Langmuir-Blodgett films of poly(p-phenylenevinylene) precursor polymers
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Chapter 5

Oxidation of monolayers of partly converted precursor polymers at the air-water interface

Abstract

We observed that the PPV units in Langmuir monolayers of partly converted di-methoxy substituted poly(p-phenylenevinylene) precursor polymers oxidize at the air-water interface. This reaction even happens in the dark and cannot therefore not be contributed to a photo-oxygenation reaction with singlet oxygen. We assume that ground state triplet oxygen is polarized at the air-water interface and forms a weakly bound complex with the double bond to give a reactive intermediate state, which lowers the activation energy of the oxidation. The air-water interface thus works as a catalyst in this reaction.
5.1 Introduction

In Chapter 2 and Chapter 3 we have reported the Langmuir monolayer and the Langmuir-Blodgett transfer behavior of (di)alkoxy-substituted precursor poly(p-phenylenevinylene) (PPVs).\(^1\)\(^2\) It appeared that the transfer improved when chloroform solutions became colored indicating the partial conversion of the precursor polymer to PPV.\(^3\)\(^4\) During stabilization experiments of these partly converted precursor monolayers, we discovered that the monolayer oxidizes at the air-water interface.

Oxidation reactions of conjugated polymers are well described\(^5\)\(^6\) and are a great disadvantage for applications of conjugated polymers in devices such as light-emitting diodes (LEDs) and photovoltaic cells, because the formed carbonyl groups are exciton quenchers.\(^7\) These oxidation reactions are photo-oxygenation reactions, wherein the conjugated polymer itself acts as the photosensitizer for singlet oxygen.\(^8\)\(^9\)

The oxidation reaction of the partly converted precursor PPV monolayers described in this Chapter is not a reaction with singlet oxygen, because it also happens in the dark. We synthesized several partly converted di-methoxy substituted precursor PPVs with different percentages of conjugated units and studied the oxidation reaction thoroughly under various conditions.

5.2 Experimental

Materials

The preparation of precursor polymer poly[2,5-di-methoxy-1,4-(α-methoxy)xylylene] (prec-DMePPV) was described in Chapter 2. Party converted DMePPVs were prepared by dissolving 300 mg (1.5 mmol) prec-DMePPV in 30 ml 1,2,4-trichlorobenzene. This solution was degassed and was allowed to reflux under an inert nitrogen atmosphere. After 5, 10 and 15 min of reflux a part of the solution was precipitated in cold methanol. The partly converted precursors obtained were redissolved in dichloromethane and were precipitated again in cold methanol.

\(^1\)H-NMR

\(^1\)H-NMR spectra were recorded in chloroform-d\(_1\) solutions at 200 MHz.
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IR
The oxidized monolayers were collected by moving the moveable barrier towards the fixed barrier until the distance between the barriers was equal to the width of a small silicon wafer and subsequently the monolayer was swept together and picked up by the silicon wafer. After that the collected monolayer was dried and analysed using in a Mattson Galaxy 6021 FT-IR spectrometer.

UV-Vis
The UV-Vis spectra of the oxidized monolayers were taken by dissolving the collected material on the silicon wafer in chloroform (Uvasol quality) after the IR spectrum was taken. The spectra were recorded on a SLM Aminco 3000 diode-array UV-Vis spectrophotometer.

Langmuir films
The surface pressure isotherms and the stabilization experiments were carried out on a computer controlled Lauda Filmbalance (FW 2). The surface pressure could be measured with an accuracy of 0.05 mN/m. The partly converted precursors were spread from chloroform solutions (Uvasol quality, concentrations 0.2-0.4 mg/mL) onto pure water subphase, which was purified by reverse osmosis and subsequent filtration through a Milli-Q purification system or onto a water subphase to which HCl, KHCO$_3$, $3 \times 10^{-3}$ M ascorbic acid or $1 \times 10^{-3}$ M 3-Carboxy-proxyl had been added. The solutions were stored in the dark, and a drop of pyridine was added to prevent premature elimination by acidic products in chloroform.\textsuperscript{3,10}

Ozone test
The presence of ozone in the laboratory air was tested with Dräger Röhrchen testing tubes with a measurable range of 0.05-1.4 ppm.

GPC
Gel permeation chromatography (GPC) measurements were performed on chloroform solutions in a Špectra Physics AS 1000 system using universal calibration with a Viscotek H-502 viscometer and a Shodex RI-71 refractive index detector. CHCl$_3$ was used as eluent. The columns were calibrated with polystyrene standards.
5.3 Results and discussion

The UV-Vis spectra of the partly converted precursors dissolved in chloroform are shown in Fig. 5.1. The strong band at $\lambda = 290$ nm corresponds to the $\pi-\pi^*$ transition of the dimethoxy-substituted phenyl ring. The bands with $\lambda_{\text{max}}$ at 360 nm and $\lambda_{\text{max}}$ at 410 nm correspond to conjugated units, the tetramethoxy-stilbene unit and the hexamethoxy-distyrylbenzene units, respectively.\textsuperscript{11} Using $^1$H-NMR spectroscopy, the degree of conversion was calculated on the basis of the peaks between 3.5 - 4 ppm originating from the methyl protons of the aromatic methoxy groups of the PPV and the precursor-PPV units and the bands between 2.7 - 3.3 ppm which originate only from groups of the precursor-PPV unit. The conversion of the polymer was determined to be 10%, 20% and 32% after 5, 10 and 15 min of reflux, respectively.

Various stabilization curves of the 32% partly converted prec-DMePPV (32%-pcDMePPV) at 15 mN/m and 15 °C are shown in Fig. 5.2. It can be seen that this experiment is not reproducible. All experiments show the same large
decrease in area, but the moment at which the decrease started and the rate differed from experiment to experiment. After the initial decrease in area a more or less stable monolayer is formed. The stabilization curves of 10%-pcDMePPV, 20%-pcDMePPV and 32%-pcDMePPV stabilized at a surface pressure of 15 mN/m and at 15 °C are shown in Figure 5.3. The results show that the total decrease in area depends on the degree of conversion of the polymer.

The 32%-pcDMePPV monolayer was collected after the decrease in area and UV-Vis and FT-IR spectra were taken with this material (for procedure see experimental). The UV-Vis spectra of 32%-pcDMePPV and of the collected monolayer, both being dissolved in chloroform, are shown in Fig. 5.4. The absorption bands of the longer conjugated units have disappeared in the UV-Vis spectrum of the collected monolayer and only the absorption of the stilbene units can be observed. A band with $\lambda_{\text{max}}$ at 266 nm has appeared, which can be attributed to the n-\(\pi^*\) transition of a carbonyl group.$^{12}$

Figure 5.2. Various stabilization curves of 32%-pc-DMePPV stabilized at 15mN/m and 15 °C.
In Figure 5.5 the FT-IR spectrum of 32%-pcDMePPV before spreading (Fig. 5.5, a) and the FT-IR spectrum of the collected monolayer (Fig. 5.5, b) are shown. When the spectra of Fig. 5.5 are compared the appearance of a peak at 1680 cm\(^{-1}\) and 1610 cm\(^{-1}\) is observed as well as a decrease in the vinyl bands at 3054 cm\(^{-1}\) and 963 cm\(^{-1}\). The band at 1680 cm\(^{-1}\) can be attributed to carbonyl groups, while the band at 1610 cm\(^{-1}\) originates from non-symmetrically substituted aromatic ring vibration. When the reducing agent NaBH\(_4\) or aniline is added to a solution of the collected monolayer the band at 1680 cm\(^{-1}\) diminishes, meaning that it can be attributed to an aldehyde or ketone group and not to an ester group.

Figure 5.3. Stabilization curves of a) 10%-pc-DMePPV, b) 20%-pc-DMePPV, and c) 32%-pc-DMePPV stabilized at 15mN/m and 15 °C.
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Figure 5.4. UV-Vis spectra 32%pc-DMePPV (solid line) and of the monolayer collected after the decrease in area (dashed line), both dissolved in chloroform.

Figure 5.5. FT-IR spectra of a) 32%pc-DMePPV film on silicon wafer, and b) collected monolayer of 32%pc-DMePPV after the decrease in area on silicon wafer.
Whereas the molecular weight of the 32%-pcDMePPV before spreading is about $\bar{M}_w = 1 \times 10^6$ and $\bar{M}_n = 3 \times 10^5$, the average molecular weight of the collected material, after oxidation, as determined by Gel permeation chromatography (GPC), appeared to be very low. Therefore, it is very likely that double bonds in the partly converted monolayers at the air-water interface are oxidized to aldehyde groups, thus decreasing the average molecular weight. When no pressure was applied to the monolayer after spreading and the remaining polymer at the air-water interface was collected after 24 hours and analyzed, it appeared that the oxidation reaction had occurred, meaning that an applied surface pressure is not needed for this reaction. We assume that the observed decrease in the monolayer area does not correspond with the initiation of oxidation, but with the moment that low molecular weight products with carbonyl ends that are formed by oxidation, begin to dissolve in the subphase. The oxidation reaction could be prevented when oxygen in the subphase was thoroughly removed ultrasonically and by placing the LB trough under Argon atmosphere.

The oxidation of double bonds to aldehyde groups is a very well known photo-oxygenation reaction. This reaction involves singlet oxygen that is produced by energy transfer from triplet sensitizers to oxygen. To reach the triplet state the sensitizer needs to absorb light. The PPV units in the partly converted precursor can act as sensitizers. However, in our case the oxidation reaction also happened when the monolayer was spread in complete darkness, therefore, this oxidation reaction at the air-water interface can not be a photo-oxygenation reaction.

In the literature a few other reports on oxidation reactions at the air-water interface were found. Kamel et al. reported the oxidation of the hydroxyl group of cholesterol spread on a water subphase. This reaction could be prevented by dissolving ascorbic acid in the subphase, but the real oxidation reaction mechanism is unknown. Sagisaka et al. found that an amphiphilic aniline monolayer could be oligomerized without any oxidant such as persulfate, which is normally needed in this reaction. A similar reaction was reported by our group in which a monolayer of hexadecyl-di-aminobenzoate could be polymerized without a copper catalyst. No explanations have been reported for any of these unusual reactions.

Because the oxidation reaction of the monolayer was not reproducible (Fig. 5.2), we supposed that environmental factors, such as the pH of the subphase and a variable composition of the unrestricted laboratory air, influenced the oxidation reaction. The pH of the subphase can alter a little due to variations in the dissolved amount of CO$_2$. To study the influence of the pH of the subphase it was varied between 8.5 and 2.7, but no influence on the oxidation reaction
was found. Blohm et al. observed that poly(thiophene vinylene) films are oxidized by ozone in unrestricted laboratory air. To exclude a possible oxidation reaction with ozone the LB trough was placed under pure oxygen and it was found that the oxidation reaction still took place. Moreover, the laboratory air was tested with Dräger tubes and no ozone was detected which means that the ozone concentration was below 0.05 ppm.

To elucidate whether free radicals are involved in the oxidation reaction mechanism either ascorbic acid or 3-Carboxy-proxyl, both free radical scavengers, was dissolved in the subphase prior to the spreading of 32%-pcDMePPV, but the oxidation reaction was neither inhibited nor delayed. Steinbach found an oxidative decomposition of oleic acid at the air-water interface. He assumed that oxygen at the air-water interface is polarized due to the anisotropy of the interface and that this would play an important role in this reaction. The tentative chemical structure of polarized oxygen is given in Fig. 5.6. It is known that oxygen forms weakly bound complexes with double bonds. Therefore, Steinbach assumed that a complex between the double bond and polarized oxygen is formed at the interface and that this results in some kind of reactive intermediate state, which might lower the activation energy. In this way the air-water interface works as a "catalyst", lowering the activation threshold.

We assume that the oxidation reaction described in this paper also involves a complex between the double bond and polarized oxygen. It is very likely that the reaction proceeds via a 1,2-cycloaddition of the polarized oxygen to the double bond. The 1,2-cycloaddition with ground state triplet oxygen is actually a spin-forbidden reaction, but it is observed in a few other cases and is believed to proceed via an ionic intermediate. However, the 1,2-cycloaddition can also involve a radical, ionic, peroxirane (see Scheme 5.1), or dioxetane intermediate. A radical intermediate is not very plausible because radical scavengers had no influence on the reaction. A peroxirane intermediate is more likely because similar to polarized oxygen, the O-O bond in peroxirane is very polar and the external oxygen atom carries a large negative charge just as in

![Figure 5.6. Tentative chemical structure of polarized oxygen](image-url)
polarized oxygen. Therefore, we assume that the peroxirane mechanism depicted in Scheme 5.1 is plausible for the oxidation reaction of partly converted precursor PPVs at the air-water interface but other mechanisms might also be possible.

Additional circumstantial evidence for the involvement of polarized oxygen is the (accidental) discovery that the monolayer oxidation is delayed when organic vapors are present in the air above the monolayer. When 0.5 ml toluene was allowed to evaporated in the trough before spreading and the trough was sealed with tape, the stabilization curve shown in Fig. 5.7a was obtained. For comparison the stabilization curve of a monolayer without organic vapors is also shown in Fig. 5.7b. The organic vapors are probably adsorbed at the air-water interface and might prevent in this way the polarization of oxygen.

Scheme 5.1. Peroxirane mechanism
The double bonds of the PPV units of pc-DMePPV are oxidized at the air-water interface to aldehyde groups. This reaction also happens in the dark, so singlet oxygen is not involved in this reaction. Radical scavengers and the pH of the subphase have no influence on the rate of the oxidation reaction. It is likely that oxygen is polarized at the air-water interface and forms a weakly bound complex with the double bond. It is believed that this complex is a sort of reactive intermediate state. Adding organic vapors to the air above the monolayer prevents the oxidation reaction.

**Figure 5.7.** Stabilization curves of 32% pc-DMePPV with organic vapors in the atmosphere (a) and without organic vapors in the atmosphere (b)

### 5.4 Conclusions

The double bonds of the PPV units of pc-DMePPV are oxidized at the air-water interface to aldehyde groups. This reaction also happens in the dark, so singlet oxygen is not involved in this reaction. Radical scavengers and the pH of the subphase have no influence on the rate of the oxidation reaction. It is likely that oxygen is polarized at the air-water interface and forms a weakly bound complex with the double bond. It is believed that this complex is a sort of reactive intermediate state. Adding organic vapors to the air above the monolayer prevents the oxidation reaction.
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