Chapter 4

Langmuir-Blodgett films of metal complexes of 4-(10,12-pentacosadiynamidomethyl)pyridine: a structural investigation

Summary

Complex formation between of 4-(10,12-pentacosadiynamidomethyl)pyridine and metal ions in the subphase results in stable Langmuir monolayers up to surface pressures of 35 mN·m⁻¹. Before polymerisation electron microscopy micrographs reveal a flat monomer monolayer and after polymerisation a polymer monolayer with a more striated structure was formed. Multilayers of the amphiphile can only be built up after complexation with metal ions. XPS measurements definitely confirm the presence of metal ions in the multilayers and the molar ratio between metal ion and amphiphile is derived from these spectra. These multilayers are further characterised by means of small angle X-ray reflection measurements and FT-IR spectroscopy, which show that the amphiphile has a large tilt angle (α) with respect to the surface normal.

The multilayers are polymerised by means of UV irradiation. UV/Vis spectroscopy is used to study the polymerisation process. The structural changes during polymerisation are deduced from small angle X-ray reflection measurements and FT-IR spectroscopy. In all cases the bilayer spacing decreases during the polymerisation process, while in some cases the regular plane of the all-trans conformation of the alkyl chains is converted to an irregular one containing gauche conformations. For multilayers built up from a CuCl₂ containing subphase, the whole distinct layer structure is destroyed during the polymerisation process.
**Introduction**

The interaction of metal ions in the subphase with amphiphiles is well known. The metal ions were mostly used to stabilise the monolayer [1,2,3], for example a monolayer of cadmium arachidate is much more stable than an arachidic acid monolayer alone, due to the crosslinking action of the Cd\(^{2+}\) ions, but other divalent cations like Pb\(^{2+}\), Ca\(^{2+}\), Ba\(^{2+}\), etc. also have a stabilising effect on the fatty acid monolayers as was already shown by Katherine Blodgett [4,5]. The interactions are of major importance for the manufacture of high-quality Langmuir-Blodgett (LB) films, even small amounts of cations enhance the stability of these fatty acid monolayers and condense them over a particular pH range characteristic for the metal ion dissolved in the subphase. The interaction of the metal ions with the acids depends largely on the physical and chemical properties of the metal ion. Triple valent cations for instance, like Fe\(^{3+}\) and Al\(^{3+}\), in the subphase, tend to produce extremely rigid monolayer films with fatty acids which can hardly be transferred onto substrates [1].

Nowadays there is a growing interest in making functional Langmuir-Blodgett films in which the metal ions introduce special semiconducting, magnetic or quantum physical properties into this multilayer films [1,6,7], and these films have potential applications as sensors, for chemical modification of electrodes, in catalytic systems and in microelectronical devices.

In principle the metal ions can be incorporated into the monolayer film in two ways. Firstly, by means of salt or complex formation by the amphiphile from the subphase wherein the metal ions are dissolved and secondly the metals can be bound to the amphiphile before spreading the formed salt or the metal complex at the air-water interface [8,9]. Dithiooxamides [10,11], pyridines [12,13], porphyrins [14], and phthalocyanines [15,16] are often used as ligands for complex formation with metal ions. When crown ethers and imidazoles are used as a ligand units in amphiphiles, even at very low subphase concentrations (10\(^{-6}\) M), metal ions are incorporated into the floating monolayer at the air-water interface as was shown by Lednev and Petty [17] and van Esch et al. [18]. Also metal ions could be incorporated into floating polymer monolayers with an amphiphilic character which have ligand groups like pyridine [19], bipyridine [20] or crown ethers [17].

As has been shown in Chapter 3 [21], the amphiphile 4-(10,12-pentacosadiynamido-methyl)pyridine (Scheme 4.1) can form coordination complexes with Cu(II) at the air-water interface when the copper ions are dissolved in the subphase.
It has been shown that the extent of complexation could easily be tuned by choosing the proper complexation conditions. This amphiphile contains a diacetylene functionality in the aliphatic tail, which can be polymerised upon UV irradiation, resulting in a polymer multilayer with enhanced thermal and mechanical stability. In addition to these favourable mechanical properties, polydiacetylenes are highly conjugated, linear polymers, that exhibit thermo- and solvatochromism, semiconducting as well as strong third-order nonlinear optical properties [22-25]. In principle, polydiacetylenes might find applications as ultra thin resins, protective coatings or in integrated optical devices.

In the present Chapter the morphology of the monolayer, before and after exposure to UV light, will be studied by means of electron microscopy. Furthermore, it will be shown that multilayers could only be built up of monomer monolayers, when the subphase contained Cu$^{2+}$ or Cd$^{2+}$ cations. The structure of these multilayers was deduced from XPS, small angle X-ray reflection and FT-IR measurements, revealing major changes when the cation or counter ions dissolved in the subphase were changed. Polymerisation of the multilayers was followed by UV/Vis spectroscopy. The structural changes during the polymerisation process were studied by means of small angle X-ray reflection and FT-IR measurements. From these studies it is concluded that the layer structure is preserved well with one exception: in the case of multilayers built up from a CuCl$_2$ containing subphase, the layer structure is destroyed during exposure to UV light.

**Experimental**

The synthesis and characterisation of the amphiphile have been outlined in the experimental section of Chapter 3.
**Langmuir-Blodgett films**

The monolayer properties were studied by measuring pressure-area isotherms using a commercially available computer controlled Lauda-Filmbalance (FW 2). The water used for the subphase, was purified by a Milli-Q filtration system preceded by a reversed osmosis filtration (Elgastat spectrum SC30). The amphiphile was dissolved in chloroform (Merck, spectroscopic quality), with a concentration of 0.1 wt%, and the isotherms were recorded with a compression speed of 10 Å²·(molecule·min)⁻¹ at different temperatures. Glass slides, quartz slides and silicon wafers, used as substrates, were subsequently treated with a mixture of H₂O₂ (30%) / NH₃ (25%) / H₂O (1:1:5 v/v) for 30 minutes at 60 °C, ultrasonically treated with a mixture of HCl (37%) / H₂O (1:6 v/v) for 15 minutes, washed several times with Milli-Q water, again ultrasonically cleaned with methanol (Merck p.a.), methanol / chloroform (3:1 v/v) mixture and chloroform (Merck p.a.) for 15 minutes, and finally stored in methanol. Before use the substrates were hydrophobised by treating them with a mixture of chloroform and hexamethyldisilazane (Acros, 98%) (4:1 v/v) at 50 °C, and finally rinsed with chloroform. Gold substrates were obtained by sputtering a 250 nm thick gold layer onto the cleaned glass slides. A dipping speed of 2 mm-min⁻¹ was used for both the down and upstroke transfer.

**Polymerisation**

The multilayers were polymerised using a Rayonette Photochemical Reactor, which contained UV lamps (254 nm, 16 W). The polymerisation was carried out under an argon atmosphere. The distance of the lamps to the centre of the photochemical reactor was 12 cm. After a constant flow of argon for 40 minutes, the polymerisation of the monolayer at the air-water interface was carried out at a surface pressure of 30 mN·m⁻¹, using a small UV lamp (254 nm, 1.6 W) at a 5 cm distance.

**Infrared measurements**

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

IR spectra at elevated temperatures were recorded with the Mattson Galaxy 6021 equipped with a custom made AABSPEC multi-mode FTIR cell, model #95S-E with a transmission and GIR probe (80°).
UV/Vis spectroscopy

UV/Vis absorption spectra of the multilayers on glass slides, were recorded on a SLM-Aminco 300 diode-array UV/Vis spectrophotometer.

XPS measurements

XPS spectra were obtained using a X-Probe 300 of Surface Sciences Instruments spectrometer with monochromated AlK$_\alpha$ radiation with energy of 1486.6 eV. Measurements were carried out with a resolution of 1.8 eV and 0.4 eV for the overall and narrow scan, respectively, and take-off angle of 45°. Binding energy values are referred to the aliphatic carbon 1S line, taken as 287.0 eV.

Small angle X-ray reflection measurements

Small angle X-ray reflection measurements were performed with a Philips PW1830 generator and a Philips PW1820 diffractometer in a $\theta$/2$\theta$ geometry, using CuK$_\alpha$ radiation ($\lambda$=1.542 Å).

Electron microscopy

Samples for transmission electron microscopy (TEM) were prepared by transferring the monolayer, stabilised at a surface pressure of 30 mN·m$^{-1}$, onto a carbon-coated copper grid, which has been made hydrophilic by glow discharge in air under reduced pressure, by a manual horizontal lifting method. The samples were Pt-shadowed at an angle of 20 °. TEM micrographs were recorded with a Philips EM 300 instrument using an acceleration voltage of 80 kV at a magnification of 10000×.
Results and discussion

Monolayer

Figure 4.1: Surface pressure-area isotherms of the amphiphile at 18.7 °C on an aqueous subphase (A) and on a subphase containing 5 mM CuCl₂ (B) and 5 mM Cu(ClO₄)₂ (C).

Figure 4.1 clearly shows the effect of the addition of Cu(II) ions with different counter ions (Cl⁻ and ClO₄⁻) to the subphase. On an aqueous subphase the compound forms a condensed monolayer film at 18.7 °C. When the subphase contains Cu(II) ions a liquid-expanded (LE) to liquid-condensed (LC) phase transition can be observed which indicates that complexation has taken place at the air-water interface. Upon complexation a charged monolayer is formed in which the amphiphiles start to repel each other resulting in an expanded monolayer [21]. When ClO₄⁻ was used as counter ion the surface pressure at which the phase transition (Πₑ) from the LE to LC phase appears was higher than in the case when Cl⁻ was used as counter ion. This indicates that when ClO₄⁻ is used as counter ion a more complete complexation takes place as has already been pointed out in Chapter 3 [21].
With or without metal ions in the subphase, these monolayers could be stabilised at surface pressures up to 35 mN·m⁻¹ with subphase temperatures up to 25 °C and form stable monolayers within 30 minutes at a surface area of about 27 Å²-molecule⁻¹.

These monolayers could be polymerised at the air water interface after 40 minutes of a constant flow of argon, by means of a small UV lamp (254 nm, 1.6 W) for 2 minutes, resulting in a small contraction of the monolayer. The polymerised monolayer was very brittle and appeared blue which could be seen by the naked eye. Figure 4.2 shows the transmission electron micrographs of the monomer (4.2A) and polymer (4.2B) monolayers picked up at a surface pressure of 30 mN·m⁻¹ on a 5 mM Cu(ClO₄)₂ subphase.

![Figure 4.2: Transmission electron micrographs of transferred monomer (A) and polymer (B) monolayers at a subphase temperature of 19 °C and a surface pressure of 30 mN·m⁻¹. The polymer monolayer was formed after UV irradiation of the monomer monolayer at the air-water interface for 2 minutes under an argon atmosphere. The scale bar corresponds to 0.2 μm.](image)

The monomer monolayer appeared to be very smooth, the fold on the left upper side of Figure 4.2A, is formed during the preparation of the sample, and will therefore not be present in the monolayer at the air-water interface. The polymer monolayer has a striated texture, which is often seen for polydiacetylene monolayers (Sarkar et al. [26], Putman et al. [27]). The crack on the upper left side of Figure 4.2B, again was formed during the preparation. This crack was exactly formed on the border of two crystals as can be seen from direction of the striations, indicating the chain direction of the polymer backbone [26]. From picture 4.2B it is possible to estimate the thickness of one polymer monolayer, by measuring the length of the shadow. From the equation \( h = l \times \tan \alpha \) in which \( h \) is the thickness of the
monolayer, \( l \) is the length of the shadow and \( \alpha \) is the angle at which the samples were Pt-shadowed, the monolayer thickness can be calculated. The estimated thickness is in the order of 33 Å ± 8 Å.

**Multilayer formation**

Transfer experiments were carried out at surface pressures between 18 and 30 mN·m\(^{-1}\) and with a subphase temperature of 19 °C. The polymer monolayer could not be transferred onto solid substrates because it was too brittle and too stiff. When the monolayers were deposited onto a solid substrate (glass, quartz, gold or silicon), Z-type transfer was observed with transfer ratios of 0.0 on the downstroke and 1.0 on the upstroke, irrespective of the counter ions used (Cl\(^-\), ClO\(_4\)\(^-\) or Br\(^-\)). In Table 4.1 the different samples used in this study are listed.

**Table 4.1:** *Samples used in this study.*\(^{a,b}\)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Substrate</th>
<th>Subphase</th>
<th>Surface pressure (mN·m(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Silicon</td>
<td>5 mM Cu(ClO(_4))(_2)</td>
<td>30</td>
</tr>
<tr>
<td>B</td>
<td>Glass</td>
<td>5 mM Cu(ClO(_4))(_2)</td>
<td>30</td>
</tr>
<tr>
<td>C</td>
<td>Au with 3 layers of cadmium arachidate</td>
<td>5 mM Cu(ClO(_4))(_2)</td>
<td>30</td>
</tr>
<tr>
<td>D</td>
<td>Au with 3 layers of cadmium arachidate</td>
<td>1 mM Cu(ClO(_4))(_2)</td>
<td>30</td>
</tr>
<tr>
<td>E</td>
<td>Silicon</td>
<td>5 mM CuCl(_2)</td>
<td>30</td>
</tr>
<tr>
<td>F</td>
<td>Silicon</td>
<td>5 mM CdBr(_2)</td>
<td>19</td>
</tr>
</tbody>
</table>

\(^{a}\) *All samples consisted of 16 layers of the amphiphile.*

\(^{b}\) *Subphase temperature is 19 °C.*

**Cu(II) containing multilayers**

XPS measurements were performed on these multilayers to confirm the presence of metal ions in these samples and to give quantitative information about the amount of metal ions incorporated into the LB films. The XPS spectrum of a multilayer built up from a 5 mM Cu(ClO\(_4\))\(_2\) subphase (Sample A), is shown in Figure 4.3.
The copper peaks can clearly be seen, but it appeared to be a mixture of Cu (II) (peaks at 936.5 and 956.5 eV with the associated satellites) and Cu (I) (peaks at 933.5 and 954.0 eV). This is somewhat surprising because only Cu(II) was expected in the multilayers and no reduction to Cu (I). So, the behaviour of these multilayers inside the XPS spectrometer was studied more closely. Upon longer exposure of the multilayer to soft X-rays, the Cu(I) peaks increased in time while the Cu(II) peaks decreased in intensity, also the satellites associated with Cu(II) disappeared. Finally, after 20 hours of exposure to X-rays, almost all the Cu(II) is reduced to Cu(I). In Figure 4.4 the Cu(II) and Cu(I) fractions are plotted as function of the exposure time to the soft X-rays in the XPS apparatus. It can be seen clearly that the fraction of Cu(I) increases at longer irradiation time and the Cu(II) ions are reduced.

This phenomena has been described before for Cu$^{2+}$ and some other metal ions (like Cr$^{6+}$ and Fe$^{3+}$) in the literature [28-33]. This reduction is mainly caused by secondary electrons, those produced inside the sample by slowing down of primary electrons and those falling on the sample from the surroundings [30]. When the multilayers were built up from a 5 mM CuCl$_2$ subphase, it could be seen that the initial X-ray induced reduction of Cu(II) proceeded much slower than when ClO$_4^-$ was used as a counter ion (Figure 4.4, curve B). After 1 hour of exposure to X-rays only a weak shoulder of Cu(I) can be seen in the case of Cl$^{-}$ containing multilayers (about 7%), whereas in the case of ClO$_4^-$ containing multilayers
there is already a pronounced amount of Cu(I) present after 1 hour of exposure to the soft X-rays. This lower reduction rate of the Cu(II) ions, is probably caused by the difference in packing of multilayers which contain Cl⁻ or ClO₄⁻ as counter ion. Probably, the multilayers which contain Cl⁻ as counter ion, have a more dense packing than the multilayers which contain ClO₄⁻ as a counter ion, causing a slower reduction of the Cu(II) ions upon exposure to soft X-rays. This was also the case for the X-ray induced Cu(II) reduction inside α- and γ-zirconium phosphates [33]. These layered compounds differ in structure and packing sequence of layers, resulting in a different reduction rate of Cu(II) during the XPS experiments. In α-zirconium phosphate (which has the less dense structure of the two zirconium phosphates) the Cu(II) ions are reduced much faster than in γ-zirconium phosphate. When the floodgun was used for compensation of charging effects, immediately a total reduction of Cu(II) could be observed for multilayers which contain ClO₄⁻ as counter ions, whereas with Cl⁻ as counter ion the reduction still appeared very slow.

**Figure 4.4:** Percentage of Cu(I), calculated by the formula: \[
\left[ \frac{\text{Cu(I) } 2p_3}{\text{Cu(I) } 2p_3 + \text{Cu(II) } 2p_3} \right] \times 100\%
\]
at different irradiation times for Cu(II) containing multilayers, built up from a 5 mM Cu(ClO₄)₂ (A, sample A) and 5 mM CuCl₂ (B, sample E) subphase at 19 °C at 30 mN·m⁻¹ on silicon. In determining the amount of Cu(II), the integrated area of the satellite was also taken into account and the deconvolutions were performed by a best-fit Gaussian computer program.
The amount of Cu(II) ions incorporated in the multilayers can easily be varied by changing the subphase concentration of Cu(II) ions, as can be seen in Table 4.2.

Table 4.2: The ratio N:Cu of the multilayers, calculated from the XPS spectra, as a function of the Cu(ClO₄)₂ concentration in the subphase.¹

<table>
<thead>
<tr>
<th>[Cu(ClO₄)₂] (mM)</th>
<th>ratio N:Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>4.2</td>
</tr>
<tr>
<td>5</td>
<td>4.7</td>
</tr>
<tr>
<td>1</td>
<td>17.2</td>
</tr>
<tr>
<td>0.5</td>
<td>25.8</td>
</tr>
</tbody>
</table>

¹ For all multilayers the ratio of Cu:Cl was 1:2.

Stable monolayers can be formed on a Cu(ClO₄)₂ containing subphase up to concentrations of 10 mM. When the subphase contained more than 10 mM Cu(ClO₄)₂, stable monolayers cannot be formed anymore, probably because too much Cu(II) ions are coordinated to the monolayer, forming a heavily charged monolayer and on compression molecules are probably forced to dissolve in the subphase.

The maximum amount of Cu(II) ions in the multilayers (built up from a 10 mM Cu(ClO₄)₂ containing subphase) with ClO₄⁻ as counter ion was about 1 Cu(II) ion to 2 amphiphiles, because each amphiphile contains 2 nitrogen atoms. When the subphase contained 5 mM CuCl₂, the multilayer contained about 1 Cu(II) ion to 3 amphiphiles. Thus, the ClO₄⁻ counter ion causes a better complexation in the monolayer to occur, as has been discussed already in Chapter 3 [21].

In Figure 4.5, the GIR spectra of sample C and D are shown. The peak at 1621 cm⁻¹ corresponds to the νC-N of the pyridine moiety coordinated to the metal and the 1600 peak corresponds to νC-N of a free pyridine ring [34,35]. It can be seen clearly that sample D contains relative high amounts of non-coordinated pyridine ligands. The coordinated and non-coordinated pyridine rings most probably have the same orientation because the bands corresponding to both vibrations appear strongly in the GIR spectrum but can hardly be seen in the transmission IR spectrum. From the XPS experiments it can be calculated that multilayers which were built up from a 1 mM Cu(ClO₄)₂ subphase contain 1 Cu(II) ion on about 8.6 amphiphiles (each amphiphile having two nitrogens). Therefore it is assumed that the multilayer built up from a 1 mM Cu(ClO₄)₂ subphase (sample D), consists of CuL₄ complexes (L = amphiphile) and free amphiphiles in the ratio CuL₄ : 4L because in the GIR
spectrum of this multilayer the peaks of the coordinated non-coordinated pyridine rings have almost the same intensity.

![Absorbance vs. Wavenumber](image)

**Figure 4.5:** GIR infrared spectra of LB films consisting of 16 layers of the amphiphile on a gold coated glass with 3 layers of cadmium arachidate, built up from a 5 mM (A, sample C) and 1mM (B, sample D) Cu(ClO$_4$)$_2$ subphase at 19$^\circ$C and 30 mN·m$^{-1}$.

The following equations can be considered for complexation of the amphiphile with metal ions.

\[
L + M \leftrightarrow ML \tag{4.1}
\]

\[
L + ML \leftrightarrow ML_2 \tag{4.2}
\]

\[
L + ML_2 \leftrightarrow ML_3 \tag{4.3}
\]

\[
L + ML_3 \leftrightarrow ML_4 \tag{4.4}
\]

\[
nL + M \leftrightarrow ML_n \tag{4.5}
\]

At high Cu(II) concentrations (> 10mM Cu(ClO$_4$)$_2$) the equilibrium is shifted to the copper rich side, forming CuL complexes. This way a heavily charged monolayer is formed which is not stable. At lower Cu(II) concentrations (10 and 5 mM Cu(ClO$_4$)$_2$) the relative amount of ligands (L) at the air-water interface has increased, so, the equilibrium is shifted
and CuL₂ complexes are formed which is also indicated by the GIR measurements (Figure 4.4) in combination with the XPS measurements. At even lower concentration (1 mM Cu(ClO₄)₂ or lower) the equilibrium is totally shifted to the copper deficient side, forming CuL₄ complexes in a matrix of uncoordinated ligands. The composition of the formed complexes at the air-water interface may differ from the structure of the complexes found in the LB films, although the stoichiometry of the complexes will be the same, because during the preparation of the multilayers, the structure of the multilayers is rearranged as will be discussed in the next paragraph. This rearrangement of the multilayer structure may induce the formation of complexes which have a different structure than the complexes formed at the air-water interface.

In order to establish whether the formed multilayers had a distinct layer structure, small angle X-ray reflection measurements were performed. The small angle X-ray reflection patterns of the samples A (Fig. 4.6A) and E (Fig. 4.6B) are shown in Figure 4.6.

![Figure 4.6: Small angle X-ray reflection curves of 16 layers of the amphiphile built up from (A, sample A) 5mM Cu(ClO₄)₂ and (B, sample E) 5mM CuCl₂ subphase at 19 °C and 30 mN·m⁻¹ on silicon.](image)

A regular layer pattern is observed for these Cu(II) ion containing multilayers, with Bragg peaks representing layer spacings of 59.2 Å and 60.0 Å for the multilayers built up from 5 mM Cu(ClO₄)₂ and CuCl₂ subphase, respectively. The amphiphile, in fully stretched conformation, has a length of about 36.5 Å, so, the layer spacings found must represent a
bilayer spacing. Because these multilayers were built up by means of a Z-type transfer, a monolayer spacing between 30 and 37 Å was expected. Therefore, a rearrangement to a Y-type structure must have occurred in which the amphiphiles have a large tilt angle with respect to the surface normal, because for a perpendicular orientation of the amphiphiles to the substrate surface a bilayer spacing of about 73 Å should have been found. The rearrangement of a Z-type structure in to a Y-type structure is well-known phenomena for low molecular weight amphiphiles [1,36-39]. The Y-type structure is the thermodynamically most stable structure, with the hydrophobic aliphatic tails and the hydrophilic headgroups facing each other.

To get more information on the orientation of amphiphiles in the LB films, 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 surface will absorb maximally in this setup) 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 surface will absorb maximally in this setup) were recorded. In Figure 4.7 the different spectra can be seen for a multilayer built up from a 5 mM Cu(ClO$_4$)$_2$ subphase and the mode assignments are presented in Table 4.3.

**Table 4.3: The IR band assignments [34,35,40-43].**

<table>
<thead>
<tr>
<th>Wavenumber (cm$^{-1}$)</th>
<th>Assignment</th>
<th>Transition dipole moment, $\vec{M}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3301</td>
<td>$\nu$ (N-H)</td>
<td>$\parallel$ N–H bond</td>
</tr>
<tr>
<td>2955</td>
<td>$\nu_a$ (CH$_3$)</td>
<td>$\perp$ C–CH$_3$</td>
</tr>
<tr>
<td>2920</td>
<td>$\nu_a$ (CH$_2$)</td>
<td>$\perp$ C–C–C chain plane</td>
</tr>
<tr>
<td>2871</td>
<td>$\nu_s$ (CH$_3$)</td>
<td>$\parallel$ C–CH$_3$</td>
</tr>
<tr>
<td>2850</td>
<td>$\nu_s$ (CH$_2$)</td>
<td>$\parallel$ H–C–H plane, bisecting HCH angle</td>
</tr>
<tr>
<td>1645</td>
<td>Amide I</td>
<td>$\parallel$ C=O bond</td>
</tr>
<tr>
<td>1621</td>
<td>$\nu$ (C=N$_{ar}$)</td>
<td>$\parallel$ ring</td>
</tr>
<tr>
<td>1565</td>
<td>$\nu$ (C=C$_{ar}$)</td>
<td>$\parallel$ ring</td>
</tr>
<tr>
<td>1547</td>
<td>Amide II</td>
<td>$\perp$ C=O bond</td>
</tr>
<tr>
<td>1468</td>
<td>$\delta$ (CH$_2$)</td>
<td>$\parallel$ H–C–H plane, bisecting HCH angle</td>
</tr>
</tbody>
</table>
Figure 4.7: Infrared spectra of the amphiphile: (A) powdered in KBr (scale factor: 0.0395 ×), (B) Transmission, (C) GIR (scale factor: 0.432 ×). Samples: In case of GIR, 16 layers transferred onto a gold coated glass slide from a 5 mM Cu(ClO₄)₂ subphase (sample C) and in case of transmission, 16 layers transferred onto silicon at a subphase concentration of 5 mM Cu(ClO₄)₂ (sample A). In both cases the subphase temperature was 19 °C and the surface pressure was 30 mN·m⁻¹.

In order to scale the bulk, transmission and GIR spectra in a proper way, transmission and GIR spectra were also recorded at 60 °C. At this elevated temperature the side chains are molten and all preferred orientation is lost. Also a bulk spectrum of the amphiphile powdered in KBr was recorded at 80 °C, at this temperature the amphiphile is in the molten state. All these spectra were scaled in such a way that the vibrations in the CH stretching vibration region have the same intensity as in the transmission spectrum of sample A at 60 °C. These scaling factors were used for the bulk and GIR spectra at room temperature in Figure 4.7.

For the GIR measurements gold substrates were used on which 3 layers of cadmium arachidate were deposited on both the sample and reference side, therefore the 3 cadmium layers make no contribution to the GIR spectrum. 16 monolayer were deposited on top of these 3 cadmium arachidate layers. Furthermore, also a GIR spectrum was recorded when gold substrates were used on which 3 layers of poly((S)-1-acetoxy methyl ethylethyl isocyanide) were deposited (sample and reference side) on top of which 16 layers of the
amphiphile from a 5 mM Cu(ClO$_4$)$_2$ subphase were transferred. This spectrum was identical to the GIR spectrum of Figure 4.7 which indicates that the 3 cadmium arachidate layers probably do not influence the structure of the LB film on top of these layers which allows a proper comparison of the transmission and reflection IR spectra.

In the transmission spectrum of the amphiphile, powdered in KBr, the individual groups have no preferred orientation. In the transmission spectrum (Fig. 4.7B), the N–H (3301 cm$^{-1}$) and amide I (1645 cm$^{-1}$) can be clearly seen, while these absorption bands are nearly absent in the GIR spectrum. The integrated area of the amide I peak of the transmission spectrum is one and a half time larger then the amide I peak of the bulk spectrum. The amide II (1545 cm$^{-1}$) vibration on the contrary is strongly present in the GIR spectrum and very weak in the transmission spectrum. From this it is concluded that the amide groups are oriented parallel to the substrate surface. Furthermore, the pyridine group vibration at 1621 cm$^{-1}$ is strongly absorbing in the GIR spectrum and only weakly in the transmission spectrum, so, the pyridine group is oriented with a small angle with respect to the surface normal. Also in the absorption region of the aliphatic tail vibrations, major differences could be observed. It can be seen that the intensities of the bands at 2920 ($v_a$ CH$_2$) and 2850 cm$^{-1}$ ($v_s$ CH$_2$) differ tremendously in intensity comparing the transmission and GIR spectra. The asymmetric stretch vibrations of the methylene is absorbing strongly in the GIR spectrum while the symmetric stretch vibration absorptions can hardly be seen. Both vibration absorptions are present in the transmission spectrum. These differences in intensity of the $v_a$ (CH$_2$) and $v_s$ (CH$_2$) between the GIR and transmission spectra are usually not observed when an all-trans CH$_2$ chain is oriented with an angle, $\alpha$, with respect to the surface normal [40-45] and the C–C–C plane in the all-trans alkyl chain can take on any orientation around the chain axis. So, in the normal case, the intensities of $v_a$ (CH$_2$) and $v_s$ (CH$_2$) in the GIR or transmission spectrum, depend only on the tilt angle, $\alpha$, and the ratio of their intensities does not change significantly between both spectrum measurement methods.

In the literature [40,46-49], several reports have been published in which comparable changes in intensities of $v_a$ (CH$_2$) and $v_s$ (CH$_2$) have been described. Those results have been explained by assuming a special packing of the alkyl chains. Nuzzo et al. [46] and Evans et al. [47] interpreted their results as due to a close packing of the CH$_2$ chains in a triclinic lattice instead of an orthorhombic. This close packing was supposed to be induced by strong dipoles of the sulfone groups incorporated in the alkyl chain. In that way the all-trans C–C–C plane had a preferred orientation, in which this plane was oriented at a certain angle with respect to the substrate surface and could not take on all possible orientations around the chain director. This result was also found by Walsh and Lando [50] for alternating multilayers of
diacetylenes. Figure 4.8 shows a schematic representation of the two extreme orientations of a tilted all-trans aliphatic chain.

From Figure 4.7, it can be deduced that $\nu_s$ (CH$_2$) has a preferred orientation nearly parallel to the substrate surface, because it appeared strong in the transmission spectrum and relatively weak in the GIR spectrum. On the other hand, $\nu_a$ (CH$_2$) was relatively strong in the GIR spectrum, compared with the $\nu_s$ (CH$_2$) vibration in this spectrum. However, the absolute value of the $\nu_a$ (CH$_2$) vibration in the GIR spectrum is smaller as compared to the transmission and bulk spectrum, indicating a large tilt angle ($\alpha$) of the chain director with respect to the surface normal. Figure 4.8A represents the suggested situation, in which the transition dipole moment of the $\nu_s$ (CH$_2$) vibration is parallel to the substrate surface and the transition dipole of the $\nu_a$ (CH$_2$) vibration has a considerable component perpendicular to the substrate surface.

**Figure 4.8:** Schematic representation of the two extreme orientations of an all-trans aliphatic chain.
From the results obtained from the small angle X-ray reflection measurements together with the result from the FT-IR spectra a model for the multilayer film (Figure 4.9), built up from a 5 mM Cu(ClO₄)₂ subphase, is proposed.

α is the tilt angle relative to the surface normal. From the experimental data, a value of 35° was found for α, taking into account a bilayer spacing of 59.2 Å and a large tilt angle of the aliphatic tail as is deduced from the IR spectra, which is not unusual for diacetylenes, where normally values between 20 and 45° are found [51]. The C–C–C plane of the aliphatic tail has a preferred orientation in which the transition dipole moment of the νᵢ (CH₂) vibration must lie nearly in the plane of the substrate [47].

**Figure 4.9:** Schematic representation of the structure of amphiphiles inside the multilayers.

When the subphase contained 5 mM CuCl₂, monolayers could only be transferred onto silicon or glass substrates and not onto gold substrates. That is why only transmission IR spectra could be recorded. These spectra (not shown here) closely resemble the transmission spectra of multilayers built up from a 5mM Cu(ClO₄)₂ subphase. Furthermore, the multilayers built up from both subphases have nearly the same bilayer spacing as was derived from the
small angle X-ray reflection measurements, so, it is assumed the multilayers built up from both subphases nearly have the same structure.

**Cd(II) containing multilayers**

Multilayers could also be built up from a 5mM CdBr$_2$ subphase by Z-type transfer at a subphase temperature of 20 °C and surface pressures between 15 and 20 mN·m$^{-1}$.

XPS measurements were performed for a direct observation of Cd(II) ions in these LB films. The Cd(II) peaks can be seen clearly at about 405 (3d$_3$) and 412 (3d$_5$) eV [52]. The amount of Cd(II) incorporated is about 1 Cd(II) to 2 amphiphiles, as calculated from the ratio of the integrated peak areas of Cd(II) to N.

**Figure 4.10:** Small angle X-ray reflection curve of a LB film consisting of 16 layers of the amphiphile on silicon, built up from a 5 mM CdBr$_2$ subphase (sample F) at 19 °C and 19 mN·m$^{-1}$.

Small angle X-ray reflection measurements (Fig. 4.10), showed a regular layer structure with a layer spacing of about 42 Å. This might be ascribed to a monolayer spacing, assuming that the amphiphiles are oriented perfectly perpendicular to the substrate (α = 0°) or
it represents a bilayer spacing with a very large tilt angle, $\alpha$, of the chain director with respect to the surface normal.

In Figure 4.11, the transmission IR spectrum of sample F can be seen. It was not possible to transfer monolayers onto gold or silver coated glass substrates even when these substrates were covered first with 5 layers cadmium arachidate or 4 layers of amylose-acetate [40] or poly((S)-1-acetoxymethylethylisocyanide) [53], so GIR spectra could not be recorded.

For the bulk spectrum, the same scaling factor was used as in Figure 4.7. In the transmission spectrum (fig. 4.11 B), the N-H (3290 cm$^{-1}$) and Amide I (1644 cm$^{-1}$) absorption bands can clearly be seen but their relative intensity is weaker than in the bulk spectrum indicating, that the amide bond has a large tilt angle with respect to the surface normal. Also the aliphatic tail vibrations (2920 cm$^{-1}$ for $\nu_a$ (CH$_2$) and 2850 $\nu_s$ (CH$_2$)) should have a much stronger absorption in the transmission spectrum when the aliphatic tails were oriented almost perpendicular to the substrate. However from Figure 4.11 it can be concluded that the aliphatic tail has a large tilt angle ($\alpha$) with respect to the substrate surface. The carbon-nitrogen stretch vibration absorption is present at 1618 cm$^{-1}$, indicating that the Cd(II) ions are indeed coordinated to the pyridine ring of the amphiphile.

![Infrared spectra of the amphiphile](image_url)

**Figure 4.11:** Infrared spectra of the amphiphile: (A) bulk spectrum of the amphiphile, powdered in KBr (scale factor: 0.0395$\times$), (B) transmission, 16 layers of the amphiphile on silicon built up from a 5mM CdBr$_2$ subphase (sample E) at 19 $^\circ$C and 19 mN-m$^{-1}$.
The transmission spectrum suggests a large tilt angle ($\alpha$), so from the IR spectrum it can be concluded that the spacing of 42 Å, represents a bilayer spacing. Again a “turnover” from a Z-type structure to a Y-type structure must have occurred, because these multilayers were also built up with a Z-type transfer. From these results a structure for the multilayer is proposed which deviates a little from the LB film built up from a Cu(II) subphase. The tilt angle ($\alpha$) of the chain director with respect to the surface normal is approximately 55°.

Thus, when the multilayers contain Cd(II) ions the amphiphiles have a larger tilt angle with respect to the surface normal than in the case when the multilayers contain Cu(II) ions.

**Polymerisation in the multilayers**

![Graph showing polymerisation in the multilayers](image)

**Figure 4.12A:** UV/Vis spectra of a LB film of 16 layers of the amphiphile built up from a 5mM Cu(ClO$_4$)$_2$ subphase (sample B) at 19 °C and 30 mN·m$^{-1}$ on glass, at different UV ($\lambda = 254$ nm) irradiation times: (A) 0 min., (B) 2 min., (C) 5 min., (D) 20 min. and (E) 30 min.
The LB films were polymerised by means of exposure to UV light ($\lambda = 254$ nm) under argon atmosphere. The polymerisation process was followed by UV/Vis spectroscopy. Figure 4.12A exhibits absorption spectrum changes during the UV irradiation of the LB film consisting of 16 layers, built up from 5 mM Cu(ClO$_4$)$_2$ subphase. Several minutes of exposure to UV light resulted in a red form of the polymer with $\lambda_{\text{max}} = 540$ nm. Upon UV irradiation a rigid polymer with a one dimensional, conjugated backbone is formed. The conjugation resulted in the strong $\pi$ to $\pi^*$ absorption [54,55] shown in Figure 4.11A. In Figure 4.12B, the integrated area of absorbance between 400 and 800 nm as function of the polymerisation time is shown. Apparently the polymerisation is complete after 20 minutes of exposure to UV light. The optical density at 540 nm is about 0.008 per diacetylene monolayer. This is about the maximum obtainable optical density for a polydiacatylene monolayer [24]. Therefore, the polymerisation was more or less complete after 20 minutes of UV irradiation. In the case of the multilayers built up from a 5 mM CuCl$_2$ subphase, however, the polymerisation was complete only after about 50 minutes of exposure to UV light. Thus, by changing the counter ion, the polymerisation properties can be influenced, probably caused by a slightly different packing of the monomers. The polymerisation of diacetylenes is a topochemical reaction where a slightly different packing of the amphiphiles can have enormous influence on the polymerisation behaviour [56].
Upon exposure of the LB films to UV light no reduction of the Cu(II) ions inside these multilayer films to Cu(I) ions is observed as has been proven by means of XPS measurements (not shown here).

In order to examine whether the regular layer pattern was preserved during the polymerisation process, small angle X-ray reflection (SAXR) measurements were performed. In Figure 4.13 (A and B), SAXR measurements are shown of sample A (subphase: 5 mM Cu(ClO$_4$)$_2$) before and after 30 minutes of UV irradiation.

![SAXR measurements](image)

**Figure 4.13:** Small angle X-ray reflection curves of a LB film of 16 layers of the amphiphile built up from a 5mM Cu(ClO$_4$)$_2$ subphase (sample A) at 19 °C and 30 mN·m$^{-1}$ on silicon, before (A) and after 20 minutes of UV irradiation (B) and SAXR curves of a LB film consisting of 16 layers of amphiphile, built up from a 5 mM CuCl$_2$ subphase (sample E) at 19 °C and 30 mN·m$^{-1}$ on silicon, before (C) and after 50 minutes of exposure to UV light (D).

From these measurements it can be concluded that the layer structure is preserved during UV irradiation, although the bilayer spacing decreased from 59.2 down to 57.4 Å and the second order Bragg peak disappeared. The latter phenomenon can be explained by means of the well-known odd-even intensity oscillations of X-ray diffraction profiles [57-60]. In Y-type multilayer films, the juxtaposition of the two hydrophobic ends of the amphiphiles can give rise to a electron-deficient layer which will influence the intensity of the diffraction
peaks. By variation of the layer thickness of this electron-deficient layer, the intensities of the diffraction peaks can be varied which was already shown in 1977 by Matsuda et al. [57], who found that the best agreement between the calculated and experimental diffraction patterns for LB films of cadmium salts of fatty acids, was found when an electron-deficient layer of about two CH₂ groups thick was taken into account. As can be seen from Figure 4.6A and 4.13A, already before exposure to UV light the second Bragg peak had a relatively weaker intensity than the third one, which is additional proof of the existence of a Y-type structure in the LB film [60]. The shift of the Bragg peak to higher angles indicates an increased tilt of the amphiphiles inside the multilayer.

Contrary to LB films prepared from a Cu(ClO₄)₂ containing subphase, the layer structure of the LB film built up from a CuCl₂ subphase was destroyed after exposure to UV light, which is clearly demonstrated in Figure 4.13 (curves C and D).

Figure 4.14A: GIR infrared spectra of a LB film of 16 layers of the amphiphile built up from a 5mM Cu(ClO₄)₂ subphase (sample C) at 19 °C and 30 mN·m⁻¹ on gold-coated glass with 3 layers of cadmium arachidate, before and after 20 minutes of exposure to UV light. The CH₂ and CH₃ stretching vibration region.
Figure 14.4B: Transmission infrared spectra of a LB film of 16 layers of the amphiphile built up from a 5 mM Cu(ClO₄)₂ subphase (sample A) at 19 °C and 30 mN·m⁻¹ on silicon, before and after 20 minutes of exposure to UV light. The CH₂ and CH₃ stretching vibration region.

To get more insight into the structural changes during the polymerisation process inside the multilayer, FT-IR spectroscopy measurements were performed. Major changes were found in the CH stretching region for multilayers built up from a 5 mM Cu(ClO₄)₂ subphase, as can be seen in the Figures 4.14A (sample C) and 4.14B (sample B). The vibration bands near 2850, 2871, 2920 and 2955 cm⁻¹ are due to νₛ(CH₂), νₛ(CH₃), νₐ(CH₂) and νₐ(CH₃) respectively [61,62]. The vibration band near 2934 cm⁻¹ arises from the Fermi resonance between the νₐ(CH₃) band and the overtone of the CH₃ asymmetric deformation vibration near 1450 cm⁻¹ [61]. The weak vibration near 2897 cm⁻¹ was assigned to a Fermi resonance component arising from the νₛ(CH₂) band and an overtone of the CH₂ scissoring vibration [61]. After UV irradiation the νₛ(CH₂) and νₐ(CH₂) bands were slightly shifted to higher frequencies, 2852 and 2922 cm⁻¹, respectively. This indicated that the all-trans alkyl chain is partly converted into an alkyl chain containing gauche conformations. Because for an alkyl chain containing all-trans conformations, the νₛ(CH₂) and νₐ(CH₂) are situated at 2849 and 2919 cm⁻¹, respectively, while for an irregular alkyl chain containing only gauche conformations these vibrations are situated at 2854 and 2924 cm⁻¹ [61]. Furthermore, the νₛ
(CH$_3$) and the $\nu_a$ (CH$_3$) vibrations are situated at 2871 and 2955 cm$^{-1}$, respectively, irrespective of the alkyl chain conformation. This is consistent with our observations. The intensity of the $\nu_a$ (CH$_2$) band decreased in the GIR spectrum while the intensity of the $\nu_s$ (CH$_2$) band increased upon UV irradiation (Fig 4.14A). This fact together with the slight shift of these vibration bands to higher wavenumbers, could be explained by considering that the all-trans conformation of the alkyl is converted into an irregular one containing gauche conformations.

The same phenomena appeared in multilayers built up from a 5mM CuCl$_2$ subphase. But for these multilayers the intensities of the $\nu$ (N-H) and amide I absorptions also decrease in intensity and the peaks become broader, indicating that not only the structure of the aliphatic tail changes upon UV irradiation, but also the amide bond and pyridine rings are reoriented. This explains why the layer structure almost completely disappeared in the SAXR measurement (Fig. 4.13, curve D), upon exposure to UV light.

**Polymerisation of Cd(II) containing multilayers**

![Figure 4.15: Small angle X-ray reflection curves of a LB film of 16 layers of the amphiphile built up from a 5 mM CdBr$_2$ subphase (sample F) at 19 °C and 19 mN·m$^{-1}$ on silicon, before and after irradiation with UV light.](image)

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 Upon exposure to UV light (254 nm), the multilayer film built up from a 5 mM CdBr$_2$ subphase, formed a red phase polydiacetylene film. The polymerisation was complete within 30 minutes as could be seen by UV/Vis spectroscopy, in which the absorption at $\lambda_{\text{max}} = 540$ nm did not increase anymore after 30 minutes of exposure to UV light.

Small angle X-ray reflection measurements revealed that the layer structure was preserved well during the UV irradiation (Fig. 4.15). The bilayer spacing decreased from 42 to 40.5 Å, again indicating that upon polymerisation the amphiphiles make a larger tilt with respect to the surface normal. It can also be seen that the second Bragg peak is present before and after UV irradiation in contrast to the LB films built up from a Cu(II) subphase where the second Bragg peak was already somewhat weaker in intensity before UV irradiation (the well-known odd-even effect) and in the case of ClO$_4^-$ as counter ion totally disappeared upon exposure to UV light. This was a strong indication that the Cu(II) and Cd(II) ions multilayers had different layer structure.

Spectral changes in the transmission IR spectra showed up only in the CH stretching vibration region. The $\nu_a$ (CH$_2$) and $\nu_s$ (CH$_2$) absorptions did not shift to higher wavenumbers as was the case for the Cu(II) containing multilayers (Fig 4.14B). Thus, during the polymerisation process the alkyl chains maintain the all-trans conformation. Furthermore, upon polymerisation the $\nu_a$ (CH$_2$) absorption decreases in intensity while the $\nu_s$ (CH$_2$) absorption show a slight increase in intensity. These spectral changes in the transmission spectrum can only be ascribed to a larger tilt angle ($\alpha$) of the alkyl chain director with respect to the surface normal, which is in good agreement with the observed decrease in bilayer spacing derived from the SAXR measurements (Fig. 4.15).

Conclusions

Langmuir-Blodgett multilayers of 4-(10,12-pentacosadiynamidomethyl)pyridine could only be built up when the subphase contained Cu(II) or Cd(II) ions. XPS measurements confirmed that complexation had occurred in the monolayer because the multilayers contained metal ions. Care must be taken in drawing conclusions about the valence of the copper ions inside these multilayers from data deduced by XPS measurements, because upon exposure to X-rays the Cu(II) ions undergo a X-ray induced reduction to Cu(I). Small angle X-ray reflection measurements revealed that the formed multilayers had a regular layer structure with a bilayer spacing of approximately 60 Å and 42 Å for the Cu(II) and Cd(II) ions containing multilayers, respectively, although these multilayers were built up by a Z-type transfer. Therefore, a rearrangement to a Y-type structure had occurred.
Changes of metal ion had a great effect on the structure and polymerisation properties of these multilayers. Multilayers built up from a Cu(ClO$_4$)$_2$ and CdBr$_2$ containing subphase, preserve their regular layer structure during the polymerisation process. But after polymerisation, the all-trans alkyl aliphatic tail of the amphiphile in a Cu(II) ion containing multilayer, is converted into a more irregular alkyl chain, containing gauche conformations. This did not occur in the Cd(II) containing multilayers. For LB films built up from a CuCl$_2$ subphase, the regular layer structure was not preserved during the polymerisation process.

To summarise, the properties of LB film of metal complexes, largely depend on the metal and counter ions used in the subphase, from which the multilayers are built up.

References