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

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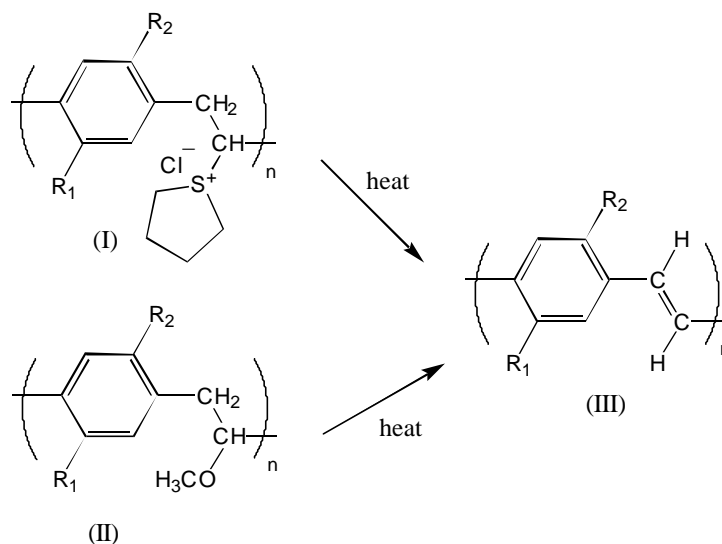
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Summary

Poly(*p*-phenylenevinylene)s (PPVs), (III) Scheme 1, are main chain π -conjugated polymers which have very interesting electrical and photoconducting properties, making them suitable for use as active component in optoelectronic and microelectronic devices, like light emitting diodes, photodiodes, photovoltaic cells and field-effect transistors. For many of these applications ultra-thin polymer films of controlled structure and thickness are needed. The Langmuir-Blodgett (LB) technique offers the possibility to prepare ordered systems with thicknesses that are controllable up to the molecular level.



Scheme 1

According to the classical LB technique, amphiphilic compounds are spread from a dilute solution in a volatile solvent on water in a Langmuir trough. The solvent evaporates leaving a *Langmuir monolayer* of the compound at the air-water interface. The monolayer behavior can be studied by measuring *surface-pressure-area isotherms*. In these experiments the molecules at the interface are compressed, by moving barriers towards each other, resulting in an increase surface pressure at a certain area per molecule because the molecules repel each other. During this decrease of area per molecule the molecules are oriented at the air-water interface. In this oriented state, the monolayer can be

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transferred onto a substrate by dipping the substrate vertically into the monolayer and a *Langmuir-Blodgett film* is obtained. There is also a horizontal lifting technique known as the *Langmuir-Schaefer* method. In this case, the horizontally oriented substrate is lowered until it just touches the monolayer and then raised.

When preformed polymers are used as spreading material a condensed or an expanded monolayer can be formed. A condensed monolayer can be compared with a polymer in the solid state, the polymer forms 2D pancakes at the air-water interface directly after spreading. An expanded monolayer can be compared with a polymer in solution and the polymer forms a homogeneous monolayer with a low segment density on the air-water interface.

PPVs are rigid rod polymers and insoluble, unless they are substituted with long alkyl chains. Therefore, non-substituted or short alkyl chain substituted PPVs can not be used for the LB technique. However, as can be seen in Scheme 1, PPVs (III) can be prepared by thermal treatment of water-soluble precursor polyelectrolytes with a sulfonium-leaving group (I), or by a chloroform soluble precursor with a methoxy-leaving group (II). The sulfonium precursor (I) has been made suitable for the LB technique by replacing the chlorine counterion with a soap-like counterion, or by a bilayer-forming amphiphile. In these cases, upon heat treatment a large volume fraction of the multilayer has to leave the film, likely causing severe disruption of the film structure.

This thesis focuses on Langmuir monolayer behavior and the transfer behavior of different chloroform soluble precursor PPVs with a methoxy-leaving group, (II) Scheme 1, because it is expected that this small group causes minimal damage to the multilayer structure when the precursor is converted to PPV. The precursors were substituted with hydrophilic ether groups to increase the interaction with the water subphase. The used precursors and their denominations are given in Table 1.

The orientation of the polymer chains at the air-water interface and in the

Table 1

Precursor polymer (II)	R ₁	R ₂
prec-MePPV	H	OCH ₃
prec-DMePPV	OCH ₃	OCH ₃
prec-DBuPPV	OC ₄ H ₉	OC ₄ H ₉
prec-BuMePPV	OCH ₃	OC ₄ H ₉
copolymer	OCH ₃ or OC ₄ H ₉	OCH ₃ or OC ₄ H ₉
prec-MEHPPV	OCH ₃	OCH ₂ CH(CH ₂ CH ₃)C ₄ H ₉

LB-films is mainly determined by (polarized) transmission- and grazing angle reflection infrared spectroscopy. These measurements were done in combination with spectrum simulations (described in the Appendix) to exclude misinterpretation due to optical effects. Additional information about the orientation of the polymer chains was obtained from polarized UV-Vis spectroscopy. Small angle X-ray reflection (SAXR) measurements were done on multilayer assemblies to determine the overall thickness, the surface roughness and the quality of the layer structure.

In Chapter 2, the behavior and structure of monolayers of different (di)alkoxy substituted precursor PPVs are studied by surface pressure-area isotherms, FT-IR reflection measurements at the air-water interface and hysteresis experiments. All precursor polymers form a true 2D polymer monolayer at the air-water interface in which all polymer segments are in contact with the water subphase. The isotherms of the precursors, except prec-DBuPPV, showed no special transitions, and the closely-packed monolayer is formed in the range of 36-45 Å²/repeating unit. Directly after spreading, the aromatic rings take on a more or less perpendicular orientation to the surface and the monolayers can be considered to be in a condensed state with lateral cohesive π - π interactions between aromatic rings. The chain conformation and the orientation of these precursors are predominantly determined by the main chain and not by the alkyl chains. Prec-DBuPPV is, in contrast to the other precursors, di-substituted with longer alkyl chains and the isotherm of this precursor shows two transitions. The first transition is found at about 100 Å²/repeating unit and a second transition at about 48 Å²/repeating unit. In the prec-DBuPPV case the side chains determine the conformation and orientation of polymer chains in the monolayer. The prec-DBuPPV monolayer is assumed to be in an expanded state until the first transition. In this expanded state the aromatic rings and the butyl chains are lying completely flat on the water surface with all ether groups in contact with the water subphase. Upon further compression the butyl chains are pushed out of the air-water interface and the rings take on a more tilted orientation. At the second transition one butyl chain per repeating unit is pushed into the water phase and the aromatic rings take on an almost perpendicular orientation to surface with favorable lateral cohesive π - π interactions between aromatic rings.

The monolayer stability, transfer properties and multilayer structure of these precursors is discussed in Chapter 3. All the precursor polymers form stable monolayers at the air-water interface. Prec-DBuPPV can be stabilized before and directly after the second transition at 48 Å²/repeating unit, but it was not possible to stabilize this polymer just before the first transition at 100 Å²/repeating unit. The packing of prec-DBuPPV stabilized before the second

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transition and the packing of prec-MEHPPV is less dense than is the case for the other precursors, the reason for this can be ascribed to the effect of the substituents. In the prec-MEHPPV case, closer packing is prevented by repulsive forces between the branched side chains, whereas in the prec-DBuPPV case (stabilized before the second transition) both butyl chains are oriented out of the water subphase and in this orientation the aromatic rings are more or less shielded from each other by butyl chains.

The transfer behavior was studied with the conventional LB-technique. The less closely-packed monolayers of prec-MEHPPV and prec-DBuPPV (stabilized before the second transition) can be transferred very well with the Langmuir-Blodgett technique and the transfer is Y-type. However, the closely-packed monolayers with strong π - π interaction between the aromatic rings, appeared to be too stiff to be transferred with the Langmuir-Blodgett technique. The transfer behavior of prec-DMePPV is a borderline case in this series, because only transfer of the first monolayer is successful. Multilayers of Prec-DMePPV can be prepared by the Langmuir-Schaefer method. From FT-IR measurements of the multilayer films can be concluded that the aromatic rings of prec-DMePPV and prec-DBuPPV in the multilayers have lost some of their perpendicular orientation with respect to their orientation in the Langmuir monolayer. However, the aromatic rings are still predominantly perpendicular to the substrate surface.

In the multilayer assembly of 20 monolayers of prec-MEHPPV no orientation is found due to sterical hindrance between the bulky side chains. Thinner multilayers do reveal orientation, but this is probably substrate induced.

During the transfer experiments of prec-DMePPV we discovered that the transfer improved significantly when the chloroform precursor solution was exposed to ordinary daylight and had become colored. What happens during exposure to light, and the Langmuir monolayer and the Langmuir-Blodgett transfer behavior of these colored precursors is described in Chapter 4. When chloroform is exposed to light acidic photoproducts are formed. These products catalyze the conversion reaction and a partly converted precursor (pc-DMePPV) is formed. Besides this reaction also photo-oxidation of the vinyl bonds occurs leading to chain cleavage and formation of aldehyde end groups.

Stabilization curves of pc-DMePPVs show an enormous decreasing area because the monolayers oxidize at the air-water interface. This oxidation reaction of partly converted precursor PPVs is studied thoroughly and described in Chapter 5.

Oxidation reactions of conjugated polymers are well known and are a great disadvantage for applications of conjugated polymers in devices because the

formed carbonyl groups are exciton quenchers. However, these oxidation reactions are photo-oxygenation reactions, in which light is needed to produce singlet oxygen. The oxidation reaction described in Chapter 5 even happens in the dark and can therefore not be attributed to a photo-oxygenation reaction. We assumed that oxygen forms a weakly bound complex with the double bond and is polarized at the air-water interface. In this way an activated form of oxygen is formed and the double bond is oxidized. We accidentally discovered that the monolayer oxidation is delayed when organic vapors (toluene, acetone, chloroform) are present in the air above the monolayer. It is assumed that the organic vapors adsorb at the interface and prevent in this way the polarization of oxygen.

The transfer of pc-DMePPV under "oxidation-free conditions" is good and Z-type. Thus, in contrast to what was found for non converted precursor (prec-DMePPV), it is possible to build up multilayers of more than one monolayer. The reason for this is probably that in the pc-DMePPV case the cohesion forces between the monolayer and the already transferred monolayer are improved with respect to prec-DMePPV due to hydrophobic interaction between conjugated parts. However, the observed transfer behavior is peculiar, because the transfer ratio upwards is higher than 1 and after deposition the monolayer on the air-water interface expands. From polarized UV-Vis and FT-IR measurements it was concluded that the polymer chains in the multilayers are oriented in the dipping direction. Generally, dipping induced in-plane orientation is only found for rod like polymers or rod like crystals. Pc-DMePPV can not be considered as rigid rod like molecule because the conjugated units are very short. It is assumed that, due to hydrophobic intra- and intermolecular interactions between the conjugated parts in the chains, the monolayer of pc-DMePPV can be considered as a 2-D physical network and the obtained orientation in the dipping direction is due to the stretching of this network during deposition. After each dip the monolayer relaxes, restoring the free volume again as observed by the expansion of the film.

After full conversion to di-methoxy-PPV (DMePPV) by thermal treatment of the multilayer the more or less perpendicular orientation of the aromatic rings is lost, probably because the ring had to turn over to obtain π - π overlap. However, the dipping induced in-plane orientation was preserved.

Summary
