Feringa, B. L. *Langmuir* **1992**, *8*, 1852.

(10) Walsh, S. P.; Lando, J. B. *Langmuir* **1994**, *10*, 246.

(11) Caminati, G.; Margheri, E.; Gabrielli, G. *Thin Solid Films* **1994**, *244*, 905.

(12) Caminati, G.; Margheri E.; Gabrielli, G. *Prog. Colloid Polym. Sci.* **1994**, *97*, 12.

(13) Susuki, A.; Ohkawa, K.; Kanda, S.; Emoto, E.; Watari, S. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 2634.

(14) Sasakawa, K.; Iwata, S. *Annu. Rep. Res. React. Inst., Kyoto Univ.* **1984**, *17*, 146.

(15) Kalvoda, L.; Brynda, E. *Thin Solid Films* **1993**, *232*, 120.

(16) van Esch, J. H.; Nolte, R. J. M.; Ringsdorf, H.; Wildburg, G. *Langmuir* **1994**, *10*, 1955.

(17) Nagel, J.; Oertel, U. *Polymer* **1995**, *36* (2), 381.

(18) Miyashita, T.; Saito, S.; Matsuda, M. *Chem. Lett.* **1991**, 859.

(19) Werkman, P. J.; Wieringa, R. H.; Schouten, A. J. *Langmuir* **1997**, submitted for publication.

So, by using the alternating deposition technique, stable ABAB, Y-type films are obtained. XPS measurements confirmed the presence of Cd(II) ions in the multilayers. The structure of these films was studied by means of SAXR and FT-IR measurements. The SAXR curve shows seven Bragg peaks, indicating that the multilayers have a regular layer structure. The multilayers were polymerized by exposure to UV light (λ = 254 nm), maintaining their regular layer structure. Also the structural changes, in the multilayer film, induced by the photopolymerization process will be shown.

Experimental Section

Materials. 10,12-Pentacosadiynoic acid (Hüls-Petrarch) and $CdBr_2$ (Merck) were used without further purification. 4-[(10,12-Pentacosadiynamido)methyl]pyridine was prepared as previously described.[19]

Alternating Deposition. A commercially available computer-controlled KSV-5000 alternate layer system, manufactured by KSV Corp. (Finland), was used for the preparation of the alternating LB films. The water used for the subphase was purified by a reversed-osmosis system (Elgastat spectrum SC 30) and subsequent filtration through a Milli-Q purification system. The amphiphiles were dissolved at a concentration of 0.1 wt % in chloroform (Merck, spectroscopic quality). For the cleaning procedures of the substrates and the preparation of the gold-coated glass slides, a standard method was used.[19] The subphase contained 5 mM $CdBr_2$ and had a temperature of 20.0 °C. Amphiphile A was stabilized at a surface pressure of 17 mN·m^{-1}, while amphiphile B was stabilized at a surface pressure of 20 mN·m^{-1}. Monolayers of both amphiphiles were transferred onto substrates with a dipping speed of 2 mm·min^{-1} for the down- and upstroke. Amphiphile A was transferred at the downstroke with transfer ratios between 0.9 and 1.0, and amphiphile B was transferred at the upstroke with a transfer ratio of 1.0.

Polymerization. The alternating multilayers were polymerized using a Rayonette photochemical reactor, which contained UV lamps (254 nm, 16 W). Photopolymerization was carried out under an argon atmosphere; the distance of the lamps to the center of the photochemical reactor was 12 cm.

Infrared Measurements. The transmission infrared measurements were carried out with a Mattson Galaxy 6021, while the grazing incidence reflection (GIR) measurements were performed on a Bruker IFS-88 FT-IR spectrophotometer equipped with a Spectra-Tech Inc. fixed-angle (80°) GIR accessory. The spectra were recorded with a 4 cm^{-1} resolution.

UV/Vis Spectroscopy. UV/Vis absorption spectra of the multilayer films were recorded on a SLM Aminco 300 diode-array UV/vis spectrophotometer.

XPS Measurements. XPS spectra of the multilayer films were obtained using a Surface Sciences Instruments X-Probe 300 spectrometer with monochromated Al Kα radiation with an energy of 1486.6 eV; each sample was measured with a resolution of 1.8 and 0.4 eV for the overall scan and narrow scan, respectively, and a take-off angle of 45°. Binding energy values were referred to the aliphatic 1s line, taken as 287.0 eV.

Small-Angle X-ray Reflection (SAXR) Measurements. SAXR measurements of the multilayer films were performed with a Philips PW 1830 generator and a Philips PW 1820 diffractometer in a $\theta/2\theta$ geometry, using Cu Kα radiation (λ = 1.542 Å).

Results and Discussion

Alternating Multilayer Formation. On a subphase containing 5 mM $CdBr_2$ at 20 °C, amphiphile A was stabilized at a surface pressure of 17 mN·m^{-1}, while amphiphile B was stabilized at a surface pressure of 20 mN·m^{-1}. First, a monolayer of the Cd(II) salt of amphiphile A was transferred onto a solid substrate on the upstroke (transfer ratio: 1.0), after which an alternating multilayer was built up with transfer of the Cd(II) salt of amphiphile A on the downstroke and transfer of the Cd(II) complex of amphiphile B on the upstroke until the
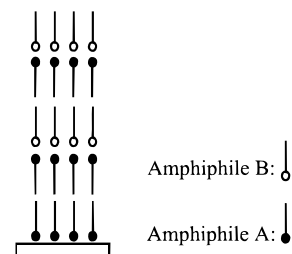

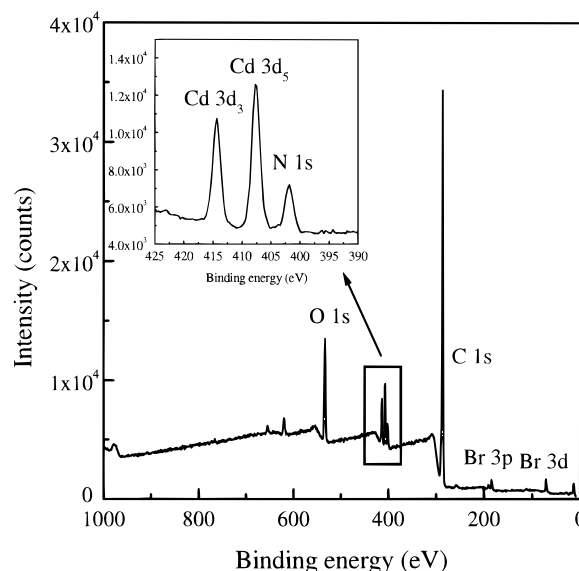**Figure 1.** Schematic representation of the alternating multilayer.

Figure 2. XPS spectrum of an alternating multilayer on silicon of amphiphiles A and B, consisting of 19 layers, built up from a 5 mM $CdBr_2$ subphase at 20 °C.

multilayer contained 18 alternating monolayers. Figure 1 shows a simplified schematic illustration of the obtained structure.

XPS Measurements. In order to reveal the presence and amount of incorporation of Cd(II) ions in the multilayers, XPS measurements were performed on an alternating multilayer built up from a 5 mM $CdBr_2$ subphase (Figure 2).

The Cd 3d$_3$ and Cd 3d$_5$ peaks can clearly be seen in Figure 2 and also the N 1s peak, originating from amphiphile B, can be seen, indicating that indeed both amphiphiles are present in the multilayers, while also a large O 1s peak could be observed. This O 1s peak is much larger than that in the case of multilayers composed entirely of amphiphile B.[19] Each Cd(II) ion, coordinated to amphiphile B, has two Br$^-$ ions for charge compensation; so from the ratio N to Br$^-$ (about 2:1) it can be concluded that two amphiphiles B are coordinated to one Cd(II) ion while each amphiphile B contains two nitrogen atoms. This Cd(II) content in the amphiphile B layer corresponds to the Cd(II) ions content of multilayers of amphiphile B, built up from a 5 mM $CdBr_2$ subphase.[19] Further, it was found that two amphiphiles A form a salt with one Cd(II) ion which is consistent with the IR measurements (Figure 4) which show no vibrations at 1700 cm^{-1}, indicating a complete salt formation of the carboxylic acid groups.

SAXR Measurements. In order to examine if the alternating layer multilayers built up from a 5 mM $CdBr_2$ subphase had a regular layer structure, SAXR measurements were performed on the alternating multilayers. Figure 3 shows that the alternating LB film had a regular layer pattern, indicated by the presence of seven Bragg peaks, which corresponded to a spacing of 55.2 Å. This
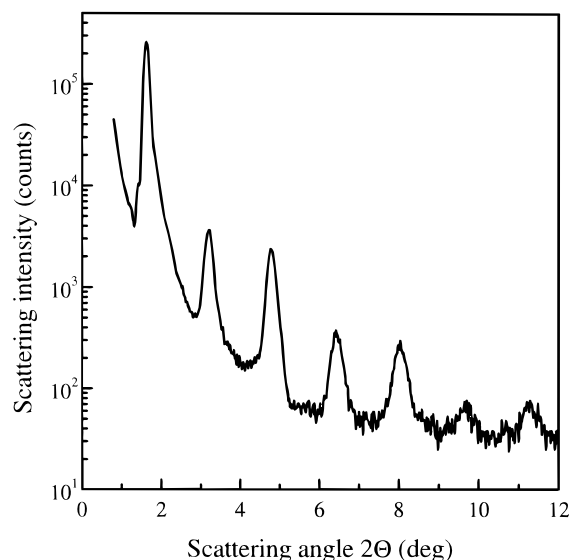
Figure 3. SAXR curve of an alternating multilayer on silicon of amphiphiles A and B, consisting of 19 layers, built up from a 5mM CdBr$_2$ subphase at 20 °C.
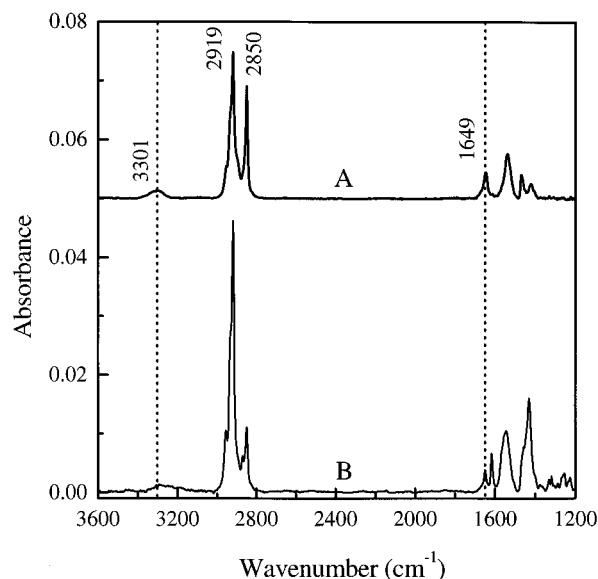

Figure 4. Infrared spectra of alternating multilayers of amphiphiles A and B, consisting of 19 layers, built up from a 5 mM CdBr$_2$ subphase at 20 °C: (A) transmission, with silicon as the substrate (2×19 layers); (B) GIR, with gold-coated glass slide as the substrate.

Table 1. IR-Band Assignments[8,9,19,23]

wavenumber (cm^{-1})	assignment	transition dipole moment, M
3301	ν(N−H)	‖ N−H bond
2954	ν_a(CH$_3$)	⊥ C−CH$_3$ bond
2919	ν_a(CH$_2$)	⊥ C−C−C plane
2871	ν_s(CH$_3$)	‖ C−CH$_3$ bond
2850	ν_s(CH$_2$)	‖ H−C−H plane, bisecting HCH angle
1649	amide I	‖ C=O bond
1615	ν(C−N$_{ar}$)	‖ ring
1539	ν_a(COO$^-$)	⊥ C−COO$^-$ bond
1465	γ(CH$_2$)	‖ H−C−H plane, bisecting HCH angle
1434	ν_s(COO$^-$)	‖ C−COO$^-$ bond

spacing corresponds to a bilayer spacing as expected. Also multilayers of pure amphiphile A were built up from a 5 mM CdBr$_2$ subphase. These LB films had a bilayer spacing of 54.9 Å, which corresponds well to values observed in the literature[20-22] for multilayers of the diacetylene acid, in which the aliphatic tails had a tilt angle (α) of approximately 34° with respect to the surface normal.

Infrared Measurements. In order to study the structure of the multilayers in more detail, transmission IR spectra (electrical field vector parallel to the substrate surface, so all individual group vibrations with transition dipole moment components parallel to the substrate will absorb in this mode) and grazing incidence reflection (GIR) IR spectra (electrical field vector perpendicular to the substrate surface, so all individual group vibrations with transition dipole moment components perpendicular to the substrate will absorb in this mode) were recorded. Figure 4 shows the transmission and GIR IR spectra of the alternating multilayers built up from a 5 mM CdBr$_2$ subphase. The mode assignments are listed in Table 1.

From Figure 4 it can be seen that in the transmission mode the N−H (3301 cm^{-1}) and amide I (1649 cm^{-1}) vibrations are strongly present. These vibrations are also present in the GIR spectrum but weaker in intensity, indicating that the amide bond makes a tilt with respect to the surface normal and is not oriented perpendicular to the substrate surface; otherwise, these vibrations would not be observed in the GIR spectrum. Furthermore, the pyridine group vibration near 1615 cm^{-1} is clearly present in the GIR spectrum but is very weakly present in the transmission mode, from which it can be concluded that the pyridine ring has a small tilt angle with respect to the surface normal. The ν_a (COO$^-$) vibration of amphiphile A at 1539 cm^{-1} is present in both the transmission and GIR spectra, while the ν_s(COO$^-$) vibration at 1434 cm^{-1} is only strongly present in the GIR spectrum.

There are also major differences observed between both IR modes, in the region of the CH stretching vibrations of the aliphatic tail. The intensity of the band at 2919 cm^{-1} (ν_a(CH$_2$)) is very strong in the GIR mode, while the ν_s(CH$_2$) band (2850 cm^{-1}) has a much weaker intensity.

Both vibrations can clearly be seen in the transmission mode. As already has been discussed in our previous publication[19] and by other authors,[9,10,23,24] the different ratio of intensities between the ν_a(CH$_2$) and ν_s(CH$_2$) bands, comparing the transmission and GIR modes, is usually not observed when the C−C−C plane of the all-trans alkyl chain can take on any orientation around the chain axis, i.e., when this chain axis is oriented with a tilt angle (α) with respect to the surface normal. So, in our case the C−C−C plane has a preferred orientation, in which this plane is oriented almost parallel to the substrate surface and does not take on all possible orientations around the chain director. This way the ν_s(CH$_2$) vibration has a large component parallel to the substrate and will therefore absorb strongly in the transmission mode and relatively weakly in the GIR mode, as can be seen in Figure 4. The asymmetric stretch vibration of the methylene (ν_a(CH$_2$)) absorbs relatively strongly in the GIR mode, which indicates that the chain director has a large tilt angle (α) with respect to the surface normal. These results were also found by Walsh and Lando[10] for alternating multilayers of other diacetylene group containing amphiphiles.

(20) Tieke, B.; Lieser, G.; Weiss, W. *Thin Solid Films* **1983**, *99*, 95.
(21) Ogawa, K. *J. Phys. Chem.* **1991**, *95*, 7109.
(22) Dhanabalan, A.; Talwar, S. S.; Major, S. *Thin Solid Films* **1996**, *279*, 221.

(23) Nuzzo, R. G.; Fusco, A.; Allara, D. L. *J. Am. Chem. Soc.* **1987**, *109*, 2358.
(24) Evans, S. D.; Goppert-Berarducci, K. E.; Urankan, E.; Gerenser, L. J.; Ulman, A.; Snyder, R. G. *Langmuir* **1991**, *7*, 2700.
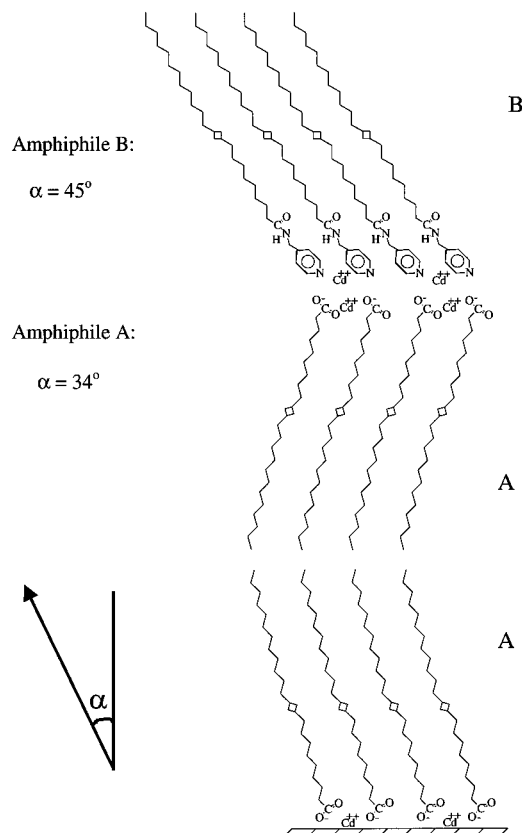
Figure 5. Proposed structure of the amphiphiles in the alternating multilayer.

In Figure 5 the proposed model for the alternating multilayers can be seen. The model was deduced from SAXR and FT-IR measurements. From the SAXR measurements of multilayers from the pure amphiphile A, built up from a 5 mM $CdBr_2$ subphase, a bilayer spacing of 54.9 Å was found. Therefore, the separate monolayers have a thickness of 27.45 Å. The total length of a fully stretched amphiphile A which forms a salt with a Cd(II) ion has a length of approximately 33 Å.[21,22] Assuming that the amphiphiles are fully stretched, the found monolayer thickness of 27.45 Å results in a tilt angle (α) of the amphiphile of approximately 34° with respect to the surface normal.

It is assumed that amphiphile A has the same orientation in the alternating multilayer as in the multilayer film of the pure amphiphile[10] because in both cases the multilayers were built up with a Y-type transfer. However, analogous to Ogawa,[21] amphiphile B is expected to have a different orientation in the alternating multilayer compared to a LB film of pure amphiphile B, because the latter multilayer film is built up with a Z-type transfer but rearranges to the thermodynamically more stable Y-type structure. This multilayer film had a bilayer spacing of approximately 42 Å.[19] The alternating multilayer film is built up with a Y-type structure, so no rearrangement of amphiphile B in this film is expected.

The alternating multilayers have a bilayer spacing of approximately 55.2 Å. Assuming that amphiphile A has the same orientation in the alternating layers as in multilayer films of the pure amphiphile (monolayer thickness 27.45 Å), it can easily be calculated that a monolayer of amphiphile B is 27.75 Å thick in the alternating multilayer film.

From the FT-IR spectra it can be seen that the pyridine ring and amide bond have small tilt angles with respect to the surface normal, and while amphiphile B has a length
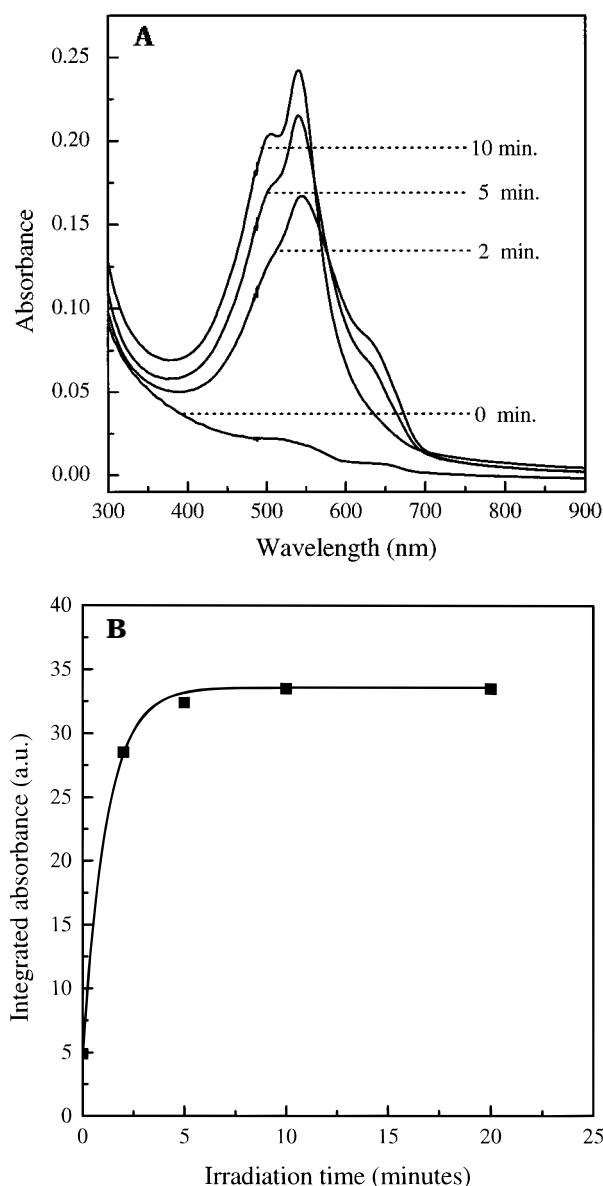

Figure 6. (A) UV/vis absorption spectra of the alternating multilayer on glass of amphiphiles A and B, consisting of 19 layers, built up from a 5 mM $CdBr_2$ subphase at 20 °C, at different times of exposure to UV light ($\lambda = 254$ nm). (B) Integrated absorbance from the UV/vis spectra of the alternating multilayer of part A, between 400 and 800 nm, at different times of exposure to UV light.

of about 36.5 Å in a fully stretched conformation, the aliphatic tail must have a large α with a value of about 45°. Both amphiphiles have a preferred orientation of the C−C−C plane of the aliphatic tail in which the transition dipole moment of the $\nu_s(CH_2)$ vibration must lie nearly in the plane of the substrate.

Polymerization in the Multilayers. The LB films were polymerized by means of exposure to UV light ($\lambda = 254$ nm) under an argon atmosphere. The polymerization process was followed by means of UV/vis spectroscopy (Figure 6A,B) because upon polymerization a rigid, one-dimensional, conjugated backbone is formed. This conjugation results in a strong π to π^* absorption in the visible region.[25−27]

(25) Bubeck, C. *Thin Solid Films* **1980**, *160*, 1.
(26) Göbel, H. D. Thesis, Universität München, München, Germany, 1989.
(27) Deckert, A. A.; Horne, J. C.; Valentine, B.; Kiernan, L.; Fallon, L. *Langmuir* **1995**, *11*, 643.
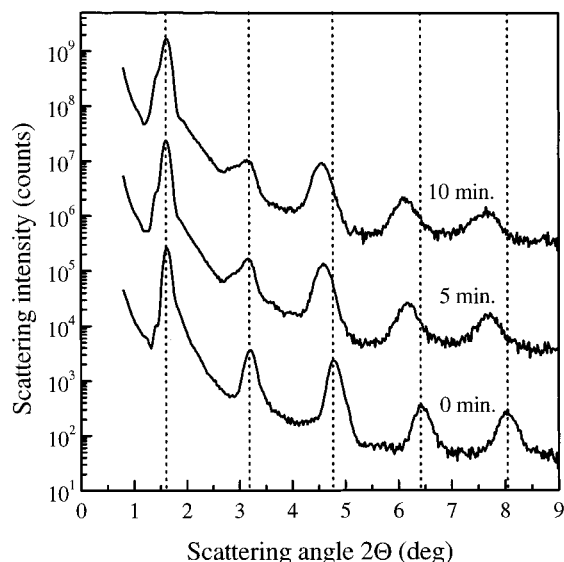
Figure 7. SAXR curves of an alternating multilayer on silicon of amphiphiles A and B, consisting of 19 layers, built up from a 5 mM $CdBr_2$ subphase at 20 °C, at different times of UV irradiation.

In Figure 6A, the absorption spectrum changes of the LB film during exposure to UV light can be seen. After a few minutes of UV irradiation, the red form ($\lambda_{max} = 540$ nm) of the polymer is formed and also a shoulder of the blue form ($\lambda_{max} = 620$ nm) of the polymer can be seen. Upon higher conversion, the blue form disappears, leaving only the red form of the polymer, which is the form with a reduced conjugation.[28] The integrated absorbance between 400 and 800 nm is plotted against the irradiation time in Figure 6B. It can clearly be seen that a maximum degree of polymerization is reached after 10 min of exposure to UV light. This corresponds to a partial conversion, while multilayers of only amphiphile A or B have an integrated absorbance between 400 and 800 nm of about 50 for multilayers consisting of 16 layers of amphiphiles. So, the packing of the amphiphiles in the alternating multilayers differs from the packing of the amphiphiles when the multilayers consist only of amphiphile A or B.

SAXR measurements were performed on the alternating multilayers, after different times of UV irradiation, in order to reveal if the regular layer structure was preserved during the polymerization process. In Figure 7, the SAXR curves can be seen of alternating multilayers built up from a 5 mM $CdBr_2$ subphase after 0, 5, and 10 min of exposure to UV light. Here we can clearly see that the layer structure is preserved during the polymerization process. The bilayer thickness increases from 55.2 to 57.9 Å, as can be concluded from the shift of the Bragg peaks to smaller scattering angles.

The SAXR curve of the polymerized multilayer film is assumed to consist of two superimposed lattices: one of the polymer lattice and one of the monomer lattice, because the polymerization process is not complete, as we have already pointed out. This is in agreement with the results of Dhanabalan et al.[22] The shoulder at the low scattering angle side of the first Bragg peak corresponds to the polymer lattice (bilayer distance = 57.9 Å), while the major peak, which is superimposed on the Bragg peak of the polymer lattice, corresponds to the monomer lattice (bilayer distance = 55.2 Å). The second Bragg peak clearly consists of two reflections, one of the polymer lattice at
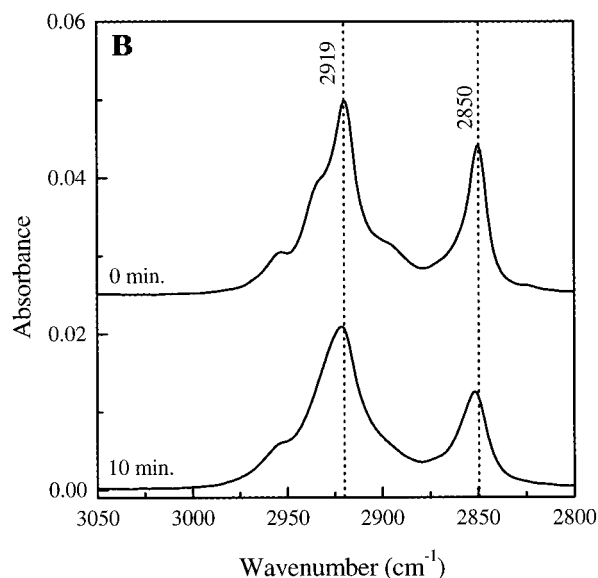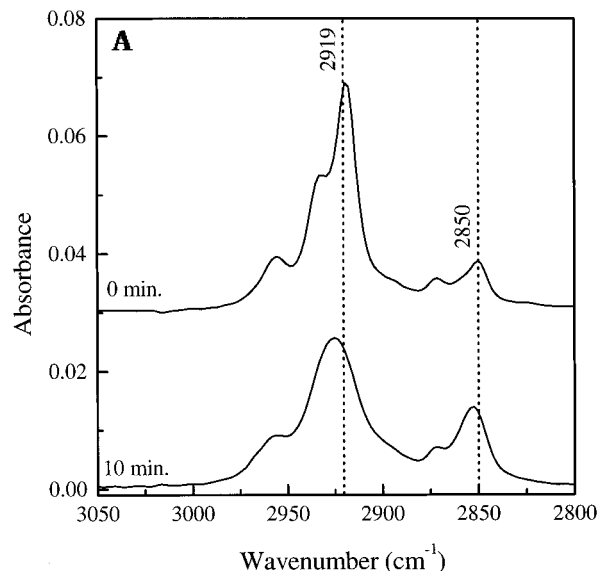
(28) Burzynski, R.; Prasad, P. N.; Biegajski, J.; Cadenhead, D. A. *Macromolecules* **1986**, *19*, 1059.

Figure 8. (A) GIR infrared spectra of the CH stretching region of an alternating multilayer of amphiphiles A and B, consisting of 19 layers on gold, built up from a 5 mM $CdBr_2$ subphase at 20 °C, before and after 10 min of UV irradiation. (B) Transmission infrared spectra of the CH stretching region of an alternating multilayer on silicon of amphiphiles A and B, consisting of 2×19 layers, built up from a 5 mM $CdBr_2$ subphase at 20 °C, before and after 10 min of UV irradiation.

the lower scattering angle side, which can be seen as a shoulder on which the reflection of the monomer lattice is superimposed. At higher scattering angles only the Bragg peaks of the polymer lattice can be seen clearly. The Bragg peaks which correspond to the monomer lattice are only weak reflections at the higher scattering angle side in the tail of the main reflection.

The increase in bilayer thickness during the polymerization process corresponds to a decrease in tilt angle (α) of the chain director of the aliphatic tail with respect to the surface normal.[20,21]

FT-IR measurements were performed in order to study the structural changes during the polymerization process. During exposure to UV light the major changes can be found in the CH stretching region of the IR spectra. The vibration bands near 2850, 2871, 2919, and 2954 cm^{-1} are due to $\nu_s(CH_2)$, $\nu_s(CH_3)$, $\nu_a(CH_2)$, and $\nu_a(CH_3)$ stretching vibrations, respectively.[29,30] Upon polymerization $\nu_s(CH_2)$ and $\nu_a(CH_2)$ are slightly shifted to higher wavenumbers,

2924 and 2852 cm^{-1}, respectively, indicating that the all-trans alkyl chain is partly converted to a more irregular one containing gauche conformations.[19,29] Furthermore, the intensity of the ν_a(CH$_2$) band decreases in the GIR spectrum upon polymerization, while the intensity of the ν_s(CH$_2$) band increases (Figure 8A), and both the intensities of the ν_s(CH$_2$) and ν_a(CH$_2$) bands decrease upon UV irradiation in the transmission mode (Figure 8B). After polymerization the ratio in intensities between the ν_a and ν_s vibration bands is approximately 1.80 for both the GIR and transmission modes. So, upon polymerization the preferred orientation of the C−C−C plane of the aliphatic tail around the chain director is lost. So, the C−C−C plane can take on any orientation around the chain director after polymerization.

(29) Saito, A.; Urai, Y.; Schlotter, N. E. *Langmuir* **1996**, *12*, 3938.
(30) Rabolt, J. F.; Burns, F. C.; Schlotter, N. E.; Swalen, J. D. *Chem. Phys.* **1983**, *78*, 946.

Conclusions

Alternating multilayers of two diacetylene group containing amphiphiles were built up from a 5 mM CdBr$_2$ subphase with a regular layer pattern. The structure of the multilayers was investigated by means of SAXR and FT-IR measurements and revealed that the molecular orientation of the amphiphiles is very similar to their parent compounds.

Upon polymerization, the layer structure is preserved and the bilayer thickness increases from 55.2 up to 57.9 Å due to a change in tilt angle of the aliphatic tail with respect to the surface normal. Also the C−C−C plane of the aliphatic tail of the amphiphiles loses its preferred orientation (in which the ν_s(CH$_2$) vibration lies nearly parallel to the plane of the substrate) around the chain director upon polymerization.