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In-Plane Orientation in Langmuir–Blodgett Multilayers of a Partly Converted Flexible Poly(p-phenylenevinylene) Precursor Polymer

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ABSTRACT: The dimethoxy-substituted precursor poly(p-phenylenevinylene) (prec-DMePPV) was partly converted to dimethoxy-PPV by exposing the precursor solution in chloroform to daylight. The monolayer and transfer behavior of this partly converted precursor (pc-DMePPV) was studied with the Langmuir–Blodgett technique. In contrast to prec-DMePPV, an excellent transfer behavior was found for pc-DMePPV, and it was possible to build up multilayer films. The observed Z-type transfer behavior was peculiar, because the transfer ratio was higher than 1, and after deposition the monolayer expanded. Although the pc-DMePPV is not a rigid-rod-like polymer, an in-plane orientation of the chain in the transfer direction was found in the multilayers. We assume 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 2D 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 dimethoxy-PPV (DMePPV) by thermal treatment of the multilayer, the dipping-induced in-plane orientation was preserved.

Introduction

Poly(p-phenylenevinylene)s (PPVs) are main-chain conjugated polymers which have very interesting electrical and photoconducting properties, making them suitable for application in optoelectronic and microelectronic devices.[1] It is becoming apparent that control of the film architecture is needed to fully exploit the optical and electrical properties of conjugated polymers.[2,3] The Langmuir–Blodgett (LB) technique offers one of the few means for the preparation of ordered systems with molecular architectures and thicknesses that are controllable up to the molecular level. The LB method induces a classical anisotropy in the film between out-of plane and in-plane properties, but in-plane properties of the multilayers are often isotropic. However, recently it has been observed that rodlike polymers,[4] rodlike polymer crystals,[5] and self-aggregating molecules (e.g., phthalocyanines)[6] are oriented during transfer, resulting in an in-plane anisotropy.

So far, LB films of PPVs have been prepared only by heat treatment of LB films of a precursor polymer consisting of a poly(p-xylylenesulfonium) salt with a long-chain perfluoroalkyl or a bilayer-forming amphiphile as counterion.[7–9] 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.

We investigated the Langmuir monolayer behavior and LB transfer properties of different chloroform soluble alkoxy-substituted PPV precursors with a methoxy leaving group.[10,11] The advantage of this precursor polymer is that the leaving group is much smaller. Therefore, it is expected that the leaving group causes less damage to the multilayer structure when the precursor polymer is converted to PPV by heat treatment.

The transfer behavior of prec-DMePPV (see Scheme 1) has been described in a previous work.[11] It was observed that transfer of only one single monolayer of prec-DMePPV was successful.

During the transfer experiments we discovered that the transfer improved significantly when the solution was exposed to ordinary daylight and had become colored.

Delmotte et al. studied what happened when a chloroform precursor solution is exposed to UV light.[12] They found that acidic photoproducts of chloroform, obtained by irradiation of chloroform in air, catalyze the elimination reaction at room temperature. Exposure by daylight is less harsh than illumination by an UV lamp, and therefore, a partly converted precursor polymer (**II**) shown in Scheme 1 will be formed. The degree of conversion will depend on the exposure time. To study this reaction in more detail, we followed the exposure to daylight of a prec-DMePPV chloroform solution with UV–vis spectroscopy, ^{1}H NMR, infrared spectroscopy, and GPC.

The monolayer behavior of partly converted dimethoxy-substituted precursors and the influence of this partial conversion on the transfer properties are reported in this paper. The in-plane and out-of-plane orientation in the obtained multilayers was studied by FT-IR spectroscopy and UV–vis spectroscopy.

Experimental Section

Materials. The preparation of precursor polymer poly[2,5-dimethoxy-1,4-(α-methoxy)xylylene] (precDMePPV) (see Scheme 1) has been described previously.[10]

Exposure to Daylight. The concentration of the solution of prec-DMePPV in chloroform exposed to daylight was about 2 mg/mL. When the desired degree of conversion was reached, further elimination by the acidic products in chloroform was prevented by adding 1 drop of pyridine per 10 mL of solution, and the solution was stored in the dark. This solution was diluted 10 times for the LB experiments and was diluted 100 times before measuring the UV–vis spectra.

^{1}H NMR. ^{1}H NMR spectra were recorded in chloroform-d_1 solutions at 200 MHz.

UV–vis. UV–vis absorption spectra were recorded on a SLM Aminco 3000 diode-array UV–vis spectrophotometer.

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Scheme 1
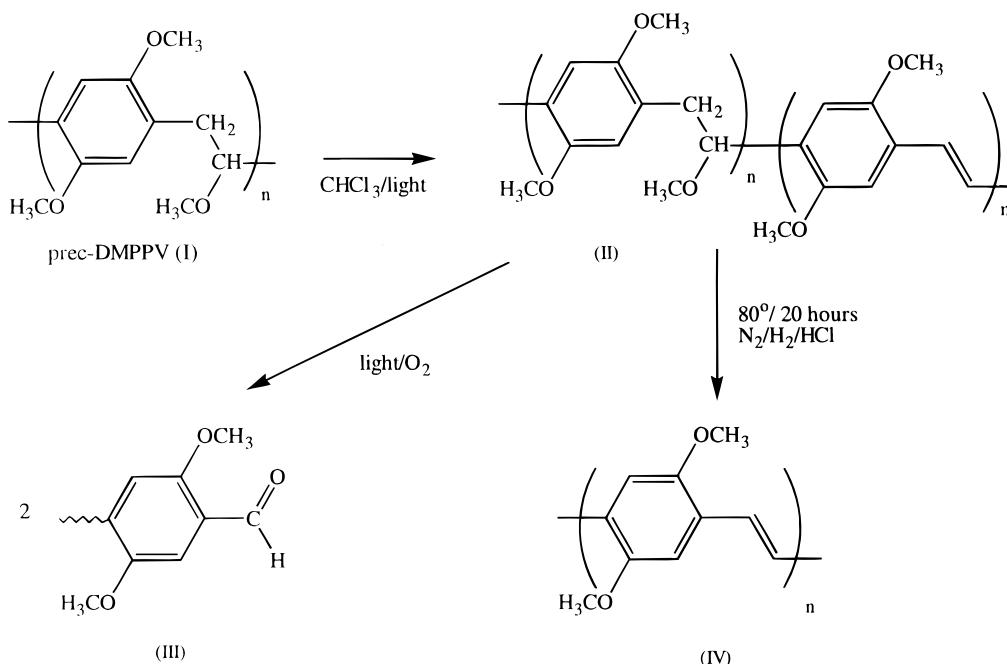
Polarized light was used to determine the preferential orientation in the multilayers before and after heating. In this experiment the uncovered part of the sample was used as reference.

Polarized Optical Microscopy. The polarized optical microscopic observations were carried out with a Zeiss photomicroscope II.

GPC. Gel permeation chromatography (GPC) measurements were performed on 2 mg/mL solutions in a Spectra 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 both solvent and eluent. The columns were calibrated with polystyrene standards.

Thermal Conversion Reaction. The thermal conversion reaction to convert the multilayers into DMePPV was done at 80–100 °C under a forming gas flow which was led through concentrated HCl. Forming gas: 95% N_2 of purity 99.998% and less than 1 ppm of O_2 and 5% hydrogen of purity 99.5% and less than 10 ppm of O_2. After heating the films were washed with water.

Langmuir–Blodgett 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 subphase was water, purified by reverse osmosis and subsequent filtration trough a Milli-Q purification system.

The surface pressure–area isotherms were obtained with a standard compression speed of 5 Å^2 repeating unit^{-1} min^{-1} at 15 °C. The compression was started 10 min after spreading, to allow the solvent to evaporate and the monolayer to fill the available area completely. Vertical dipping speeds were 10 mm/min downward and 2 mm/min upward at a temperature of 15 °C. Glass slides and silicon wafers, used as substrates, were treated with a mixture of H_2O_2 (30%)/NH_3 (25%)/H_2O (1:1:5 v/v) for 30 min at 60 °C, ultrasonically treated with a mixtures of HCl (37%)/H_2O (1:6 v/v) for 15 min, washed several times with Milli-Q water, ultrasonically cleaned again with methanol (Merck p.a.), methanol/chloroform (3:1 v/v) mixture, methanol/chloroform (1:3 v/v) mixture, and chloroform (Merck p.a.) for 15 min, and finally stored in methanol. The substrates were hydrophobized by exposing them for at least 1 day to a hexamethyldisilazane vapor (Acros, 98%) and finally rinsed with chloroform. ZnS plates were ultrasonically cleaned with chloroform. Gold substrates were prepared by evaporating a 250–300 nm thick gold layer onto cleaned glass slides.

Small-Angle X-ray Reflection (SAXR) Measurements. Small-angle X-ray measurements were performed with a Philips 1830 generator and a Phililps PW 1820 diffractometer in a $\theta/2\theta$ geometry, using Cu Kα radiation ($\lambda = 1.542$ Å). The multilayers for these measurements were deposited onto hydrophobized Si wafers.

The simulations of the diffraction pattern (Kiessig fringes) were carried out using a one-slab model and two surface roughnesses, σ.[13,14]

IR. The grazing incidence reflection (GIR) on gold and transmission measurements with ZnS (Cleartran) were preformed with a Bruker IFS-88 FT-IR spectrophotometer equipped with a MCT-A D313 detector. GIR spectra were recorded in an 80° specular setup with light polarized parallel to the plane of the incidence and referenced against the reflection of a clean gold layer. The transmission and GIR spectra were recorded using 10 cycles of 256 scans each according to the method of Arndt.[15] All spectra were recorded at 4 cm^{-1} resolution and baseline corrected.

Spectra Simulations. The optical constants of the polymers necessary for the spectra simulations were calculated according to the following procedure. A transmission spectrum of a free-standing film of the polymer was used as an input spectrum. The thickness of this film and the refractive index were estimated on the basis of the amplitude of the interference fringes and their periodic spacing. The absorption coefficients were converted into wave vector (k) values after which the refractive index (n) spectrum could be calculated from the estimated k spectrum with the Kramers–Kroning relationship. Complex refractive indices of the substrates were taken from the literature: 9.5–30i for gold[16] and 2.22 for ZnS.[17] For pc-DMePPV and DMePPV the real part of the refractive index was centered at 1.55 and 1.7, respectively.

Results and Discussion

Monolayer and Transfer Behavior of Colored Precursor Solutions. Figure 1 shows the UV–vis spectra of prec-DMePPV solutions in chloroform before and after exposure to daylight.

The freshly prepared prec-DMePPV (Figure 1, a) solution is at first colorless, and only a strong band at $\lambda = 290$ nm corresponding to the $\pi-\pi^*$ transition of the dimethoxy-substituted phenyl ring is observed. During illumination absorption bands originating from the
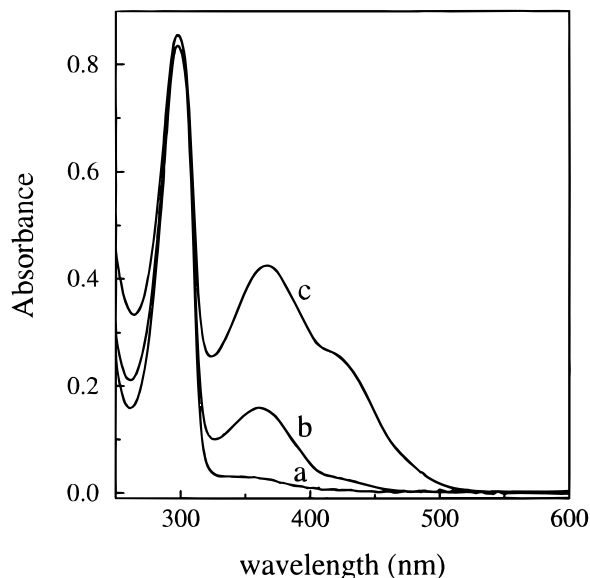
Figure 1. UV–vis spectra of prec-DMePPV solution in chloroform after exposure to daylight: (a) 0 days, 0% conversion; (b) 4 days, 10% conversion; (c) 7 days, 20% conversion.
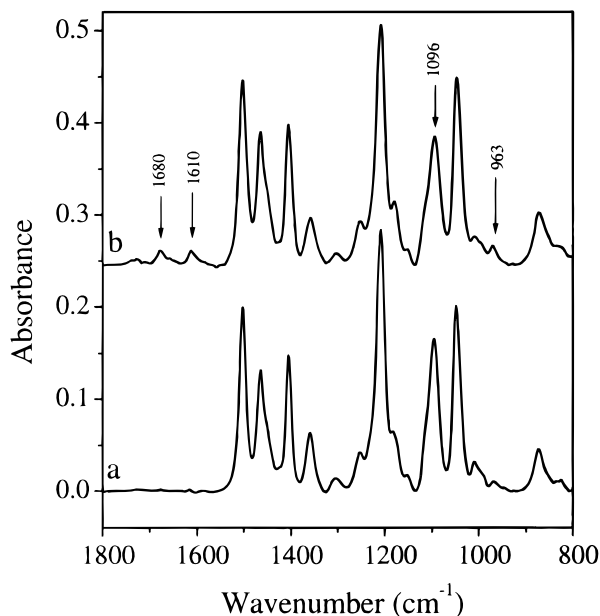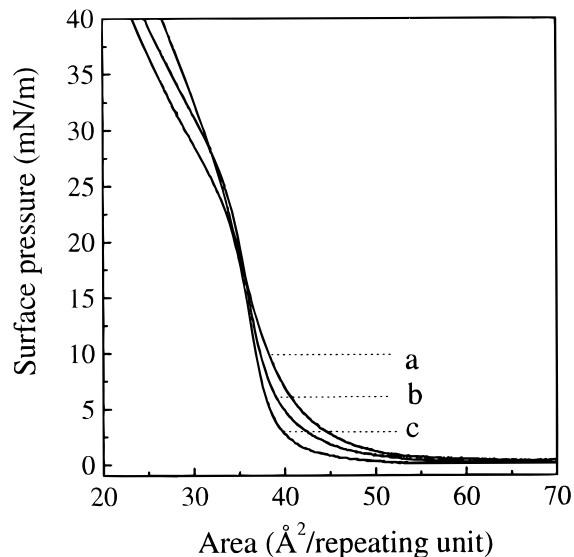

Figure 2. Infrared spectra of (a) nonconverted prec-DMePPV and (b) 20% converted precursor.

Figure 3. Surface pressure isotherms of partly converted pc-DMePPV: (a) 0 days, 0% conversion; (b) 4 days, 10% conversion; and (c) 7 days, 20% conversion. $T = 15$ °C.

tetramethoxystilbene unit with λ_{max} at 360 nm and hexamethoxydistyrylbenzene units with λ_{max} at 410 nm[18] appear (see Figure 1, b and c).

The degree of conversion was calculated on the basis of the sharp peak originating from the methyl protons of methanol at 3.50 ppm in the ^{1}H NMR spectra of the illuminated solutions. The degree of conversion found was 10% after 4 days and 20% after 7 days of exposure to daylight. After an exposure of more than 7 days a severe line broadening is observed in ^{1}H NMR spectra, probably due to the presence of some radical species or molecular aggregates, and determination of the degree of conversion with ^{1}H NMR was no longer possible.

The infrared spectra of the precursor after exposure to daylight for 0 and 7 days is shown in Figure 2, a and b, respectively.

In these infrared spectra the appearance of the trans-vinyl band at 963 cm^{-1} is observed together with a

decrease of the aliphatic ether band of the methoxy leaving group at 1096 cm^{-1}. In addition, the appearance of absorption bands at 1680 and 1610 cm^{-1} is observed. The band at 1680 cm^{-1} can be ascribed to carbonyl groups, and the band at 1610 cm^{-1} originates from a nonsymmetrical substituted aromatic ring vibration. From GPC experiments we found that when the precursor is converted for 20%, the $\bar{M}_n$ decreases from 3×10^5 to 2×10^4. Thus, it appears that, during exposure to daylight, besides the elimination reaction also photo-oxidation of the vinyl bonds occurs, resulting in aldehyde end groups.

The influence of exposure of the precursor solution to daylight on the surface pressure isotherm is shown in Figure 3.

The increase of the surface pressure isotherm at about 40 Å^2/repeating unit becomes steeper and shifts to a smaller area per repeating unit, indicating that the higher converted precursor forms a more closely packed condensed monolayer. Compared to the prec-DMePPV, the partly converted precursor can be considered to be more hydrophobic at certain positions along the chain, because hydrophilic methoxy groups have been converted to hydrophobic vinyl groups. We assume that these hydrophobic parts lead to hydrophobic intra- and intermolecular interactions at the air–water interface, resulting in a more closely packed condensed polymer monolayer.

We described elsewhere[19] that Langmuir monolayers of the partly converted precursors oxidize in the dark. This is not a reaction with singlet oxygen but a reaction with oxygen in the ground state. It is assumed that this oxidation is promoted by the air–water interface. The oxidation can be prevented by applying organic vapors (chloroform, acetone, or toluene) to the air above the monolayer.

We stabilized the 20% converted precursor (pc-DMePPV) at 15 mN/m in air with and without toluene. The film stabilized in air without toluene became stable after oxidation, and at least 50 monolayers could be very well transferred onto various substrates.

The transfer ratios were 0.2 upward and 1 downward; the transfer curve is shown in Figure 4a. The transfer curve of pc-DMePPV taken under oxidation-free condi-
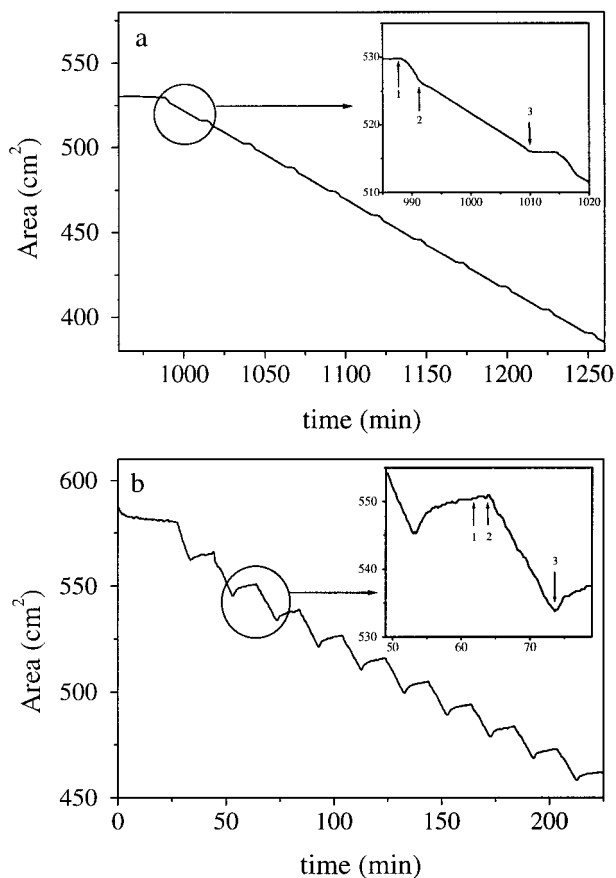
Figure 4. Stabilization and transfer curve of (a) the oxidized pc-DMePPV and (b) pc-DMePPV in oxidation-free circumstances at 15 mN/m. T = 15 °C. Point 1, start of deposition; point 2, changing point of deposition direction; point 3, end of deposition.

tions is shown in Figure 4b. This Z-type transfer behavior is peculiar, because the transfer ratio upward is higher than 1, and after deposition the monolayer expands. The expansion can be seen more clearly in the inset of Figure 4b and will be discussed later on. Thus, nevertheless, in contrast to what was found for nonconverted precursor (prec-DMePPV), it is possible to build up multilayers of more than one monolayer. The $\bar{M}_n$ of the pc-DMePPV has decreased with respect to the $\bar{M}_n$ of prec-DMePPV. In the previous article it was concluded that the high $\bar{M}_n$ is not the reason for the impossibility to create multilayer structures of prec-DMePPV, because one layer of prec-DMePPV can be transferred successfully.[11] We assume that the change in transfer behavior is generated by an increase of cohesion forces between the monolayer and the already transferred monolayer due to dipole–dipole interaction between carbonyl groups in the oxidized pc-DMePPV case (Figure 4a) and hydrophobic interactions between conjugated parts in the nonoxidized pc-DMePPV case (Figure 4b).

A polarized light UV–vis spectrum was taken from the multilayers obtained from the transfer experiments of Figure 4. In the case of the oxidized pc-DMePPV the same absorption intensity was found in both polarization directions. However, in the multilayers of nonoxidized pc-DMePPV a difference between the intensity of absorption in the dipping direction (A_s), and the intensity of the absorption perpendicular to the dipping direction (A_p) was found (Figure 5a).
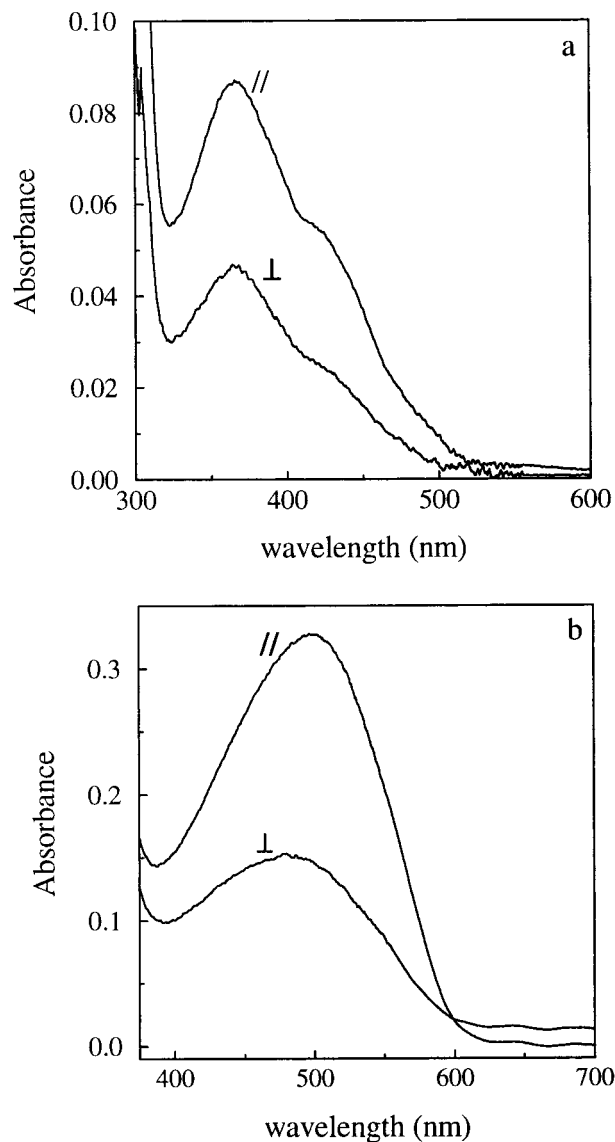

Figure 5. Polarized UV–vis spectra of (a) 15 layers of pc-DMePPV transferred onto ZnS at a surface pressure of 15 mN/m and (b) the same multilayer assembly after thermal treatment at 80 °C in a $H_2/N_2/HCl$ atmosphere.

The ratio between A_s and A_p is 2.1 ± 0.1. This can only be explained by assuming that the polymer chains are oriented in the dipping direction. Usually, a dipping-induced orientation is only found in the case of rigid-rod-like polymers or rodlike crystals.[4–6] Pc-DMePPV cannot be considered as a rigid-rod-like molecule because the conjugated units are very short. To the best of our knowledge, this is the first time a preferential orientation of a flexible polymer along the dipping direction was found.

The explanation for this phenomenon might be the following. From the isotherms it was concluded that a more condensed monolayer is formed due to hydrophobic interactions in and between the polymer chains. In this way some kind of 2D physical network is formed; see magnification in Figure 6.

First, the chains of the network are lying nonoriented and randomly in the monolayer, but during the upstroke the network in the monolayer at the air–water interface is probably stretched in the dipping direction toward the substrate (Figure 6), and the total area of the stretched network at the interface decreases as a result
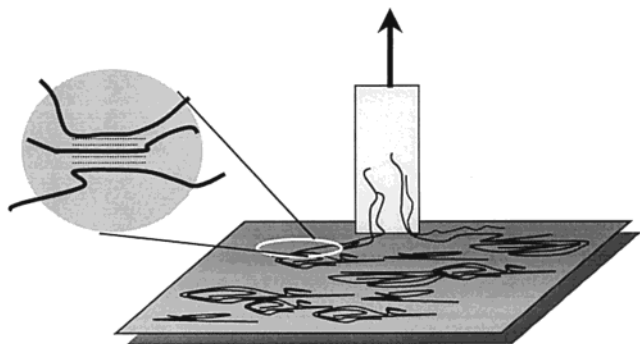
Figure 6. Schematic presentation of the stretching of the 2D physical network of pc-DMPPV during deposition. The hydrophobic interactions are represented by dotted lines.

of decreasing free volume in the 2D network. This extra decrease of the area leads to a too high transfer ratio. When the substrate leaves the film, the forces on the network are gone, but the chains in the monolayer at the air–water interface are still oriented and consequently will relax, leading to restoration of the free volume. This relaxation was observed by expansion of the film after the dip.

In the case of oxidized pc-DMePPV such a network is not built up because the longer conjugated chain parts, causing the formation of the physical network, are converted into hydrophilic carbonyl groups. Therefore, this polymer gives normal transfer behavior with no orientation in the dipping direction.

Conversion to DMePPV. To convert the pc-DMePPV multilayers into DMePPV (IV, Scheme 1), different heating procedures were carried out. These reactions were followed with FT-IR and UV–vis spectroscopy. When the multilayers were heated at 200–250 °C in a vacuum or under an inert atmosphere such as argon or nitrogen for 3 days, there was still a small 1096 cm^{-1} absorption band in the infrared spectra, and the λ_{max} was 400 nm, meaning that the conversion was incomplete. However, by adding HCl as a catalyst to the argon or nitrogen atmosphere, the elimination temperature could be lowered to 80–100 °C and full conversion could be obtained, but unfortunately carbonyl groups were formed. Papadimitrakopoulos et al.[20] discovered that the carbonyl formation could be suppressed by using a forming gas (a mixture of 95% nitrogen and 5% hydrogen) atmosphere. Therefore, a N$_2$/H$_2$/HCl atmosphere was used in the experiments, and full conversion could be obtained within 20 h at 80–100 °C for films up to 30 monolayers. After conversion of the multilayers to DMePPV a homogeneous red film is formed. The polarized UV–vis absorption spectra of the pc-DMePPV after conversion are shown in Figure 5b. The spectra show a strong band with an absorption maximum at 500 nm. The A_s/A_p ratio is 2.1, which is the same as was found before the heat treatment (Figure 5a). So, the dipping-induced orientation is preserved during conversion.

The presence of anisotropy in the converted films was also obvious from optical microscopy observations in polarized light: a change in color from yellow-green to orange was observed on 90° rotation of the sample between the two crossed polarizers.

Small-Angle X-ray Reflection (SAXR). Small-angle X-ray reflection (SAXR) measurements were done on multilayer assemblies of 15, 20, 25, and 30 layers to determine the surface roughness and thickness before and after heating at 80–100 °C in a HCl/N$_2$/H$_2$ atmo-
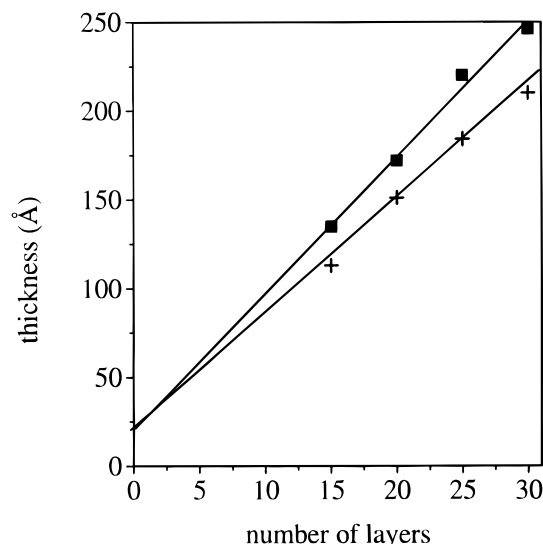
Figure 7. Thickness of the multilayers calculated from SAXR before (■) and after (+) conversion.

sphere. All scattering curves showed Kiessig fringes, but Bragg peaks were not observed, probably due to lack of contrast of the electron density profiles in these films. The Kiessig fringes could be fitted well by a theoretical model.[14] From the fit the film–air surface roughness and the total film thickness were obtained. The surface roughness appeared to be independent of the number of transferred layers and was about 8.4 ± 2.5 Å before heating and 6.9 ± 1.1 Å after conversion to PPV. Thus, the film becomes even smoother after conversion, although methanol has left the film. The film thickness of the multilayers is plotted versus the number of layers in Figure 7.

The extrapolated line intersects the Y-axis at 20 Å, which corresponds to the thickness of the SiO$_2$ + HMDS layer. A thickness per transferred monolayer of 7.8 Å before and 6.7 Å after conversion was calculated from the slope of the lines in Figure 7. From CPK models it was deduced that the thickness of the monolayer is about 4.2 Å, when the aromatic ring is lying flat, and about 8.5 Å, when the aromatic ring is perpendicular to the substrate. The thickness of 7.8 Å of pc-DMePPV is in agreement with a more or less perpendicular orientation of the aromatic rings which was also found for prec-DMePPV in previous articles.[10,11]

FT-IR Transmission and GIR Spectra of Multilayer Structures. To study in more detail the orientation of pc-DMePPV and DMePPV in the multilayers, we preformed transmission FT-IR and grazing incidence reflection (GIR) FT-IR measurements. In transmission FT-IR measurements the electrical field vector is parallel to the substrate surface, so only groups with transition-dipole moment components parallel to the substrate will absorb. In GIR FT-IR spectroscopy the electrical field vector is perpendicular to the substrate, so only groups with transition-dipole moment components perpendicular to the substrate will absorb. Comparison of the experimental GIR spectra with the transmission FT-IR spectra should be done with care. First, the experimental GIR spectra and transmission spectra must be scaled in a proper way. Second, it must be taken into account that the GIR spectra might be distorted compared to transmission spectra due to optical effects.[21,22] To determine the scaling factor and to elucidate the influence of optical effects, spectral simulations were done. The simulation procedure has been described in

**Table 1. Assignments of IR Absorption Bands Prec-DMePPV and DMEPPV Bands[23-25]**

wavenumber (cm^{-1})	assignment	dipole transition moment
3054	vinyl ν (CH)	30° with chain axis
2992–2858	ν(CH$_3$)	
2828	ν_s(CH$_3$) (OCH$_3$)	O–C direction
1502	semicircular phenyl stretch	in the plane of the phenyl ring
1465	δ_{as}(CH$_3$) asym bending	
1407	semicircular phenyl stretch	in the plane of the phenyl ring
1350	δ_s(CH$_3$) sym bending	O–C direction
1257	vinyl CH in-plane rock	30° with chain axis
1204	ν(aryl–oxygen)	=C–O direction, 83° with chain axis and in the plane of the phenyl ring
1096	ν_a(alkyl–oxygen) (OCH$_3$ leaving group)	‖ to C–C direction
1044	ν(alkyl–oxygen) (arom OCH$_3$ group)	O–C direction, 74° with chain axis
963	trans-vinyl CH out-of-plane wag	80° with chain axis
849	vinyl CH wag	73° with chain axis

the Experimental Section. The film thickness, needed for the simulations, was obtained from the SAXR measurements. From this simulation procedure the transmission spectrum of a nonoriented 114 Å thick film (thickness of 15 monolayers) of pc-DMePPV on both sides of a ZnS substrate and the GIR spectrum of a nonoriented 114 Å thick film of pc-DMePPV on gold were calculated. Some of the bands in the GIR spectrum were a little shifted due to optical effects, but when the transmission spectrum was multiplied by 2.89, both spectra almost fully coincided. This means that after proper scaling the differences between experimental GIR and transmission spectra of pc-DMePPV can be attributed to orientation effects of the polymer chains. Spectra simulations were also done for a nonoriented 100 Å thick (thickness of 15 monolayers) DMePPV film, and in this case a scaling factor of 2.0 was found. Among other things, the difference in the scaling factor between pc-DMePPV and DMePPV is caused by the difference in refractive index.

Figure 8a (solid line) shows the GIR spectrum of 15 monolayers of pc-DMePPV transferred onto gold and Figure 8a (dashed line) the nonpolarized transmission spectrum of 15 monolayers on both sides on ZnS. Figure 8b shows the spectra of these multilayers after conversion to DMePPV. The assignments of the bands and the direction of the transition dipole moments of the precursor polymer and DMePPV are given in Table 1.

Enormous differences can be seen between the transmission and grazing incidence spectra of the multilayer of pc-DMePPV (compare Figure 8a, dashed line with solid line). The bands at 1502, 1204, and 1047 cm^{-1} in the grazing incidence spectra are very strong compared to corresponding bands in the transmission spectrum. The directions of the transition dipole moments of these absorption bands are lying in the plane of the aromatic rings. Therefore, it can be concluded in agreement with earlier findings[10,11] that the chains are lying in the plain of the substrate and that the aromatic rings are oriented more or less perpendicularly to the substrate surface.

When the spectra of the pc-DMePPV (Figure 8a) are compared with the spectra after conversion to DMePPV (Figure 8b), it can be seen that the band at 1096 cm^{-1} of the aliphatic ether leaving groups is missing and that the vinyl bands at 3054, 1257, 963, and 849 cm^{-1} have appeared in the DMePPV spectrum (Figure 8b), meaning that full conversion was obtained. In these vinyl bands dichroism was observed: The bands at 963 and 849 cm^{-1} with the direction of the transition dipole moment almost perpendicular to the chains axis (see Table 1) are stronger in the GIR spectrum (Figure 8b, solid line), and the bands at 3054 and 1257 cm^{-1} with the direction of the transition dipole moment more parallel to the chain axis are stronger in the nonpolar-
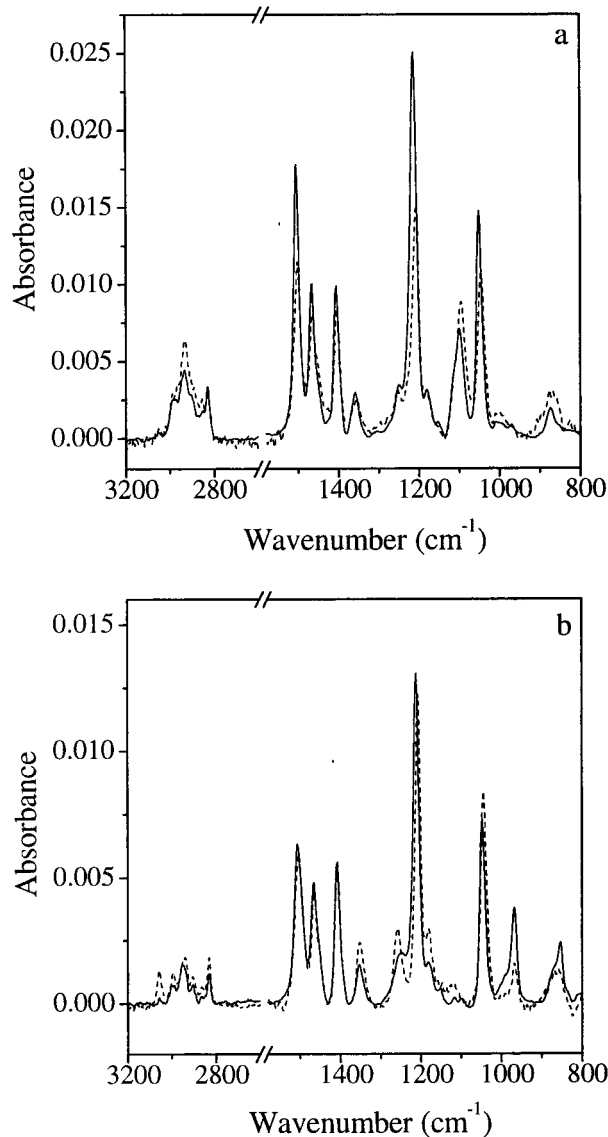
Figure 8. (a) Measured GIR spectrum of 15 LB layers of pc-DMePPV transferred onto gold (solid line) and measured transmission spectrum of 15 monolayers of pc-DMePPV deposited on both sides of a ZnS substrate (dashed line, scale factor: 2.89×). (b) Measured GIR spectrum of 15 LB layers of DMePPV transferred onto gold (solid line) and measured transmission spectrum of 15 monolayers of pc-DMePPV on both sides of a ZnS substrate (dashed line, scale factor: 2.0×).

ized transmission spectrum (Figure 8b, dashed line), meaning that the chains are still lying in the plane of the substrate. However, it can also be seen by comparing the spectra of Figure 8b that the dichroism in the bands
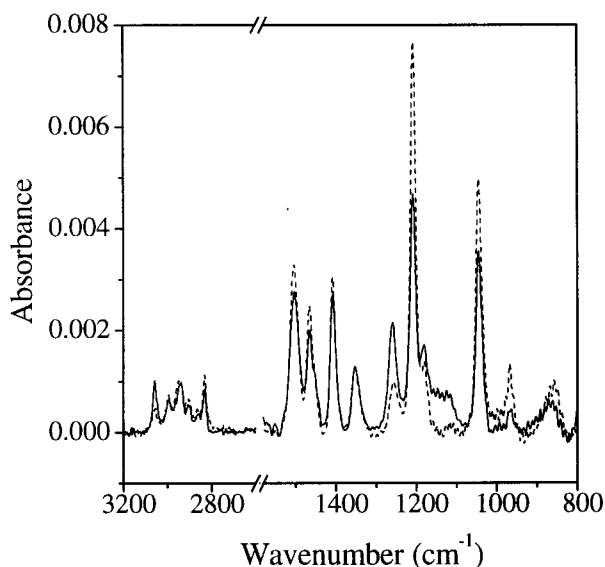
Figure 9. Measured transmission spectrum of 15 monolayers of DMePPV deposited on both sides of a ZnS substrate, with polarization perpendicular (dashed line) and parallel (solid line) to the dipping direction.

at 1502, 1204, and 1044 cm^{-1}, which was found in the nonconverted pc-DMePPV multilayers (Figure 8a), has disappeared after conversion. Thus, from the spectra of Figure 8, it can be concluded that after conversion the chains are still lying in the plane of the substrate but that the preferential perpendicular orientation of the aromatic ring is lost.

To verify the dipping-induced orientation in the multilayers, transmission spectra using light polarized either parallel or perpendicular to the dipping direction of 15 monolayers of DMePPV on ZnS were also taken (Figure 9). Dichroism can be seen in not only the bands originating from the vinyl groups but also in the bands of the aromatic ether vibrations. The bands with the transition dipole moment direction almost perpendicular to the chain axis (1204, 1044, 963, and 849 cm^{-1}) are stronger in the transmission spectrum with polarization perpendicular to the dipping direction (Figure 9, dashed line) while the bands with the direction of the transition dipole moment almost parallel to the chain axis (3054 and 1257 cm^{-1}) are stronger in the transmission spectrum polarized parallel to the dipping direction (Figure 9, solid line). We, therefore, concluded that the polymer chains are oriented in the dipping direction.

In conclusion, before conversion the chains are lying in the plane of the substrate and are oriented in the dipping direction and the aromatic rings are standing more perpendicular to the substrate. After conversion the chains are still lying in the plane of the substrate and oriented in the dipping direction, but the more or less perpendicular orientation of the aromatic rings is lost, probably because the ring had to turn over to obtain $\pi-\pi$ overlap with the vinyl bonds.

When the 10% partly converted precursor was stabilized and transferred under oxidation-free circumstances, an A_s/A_p ratio in the range 1.7–2.1 was also found, but in this case the transfer ratio decreases on successive dippings and a nonhomogeneous film is obtained after conversion to DMePPV. The number of carbonyl groups formed in the chloroform solution and the number of conjugated hydrophobic parts are probably too low to give a good cohesion between the applied monolayer and previously transferred layers.

Conclusions

During exposure of a chloroform solution of the prec-DMePPV to daylight the precursor was partly converted. In addition to this mild elimination reaction, oxidative cleavage of the double bond also took place during exposure. Compared to the monolayer of prec-DMePPV, the monolayer of pc-DMePPV can be considered as a more condensed polymer monolayer due to increased hydrophobic interactions between the polymer chains, and multilayers could be built up from pc-DMePPV. Although the pc-DMePPV is not a rigid-rod-like polymer, an in-plane orientation in the transfer direction is found in the multilayers. We assume that the monolayer of pc-DMePPV can be considered as a 2D physical network and that the obtained orientation in the dipping direction is due to stretching of this network during deposition. Before conversion of the precursor to DMePPV, the aromatic rings are oriented more or less perpendicularly to the substrate. After conversion this orientation is lost, but the in-plane orientation in the transfer direction is preserved.

References and Notes

(1) Marks, R. N.; Halls, J. J. M.; Bradley, D. D. C.; Friend, R. H.; Holmes, A. B. *J. Phys.: Condens. Matter* **1994**, *6*, 1379.
(2) Brown, A. R.; Bradley, D. D. C.; Burroughes, J. H.; Friend, R. H.; Greemham, N. C.; Burn, P. L.; Holmes, A. B.; Kraft, A. *Appl. Phys. Lett.* **1992**, *61* (23), 2793.
(3) Brown, A. R.; Greemham, N. C.; Burroughes, J. H.; Bradley, D. D. C.; Friend, R. H.; Burn, P. L.; Kraft, A. *Chem. Phys. Lett.* **1992**, *200*, 46.
(4) Duda, G.; Schouten, A. J.; Arndt, T. A.; Lieser, G.; Schmidt, G. F.; Bubeck, C.; Wegner, G. *Thin Solid Films* **1988**, *159*, 221.
(5) Brinkhuis, R. H. G.; Schouten, A. J. *Macromolecules* **1992,** *25*, 2717.
(6) Sauer, T.; Arndt, T.; Batchelder, D.; Kalachev, A. A.; Wegner, G. *Thin Solid Films* **1990**, *187*, 357.
(7) Nishikata, Y.; Kakimoto, M.; Imai, Y. *Thin Solid Films* **1989**, *179*, 191.
(8) Wu, A.; Yokoyama, S.; Watanabe, S.; Kakimoto, M.; Imai, Y.; Araki, T.; Iriyama, K. *Thin Solid Films* **1994**, *244*, 750.
(9) Era, M.; Kamiyama, K.; Yoshiura, K.; Momii, T.; Murata, H.; Tokito, S.; Tsutsui, T.; Saito, S. *Thin Solid Films* **1989**, *179*, 1.
(10) Hagting, J. G.; de Vos, R. E. T. P.; Sinkovics, K.; Vorenkamp E. J.; Schouten, A. J. *Macromolecules* **1999**, *32*, 3930.
(11) Hagting, J. G.; de Vos, R. E. T. P.; Sinkovics, K.; Vorenkamp E. J.; Schouten, A. J. *Macromolecules* **1999**, *32*, 3939.
(12) Delmotte, A.; Biesemans, M.; Rahier, H.; Gielen, M.; Meijer, E. W. *Synth. Met.* **1993**, *58*, 325.
(13) Waren, B. E. In *X-ray diffraction*; Addison-Wesley: Reading, MA, 1969.
(14) Leuthe, A.; Riegler, H. *J. Phys.* **1992**, *25*, 1786.
(15) Arndt, T.; Schouten, A. J.; Schmidt, G. F.; Wegner, G. *Makromol. Chem.* **1991**, *192*, 2215.
(16) Allara, D. L.; Baca, A.; Pryde, C. A. *Macromolecules* **1978**, *11*, 1215.
(17) *Handbook of Optical Constants of Liquids and Solids*; Palk, E. D., Ed.; Academic Press: New York, 1985.
(18) Manecke, G.; Zerpner, D. *Makromol. Chem.* **1969**, *129*, 183.
(19) Hagting, J. G.; Schouten, A. J. Submitted to *Macromolecules.*
(20) Papadimitrakopoulos, F.; Miller, T. M.; Chandross, E. A.; Galvin, M. E. *Polym. Perpr.* **1994**, *35*, 215.
(21) Greenler, R. G. *J. Chem. Phys.* **1966**, *44*, 310.
(22) Brinkhuis, R. H. G.; Schouten, A. J. *Macromolecules* **1991,** *24*, 1496.
(23) *Introduction to Infrared and Raman Spectroscopy*; Colthup, N. B., Daly L. H., Wiberley, S. E., Eds.; Academic Press: New York, 1964.
(24) Bradley, D. D. C.; Friend, R. H.; Lindenberger, H.; Roth, S. *Polymer* **1986**, *27*, 1709.
(25) Liang, W.; Karasz, E. *Polymer* **1991**, *32*, 2363.