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Oxidative Coupling Polymerization in a Langmuir Monolayer of Octadecyl 3,5-Diaminobenzoate

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In a Langmuir monolayer of the surface active monomer octadecyl 3,5-diaminobenzoate (ODDB), stabilized at a surface pressure of 10 mN/m and a temperature of 23.7 °C at the air-water interface, oxidative coupling polymerization occurs when copper(II) chloride was added or already was present in the subphase. Even in the absence of the catalyst this reaction takes place. Deposition of the polymerized monolayer onto glass, zinc sulfide, or gold substrates, using the vertical dipping method, gave transfer ratios between 0 and 0.4 on the downstroke and 1 on the upstroke. The multilayer films on zinc sulfide and gold substrates were characterized by means of Fourier transform IR spectroscopy, and multilayer films on quartz were characterized by means of UV/vis spectroscopy. Collected monolayers were characterized by means of size exclusion chromatography and again Fourier transform IR and UV/vis spectroscopy. During the stabilization of the monolayer without addition of copper(II) chloride to the subphase, the area per molecule decreased very slowly. Addition of copper(II) chloride enhanced this effect. The reduction of the area per molecule is probably caused by the polymerization itself accompanied by a reorientation of the molecules in the monolayer at the air-water interface. After stabilization the area per molecule was found to be about 27 Å². and electron micrographs showed the formation of a smooth monolayer. From this it has been concluded that a closely packed monolayer was formed. Fourier transform IR and UV/vis spectra of poly[(p-phenylenevinylene) and poly((p-thienylenevinylene), flexible nonconjugated precursor polymers have been used. Langmuir monolayers of poly-anion complexes of these precursor polymers could be transferred by a conventional LB dipping process. The formed LB multilayer films were exposed to heat in order to obtain a π-conjugation.11–13

Introduction

Over the past few years the Langmuir–Blodgett (LB) technique has been used to manipulate a number of π-conjugated polymers into multilayer thin films with well-defined layered structures and ordered molecular organizations.4 Because of the failure of π-conjugated polymers to dissolve in common organic solvents, caused by the stiffness of the backbone, these polymers cannot directly be used to prepare Langmuir monolayers and LB multilayer films. In order to obtain solubility, linear aliphatic side chains can be attached to the backbone. These polymers can directly be processed by means of the LB technique.2–10

Alternatively, to obtain multilayer films of poly(p-phenylenevinylene) and poly(p-thienylenevinylene), flexible nonconjugated precursor polymers have been used. Langmuir monolayers of poly-anion complexes of these precursor polymers could be transferred by a conventional LB dipping process. The formed LB multilayer films were exposed to heat in order to obtain a π-conjugation.1–10

In order to circumvent solubility problems, direct processing of a surface active monomer is also a method used for the preparation of LB multilayer films of π-conjugated polymers. After deposition of the Langmuir monolayer onto a solid substrate, π-conjugation can be obtained by forcing the monomer to polymerize.11–14 In the Langmuir monolayer polymerization of the ‘preoriented’ monomers can also be performed by adding a catalyst or reagents to the subphase.15–27 Recording of the area per repeating unit in time during the polymerization, at constant pressure and temperature, can be regarded as volume dilatometry in two dimensions.

Tsuchida et al.28 showed that 1,4-diaminobenzene can be polymerized oxidatively to the corresponding azo...
polymer at room temperature by Fe(III) chelates, like the Fe(III) salt of ethylenediaminetetraacetic acid, in aqueous solution. Moreover, it is known that, in particular cases, a copper(II) chloride salt/dioxygen combination can give azo coupling of primary aromatic amines. With this in mind, the possibility of polymerization in a Langmuir monolayer of the surface active monomer, octadecyl 3,5-diaminobenzoate, by adding copper(II) chloride to the subphase (water) was examined.

**Experimental Details**

**Materials.** Octadecyl 3,5-diaminobenzoate, (ODDB) was synthesized from octadecyl 3,5-dinitrobenzoate by reduction, and octadecyl 3,5-dinitrobenzoate was synthesized from 3,5-dinitrobenzoic acid and 1-octadecanol by esterification. CuCl2-2H2O was obtained analytically pure from Merck.

**LB Measurements.** LB measurements were performed on a computer-controlled Lauda Filmbalance F2W. The water used for the subphase was purified with a Elga distilled water system coupled with a Milli-Q purification system, delivering water with a resistance greater than 18 MΩ. For spreading, ODDB was dissolved in a mixture of chloroform, acetone, and toluene (1:1:1 by volume). The concentration of the spreading solution varied between 0.7 and 0.9 mg/mL. Surface pressure—area isotherms were measured with a standard compression rate of 5 Å2 monomer−1 min−1. Transfer experiments were carried out by a vertical dipping method after stabilization of the Langmuir monolayer at the air—water interface at constant pressure and temperature for about 18 h. A dipping speed of 5 mm/min was used for the downstroke and upstroke transfer. For the cleaning of glass slides a standard method was used. Just before use, the glass slides were rinsed with 2-propanol and chloroform, partly hydrophobized by treatment with a mixture of octadecyl and hexamethyldisilazane (1:4 by wt) at 50 °C, and finally rinsed with chloroform. ZnS plates (Cleartran Spectra-Tech) were cleaned ultrasonically with chloroform. Gold substrates were obtained by sputtering a 50 nm thick gold layer onto the clean glass slides with a Biorad Turbocoater E-6700. The cleaning method of quartz substrates was identical to the cleaning method of glass substrates.

The collected polymerized Langmuir monolayer material was compared with the azo-coupling product of ODDB formed in bulk solution. For the oxidative coupling polymerization in bulk solution a catalyst prepared from copper(I) chloride (CuCl), pyridine, and dioxygen was used. The standard conditions for this polymerization in bulk solution were as follows: [ODDB]0 = 0.06 mol/L; [CuCl]0 = 0.03 mol/L; reaction volume 15 mL of pyridine; reaction temperature 50 °C; dioxygen consumption ∼0.063 mol/L.31,33 Langmuir monolayer material was also characterized by size exclusion chromatography (SEC) (PSS Gel type 105 + 104 Å columns, Shodex RI-71 refractive index detector, tetrahydrofuran as eluent).

**Results and Discussion**

In Figure 1 the surface pressure—area isotherms of ODDB at different temperatures are shown. Because 1,3-diaminobenzene is soluble in water, the phenyl ring with the two amino groups and the ester group of ODDB are expected to be located in the water phase. With increasing surface pressure the long linear aliphatic chains are expected to adopt a perpendicular orientation with respect to the water surface (Figure 2). Isotherms were recorded at temperatures of 11 and 23 °C. The isotherm at 30 °C published by Lupo et al.35 corresponds with this isotherm. During the compression of the spreaded material, at the air—water interface, the formation of a condensed phase starts at an area per molecule of about 33 Å2. From Corey Pauling Koltun (CPK) models it was calculated that the area per molecule, in the vertical position with respect to the water surface (Figure 2), is about 28–30 Å2. The molecules in the monolayer will therefore be closely packed. With increasing temperature the crystallinity of the monolayer decreases and the resulting isotherm points to a combination of a liquid and a condensed phase. As a result the area per repeating unit where the surface pressure starts to rise increases and the collapse pressure decreases (isotherms b and c).

![Figure 1. Pressure—area isotherms of ODDB at 11 and 23.7 °C (a), 35 °C (b), and 44 °C (c).](image1)

![Figure 2. Schematic picture of ODDB at the air—water interface.](image2)
The stabilization of a Langmuir monolayer of ODDB, at a pressure of 10 mN/m and a temperature of 23.7 °C, is shown in Figure 3, curve a. At first the area per molecule reduces slowly from 31 to 28 Å² in about 6 h. Subsequently, a more or less stable Langmuir monolayer, with an area per molecule of about 27 Å², is formed. When, after a stabilization period of about 100 min, 20 mL of an aqueous solution of CuCl₂ was added to the subphase, resulting in a concentration of about 0.014 mol/L, the reduction of the area per molecule in time was accelerated. The surface area per molecule remains more or less constant after reaching a value of about 27 Å² (Figure 3, curve b). Curve c in Figure 3 shows the area per molecule in time of a Langmuir monolayer of ODDB at 10 mN/m and 23.7 °C, directly spread on a CuCl₂-containing subphase (total concentration ∼ 0.014 mol/L). After a very fast reduction of the area per molecule to about 27 Å², the area increases slowly to about 28 Å² and then again decreases slowly to about 27 Å². The small increase of the area per molecule can also be seen more or less in Figure 3, curve b.

After a stabilization period of about 18 h the Langmuir monolayers were transferred onto solid substrates of glass, zinc sulfide, and gold by a vertical dipping method. The transfer ratio on the downstroke usually was between 0 and 0.4. On the upstroke the transfer ratio was about 1.

The FTIR spectra of the collected black Langmuir monolayer material, after a stabilization period of about 18 h, at 10 mN/m and 23.7 °C, without and with CuCl₂ in the subphase are shown in Figures 4c and d, respectively. These spectra are very much identical. Moreover, comparison of these spectra with the IR spectrum of the azo polymer prepared in bulk solution (Figure 4, spectrum b) revealed a strong similarity. Obviously, an azo coupling product is formed during the stabilization of the Langmuir monolayer with and without copper chloride in the subphase. Spectra b, c, and d differ from the spectrum of ODDB (Figure 4, spectrum a). A detailed discussion of these differences has been given in another paper.³³

The UV/vis spectra of the collected Langmuir monolayer material, after a stabilization period of about 18 h, without and with CuCl₂ in the subphase (a and b, respectively) and the corresponding azo polymer prepared in bulk solution (c) are shown in Figure 5. The UV/vis spectra of the Langmuir monolayer material without CuCl₂ and of the azo polymer prepared in bulk solution are almost identical. The spectrum of the azo polymer prepared in bulk solution, which is expected to have a trans-azo configuration, shows a long tail up to 900 nm, caused by transitions in the π-conjugated system along the backbone.³⁶ This tail is also present in spectrum a but reaches only to about 700 nm. Spectrum b is very much similar to spectrum a, except that the peak at about 335 nm has disappeared. From the FTIR and the UV/vis spectra it is concluded that during the stabilization of a Langmuir monolayer of ODDB at 10 mN/m and 23.7 °C coupling of the amino groups to the zero group occurs. A larger π-conjugation length results in absorptions at higher wavelength in the UV/vis spectrum; therefore, the material prepared by coupling in a Langmuir monolayer might have a smaller conjugation length than the azo polymer prepared in bulk solution. The origin for the absence of the peak at about 335 nm in UV/vis spectrum b of Figure 5 is not clear at the moment.

The reduction of the surface area in time appears to be the result of a better packing of the molecules in the

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Langmuir monolayer at the air–water interface, which is introduced by the coupling. When the subphase contains no CuCl₂, the coupling is very slow, resulting in a slow reduction of the surface area in time (Figure 3, curve a). When CuCl₂ is added or already present in the subphase, the rate of coupling is enhanced, resulting in a faster reduction of the surface area in time (Figure 3, curves b and c). The very fast coupling in the Langmuir monolayer on an already CuCl₂-containing subphase (Figure 3, curve c) forces the molecules to organize very fast in a closely packed system. After the coupling, reorientations of the polymer chain probably occur, resulting in the small increase followed by a small reduction of the surface area in time.

Formation of the azo polymer can also be seen with SEC. Before the SEC measurements, the collected Langmuir monolayer material was dissolved in chloroform, which was washed (three times) with water. The chloroform was removed by evaporation, and the material was dried under vacuum. Figure 6 shows the SEC diagrams of ODDB (a), the reaction product of the polymerization of ODDB in bulk solution (b), and the collected Langmuir monolayer material after a stabilization period of about 18 h at 10 mN/m and 23.7 °C without and with CuCl₂ in the subphase (c and d, respectively). The peak at about 23.2 mL originating from the tetrahydrofuran stabilizer (butylated hydroxytoluene) can be regarded as an internal standard. For the determination of the molecular weight by using SEC in combination with a Viscotek viscometer detector, it is necessary to know the concentration of the solution of Langmuir monolayer material. Because the amount of Langmuir monolayer material was very small, the concentration is difficult to determine and an exact number for the molecular weight can therefore not be given. It can be seen that without and with CuCl₂ in the subphase, the molecular weight distribution is the same.

According to SEC diagram d and diagram a, which is of pure monomer, no monomer is present in the collected Langmuir monolayer material prepared with CuCl₂ in the subphase. The small peak at about 22.7 mL in diagram c is most likely of an impurity or a small amount of monomer. The peak in SEC diagram b at about 21.1 mL originating from the dimer is also present in SEC diagrams c and d. During the polymerization in the Langmuir monolayer, without and with CuCl₂, dimer-like structures are formed. Moreover, a material with a higher molecular weight is formed. This material has a lower average molecular weight than the high-molecular-weight part of the azo polymer prepared in bulk solution (the molecular weight at the maximum of the peak at about 18.4 mL in diagram b is about 35 × 10³ D). This is consistent with the UV/vis spectra. Because of the 'preorientation' of the molecules, coupling of the reactive groups might be hindered, resulting in a lower average molecular weight of the reaction product.

From these experiments we can conclude that, during the stabilization without and with CuCl₂, dimer and high-molecular-weight coupling products are formed. The reason for the coupling in the Langmuir monolayer without CuCl₂ is not very clear. A possible explanation may be given by Terent'ev and Mogilyanski. For the oxidative coupling of primary aromatic monoamines by a catalyst prepared from CuCl₂, pyridine, and dioxygen, Terent'ev and Mogilyanski discussed two possible reaction mechanisms. Coupling of the oxidation products of the monoamine to azo and azoxy compounds could be a pathway. E.g. aniline can be oxidized via phenylhydroxylamine and nitrosobenzene to nitrobenzene. During this process coupling can occur; e.g., phenylhydroxylamine can react with nitrosobenzene to azoxybenzene and unchanged aniline can react with nitrosobenzene to azobenzene. However, Terent'ev and Mogilyanski never succeeded in finding even traces of azoxy compounds among the reaction products. According to Bamberger and Tschirner, this could be explained by the fact that...
CuCl₂ is added or already present in the subphase, the can be calculated. For the Langmuir monolayers where the shadow length a layer thickness of about 28 (present in the monolayer at the air big and small cracks are probably introduced during the period of about 18 h at 10 mN/m and 23.7 °C without CuCl₂ in the subphase. When CuCl₂ is added or already present in the subphase, the other mechanism might also occur. A Langmuir monolayer can be regarded as a very thin solid film. The CH stretching region (2800 – 3000 cm⁻¹) consists of a number of bands attributable to methyl (CH₃) and methylene (CH₂) stretching vibrations. These are the CH₃ asymmetric vibration (νₛ(CH₃)) at 2956 cm⁻¹, the CH₂ asymmetric vibration (νₐ(CH₂)) at 2920 cm⁻¹, the CH₂ symmetric vibration (ν₂(CH₂)) at 2872 cm⁻¹, and the CH₃ symmetric vibration (ν₁(CH₃)) at 2852 cm⁻¹. The corresponding transition dipole moment for each vibration is shown in Table 1.

Due to dispersion effects, comparison of the spectra should be performed with care. It can be seen clearly that the ν₂(CH₃) is present in the grazing incidence reflection IR spectrum and not in the transmission spectrum. Moreover, the νₐ(CH₂) and the ν₂(CH₂) appear as strong bands in the transmission IR spectrum and as weak bands in the grazing incidence reflection IR spectrum. From these measurements it follows that the aliphatic chains have a preferential orientation perpendicular to the substrate. The asymmetric C–O–C vibrational (νₛ(C–O– C)) at 1239 cm⁻¹ is very strong in the grazing incidence reflection IR spectrum and very weak in the transmission IR spectrum. The transition dipole moment of νₛ(C–O–C) is therefore probably more parallel to the C–O–C bond. Proof for the preferential orientation of the aliphatic chains perpendicular to the substrate can also be given by grazing incidence reflection IR spectroscopy in conjunction with thermal measurements.

In Figure 9 the grazing incidence reflection IR spectra of a sample before (a) and after heating for 5 days at 110 °C (b) are shown. After heating the intensity of νₛ(CH₃) has increased a little bit. The intensities of νₐ(CH₂) and ν₂(CH₂) show a large increase after heating. In addition,

Table 1. Transition Dipole Moment Directions of Different IR Bands

<table>
<thead>
<tr>
<th>mode</th>
<th>wavenumber (cm⁻¹)</th>
<th>direction of the transition dipole moment</th>
</tr>
</thead>
<tbody>
<tr>
<td>νₛ(CH₃)</td>
<td>2956</td>
<td>⊥ to C–CH₃ bond</td>
</tr>
<tr>
<td>νₐ(CH₂)</td>
<td>2920</td>
<td></td>
</tr>
<tr>
<td>ν₂(CH₂)</td>
<td>2872</td>
<td>⊥ to H–C–H plane</td>
</tr>
<tr>
<td>ν₁(CH₃)</td>
<td>2852</td>
<td></td>
</tr>
</tbody>
</table>

References:
after heating, the intensities of ν(C—O—C) and ν(C=O) have decreased and increased, respectively. The preferential orientation perpendicular to the substrate disappears after heating. The intensity increase of ν(C=O) after heating indicates that before heating the preferential orientation of the carbonyl group is parallel to the substrate.

In a previous paper the preparation of multilayer films of the corresponding azo polymer of ODDB prepared in bulk solution has been discussed. In the multilayer film the azo group is expected to have the trans-configuration and the aliphatic side chains form amorphous layers. Comparison of a grazing incidence reflection IR spectrum of a multilayer film of this polymer on gold with the grazing incidence reflection IR spectrum after heating for 5 days at 110 °C, shown in Figure 9, spectrum b, revealed a striking resemblance. This again is a good indication that, in the Langmuir monolayer and in bulk solution, similar products are obtained.

For the simulation of transmission and grazing incidence reflection IR spectra, a cast-free standing film of collected Langmuir monolayer material with random orientations of the different groups is needed. Unfortunately, not enough material could be collected to prepare these films. Therefore, comparison of simulated transmission and grazing incidence reflection IR spectra without orientation of the different groups with their corresponding spectra of the LB multilayer films cannot be done.

In Figure 10 the transmission IR spectra of LB multilayer films for the systems without (a) and with (b) CuCl$_2$ are shown. Compared to spectrum a, spectrum b shows two extra absorptions between 3200 and 3500 cm$^{-1}$, which are also observed in spectrum d of Figure 4. Moreover, the spectra differ between 1500 and 1600 cm$^{-1}$. The origin of these differences is not clear at the moment but could be the result of the presence of a (hydrated) copper complex or the occurrence of a side reaction. Besides these differences, the two spectra show a strong resemblance, indicating that after a stabilization period of about 18 h at 10 mN/m and 23.7 °C an identical orientation of the molecules can be expected in the Langmuir monolayers without and with CuCl$_2$ in the subphase.

For both polymers prepared with and without CuCl$_2$, no difference was found between the transmission IR spectra taken with the polarization perpendicular and parallel to the transfer direction during multilayer formation. Therefore, no flow-induced orientation has occurred during the transfer.

The small-angle X-ray diffraction pattern of a LB multilayer film (11 dipping cycles), transferred after a stabilization period of 18 h at 10 mN/m and 23.7 °C of the Langmuir monolayer at the air—water interface, without CuCl$_2$ in the subphase, is shown in Figure 11. A broad Bragg peak at 55 ± 1 Å can be seen. This reflection represents the bilayer distance of domains in the LB multilayer film where good Y-type transfer has occurred. The thickness of the monolayer is therefore about 27.5 Å, which is consistent with the thickness of the Langmuir monolayer calculated from the shadow length seen in the transmission electron micrographs. A Bragg peak corresponding to a monolayer thickness is not observed. This is probably the result of a strong disturbance of the monolayer stacking by bilayer regions. It should be noted that the transfer ratio on the downstroke usually was on the order of 0.4 (a transfer ratio of 0 was very rare). The thickness of 27.5 Å (for onemonolayer) can only be achieved when the repeating unit has a perpendicular orientation to the substrate, with the phenyl ring pointing down and the aliphatic chain pointing up, as shown for ODDB in
Figure 2. The perpendicular orientation of the aliphatic chains is consistent with the results obtained from the IR measurements. Moreover, this is in agreement with the results found for the LB multilayer films of the corresponding azo polymer prepared in bulk solution. For the LB films of the azo polymer prepared in bulk solution a bilayer distance of 42.7 Å was found. In this case, however, the aliphatic chains had no preferential orientation perpendicular to the substrate but formed amorphous layers, which results in a lower bilayer distance.

The exact configuration of the azo group in the Langmuir monolayer, after a stabilization period of about 18 h at 10 mN/m and 23.7 °C, without and with CuCl₂ in the subphase is difficult to determine. A cis-configuration as shown in Figure 12 might be a good possibility. In the transmission and grazing incidence reflection IR spectra (Figure 8) a peak at about 1507 cm⁻¹ can be observed. This peak could originate from the stretching vibration of an azo group in the cis-configuration. The appearance of this peak from the cis-azo group (with a transition dipole moment parallel with this group) in the grazing incidence reflection IR spectrum (Figure 9, spectrum a) would imply an orientation not totally parallel with the substrate of this group in the LB multilayer film. In the transmission IR spectrum for the system with CuCl₂ (Figure 10, spectrum b) the shoulder at about 1497 cm⁻¹ could be from this vibration, too.

In the grazing incidence reflection IR spectrum after heating for 5 days at 110 °C (Figure 9, spectrum b) the peak at 1507 cm⁻¹ has disappeared. This could be an indication of the configurational change of the azo group from cis to trans.

Figure 13 depicts the UV/vis spectra before (a) and after (b) heating for about 3 days at 110 °C of a LB multilayer film, prepared without CuCl₂ in the subphase.

After heating, the UV/vis spectrum corresponds with the spectrum of the collected Langmuir monolayer material in chloroform. The spectrum before heating could therefore correspond to the cis-configuration. Scaling up of the IR spectra between 1400 and 1500 cm⁻¹ revealed a shoulder at 1457 cm⁻¹. In addition, sometimes a very small shoulder at 1435 cm⁻¹ can be observed. The IR spectra of the corresponding azo polymer, prepared in bulk solution, also showed these characteristics. For this polymer it has been suggested that the shoulder at 1457 cm⁻¹ originates from the absorption of an aromatic ring vibration and the shoulder at 1435 cm⁻¹ originates from the absorption of the stretching vibration of the azo group in the trans-configuration. If this is true, a few trans-azo groups should be present in the LB multilayer films. A trans-configuration of the azo group is possible for the dimer. However, because the aliphatic side chains are preferentially orientated perpendicular to the water surface, the trans-configuration is not possible for polymer materials.

Conclusions

It was established that, in a Langmuir monolayer of ODDB, stabilized at a pressure of 10 mN/m and a temperature of 23.7 °C, autopolymerization occurs. SEC, FTIR, and UV/vis spectroscopy revealed that the formed material corresponded with the azo coupling product prepared in solution, meaning that the amino groups are able to react with each other, resulting in the formation of azo groups. Addition of CuCl₂ to the subphase results in an increase of the polymerization rate. With and without CuCl₂ in the subphase the same molecular weight distribution was obtained. SEC measurements revealed that the molecular weight of the polymer material was limited, which might be caused by the 'preorientation' of the molecules. The experimental results were explained by a coupling of the amino groups to azo groups in the cis-configuration.