

Langmuir–Blodgett Mono- and Multilayers of (Di)alkoxy-Substituted Poly(*p*-phenylenevinylene) Precursor Polymers. 2. Stability, Transfer, and Multilayer Structure of (Di)alkoxy-Substituted Precursor PPVs

J. G. Hagting, R. E. T. P. de Vos, K. Sinkovics, E. J. Vorenkamp, and A. J. Schouten*

Department of Polymer Science, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

Received January 20, 1999; Revised Manuscript Received March 25, 1999

ABSTRACT: The Langmuir monolayer stability and transfer properties of (di)alkoxy-substituted precursor PPVs were studied. All polymers formed stable monolayers, but the packing of the monomeric units in the monolayer depended strongly on the substituents. The less closely packed monolayers can be transferred with the Langmuir–Blodgett technique, while the closely packed monolayers, with strong π – π interaction between the aromatic rings, can only be transferred with the Langmuir–Schaefer technique due to the stiffness of the monolayers. Transmission and grazing incidence reflection FT-IR spectroscopy in combination with IR spectra computer simulations revealed that in many instances the orientation of the precursor at the water interface is largely preserved after transfer of the monolayer. The roughness and the thickness of the multilayers were determined by small-angle X-ray reflection.

Introduction

In part 1 we have reported on the monolayer behavior of (di)alkoxy-substituted precursor poly(*p*-phenylenevinylene)s (PPVs).¹ The isotherms of the precursors showed no special transitions, except that of the dibutoxy-substituted one, and the polymer monolayers are considered to be in a condensed or 2D collapsed state with lateral cohesive π – π interactions between almost perpendicularly oriented aromatic rings as the most prominent interaction. The dibutoxy-substituted precursor, however, is considered to be in the expanded state at large areas per repeating unit. The isotherm of this precursor showed two transitions because in this case the chain conformation is predominantly determined by the butyl chains and not by the main chain. In this part the monolayer stability, transfer properties, and multilayer structure of these precursors will be discussed.

Crisp already investigated the monolayer behavior of several preformed polymers in 1945, but the transfer of preformed polymers onto substrates to form multilayer structures is of more recent date and is sometimes only possible with unconventional methods.^{2–4} The reason why transfer is successful or fails is usually not well investigated.

We assume that for successful transfer a good adhesion between the monolayer and substrate in the first dipping and a good cohesion between the monolayer and the already transferred monolayers on successive depositions are needed. However, to comply with these properties, the monolayer should not be too stiff. The stiffness of a polymer monolayer might be ascribed to a high molecular weight of the polymer, to the crystalline nature of the polymeric monolayer, or to strong interactions between the polymers as is the case in condensed polymer films.^{2,5}

The transfer with the Langmuir–Blodgett (LB) method appeared to be successful, especially with amphiphilic preformed polymers containing distinct hydrophobic and hydrophilic parts^{6–10} and with helical or rigid rod-like polymers such as polyisocyanide,¹¹ isotactic poly(methyl

methacrylate),¹² polyglutamates,¹³ polysilanes,¹⁴ poly(β -hydroxy butyrate),¹⁵ and substituted polysaccharides.¹⁶ Although these latter polymers are not typical amphiphiles, the polar side groups point toward the water acting as the hydrophilic moiety, while the helix is sufficiently hydrophobic to prevent these materials from being soluble in water.

Alkoxy-substituted precursor PPVs are not typical amphiphiles or helical or helix forming polymers. Therefore, these precursor polymers are a new interesting class of LB polymers. The aim of present work is to study the effect of substituents on the monolayer stability and transfer properties of precursor PPVs.

Oriental effects in the multilayers were investigated by transmission and grazing incidence reflection FT-IR spectroscopy. The roughness and thickness of the multilayers were determined by small-angle X-ray reflection (SAXR) combined with computer simulations.

Experimental Section

The synthesis of materials and the experimental details of the Langmuir–Blodgett technique have been described in part 1.¹

Stabilization. The compression of the monolayer was started 15 min after spreading to allow the solvent to evaporate and the monolayer to fill the available area completely. The compression speed was 5 Å²/(repeating unit min). The starting spreading area was at least 120 Å²/repeating unit. After each experiment the subphase was renewed.

LB Films. Glass slides and silicon wafers, used as substrates, were treated subsequently with a mixture of H₂O₂ (30%)/NH₃ (25%)/H₂O (1:1:5 v/v) for 30 min at 60 °C and ultrasonically with a mixture of HCl (37%)/H₂O (1:6 v/v) for 15 min, washed several times with Milli-Q water, cleaned ultrasonically 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 organic solvents. Gold substrates were prepared by evaporating a 250–300 nm thick gold layer onto cleaned glass slides.

The Langmuir–Schaefer method¹⁷ was used to build up multilayers from prec-DMePPV. In this experiment a hydrophobized substrate was repeatedly lowered in a nearly horizontal position until it was in contact with the monolayer at the water surface. After a pause of 5 s the plate was lifted with a speed of 2 mm/min. The Langmuir–Blodgett method was carried out with dipping speeds of 4 mm/min downward and upward.

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

The simulations of the diffraction patterns (Kiessig fringes) were carried out using a simulation program designed by Leuthe which uses a one-slab model and two surface roughnesses, σ .^{18,19}

IR. The grazing incidence reflection (GIR) measurements were performed with a Bruker IFS-88 FT-IR spectrophotometer equipped with an MCT-A D313 detector. GIR spectra were recorded in 80° specular setup with light polarized parallel to the plane of incidence and referenced against the reflection of a clean gold layer. Transmission spectra were recorded from samples on ZnS or Si wafers in a Mattson Galaxy 6021 FT-IR spectrometer. The transmission and GIR spectra were recorded using 10 cycles of 256 scans each according to the method of Arndt.¹⁰ All spectra were recorded at 4 cm⁻¹ resolution and were baseline corrected.

Spectral Simulation. Spectrum simulations, necessary to elucidate optical effects, were done following the method described in the preceding paper.¹ Complex refractive indices of the substrates were taken from the literature: 9.5–30i for gold,²⁰ 2.22 for ZnS, and 3.8 for Si.²¹ For prec-DMePPV, prec-DBuPPV, and prec-MEHPPV the real part of the refractive index was centered at 1.55, 1.5, and 1.5, respectively. These refractive indexes were estimated on the basis of the amplitude of the interference fringes and the periodic spacing of a transmission spectrum of a free-standing film of the polymer concerned.

Results and Discussion

Stabilization and Transfer of the Precursor Polymers. The isotherms of the precursors are shown in part 1.¹ The isotherms of prec-MePPV, prec-DMePPV, prec-BuMePPV, and prec-MEHPPV are condensed-type isotherms with a steep rise at 36–45 Å²/repeating unit. These precursor polymers form stable monolayers at pressures below the collapse pressure. The isotherm of prec-DBuPPV showed two transitions. This polymer can be stabilized at pressures in the steep part just 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.

Figure 1 shows the stabilization curves of prec-MePPV (a), prec-BuMePPV (b), prec-DMePPV (d), prec-MEHPPV (e), and prec-DBuPPV stabilized before (f) and after (c) the second transition. The spread amount of the monomeric units was the same for all stabilization experiments.

The area per repeating unit, where a stable curve is formed, is in agreement with the isotherms. It can be seen that the packing of the monomeric units strongly depends on the substituents. The packing of prec-MePPV, prec-DMePPV, prec-BuMePPV, and prec-DBuPPV stabilized at 15 mN/m is much tighter than that of prec-MEHPPV and than that of prec-DBuPPV stabilized at 7 mN/m. From the FT-IR measurements at the air–water interface, it was found that directly after spreading the aromatic rings of all precursor

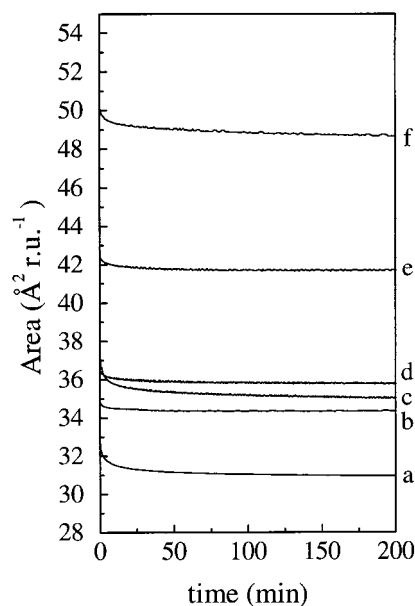


Figure 1. Stabilization curves of prec-MePPV at 10 mN/m (a), prec-BuMePPV at 15 mN/m (b), prec-DBuPPV at 15 mN/m (c), prec-DMePPV at 15 mN/m (d), prec-MEHPPV at 15 mN/m (e), and prec-DBuPPV at 7 mN/m (f). $T = 10$ °C.

polymers except prec-DBuPPV polymers are oriented almost perpendicularly to the surface.¹ The aromatic rings of prec-DBuPPV, however, are lying flat at low surface pressures, but at 7 and 15 mN/m the rings are also oriented almost perpendicularly to the surface. So, although the aromatic rings of all precursors under the conditions used in Figure 1 are oriented almost perpendicularly to the water surface, the packing of the precursors differs greatly. The reason for this can be ascribed to the effect of the substituents. In the prec-MEHPPV case, closer packing might be prevented by repulsive forces between the branched side chains, whereas in the prec-DBuPPV case (stabilized at 7 mN/m) both butyl chains are oriented out of the water subphase (see Figure 7 of part 1), and in this conformation the aromatic rings are more or less shielded from each other by butyl chains.

The transfer of these stable precursor monolayers was first studied with the conventional Langmuir–Blodgett technique. Some of the results of the transfer experiments onto hydrophobized substrates are shown in Figure 2. The transfer behavior of prec-MePPV was omitted because it is comparable to that of prec-BuMePPV. Parts a and b of Figure 2 show that the transfer of prec-BuMePPV and prec-DMePPV decreases on successive dippings. The transfer ratios of the first dipping cycle of prec-BuMePPV onto hydrophobic substrate (Figure 2a) are 0.7 on dipping and 0.4 on withdrawal and decrease to 0 on successive dippings. The transfer ratios of the deposition of a monolayer of prec-DMePPV (Figure 2b) onto a hydrophobic substrate are, however, 1.0 on dipping and 0.7 on withdrawal. When a hydrophilic substrate is used, the transfer ratios are 0.0 on dipping and 1.0 on withdrawal. However, on successive depositions on the same substrate the meniscus becomes serrated, and after deposition little drops of water remain on the substrate. The transfer ratios decrease to a value of 0 and 0.4–0.5 (Z-type) before becoming constant (see Figure 2, curve b). So, it is only possible to transfer one intact monolayer of prec-DMePPV. Changing the temperature, stabilization pres-

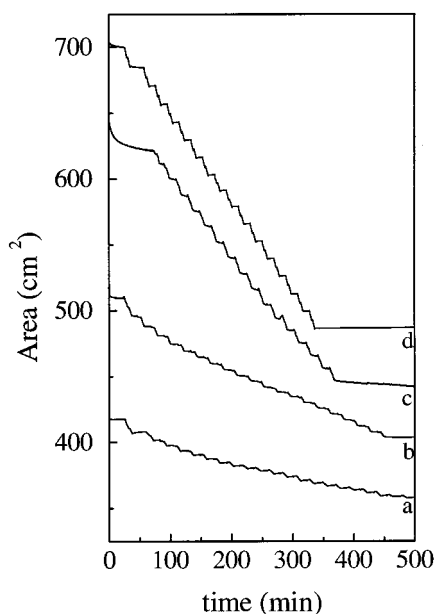


Figure 2. Stabilization and transfer curves of prec-BuMePPV at 15 mN/m (a), prec-DMePPV at 15 mN/m (b), prec-DBuPPV at 7 mN/m (c), and prec-MEHPPV at 15 mN/m (d) onto a hydrophobized substrate. $T = 10\text{ }^{\circ}\text{C}$.

sure, or the dipping speed does not improve the transfer of prec-DMePPV, prec-MePPV, and prec-BuMePPV.

The transfer of prec-DBuPPV stabilized before the second transition and the transfer of prec-MEHPPV are more successful, as can be seen in Figure 2, c and d, respectively. The transfer of prec-DBuPPV, stabilized at 7 mN/m, is constant (Figure 2c) and Y-type until 10 dippings, with transfer ratios of 0.5 downstroke and 1.0 upstroke, but after this the transfer ratios decrease to 0. The prec-DBuPPV monolayer, stabilized at 15 mN/m (after the second transition), cannot be transferred at all, not even one layer of it.

Prec-MEHPPV gives a very good transfer (Figure 2d). The transfer is Y-type and is constant at least up to 80 monolayers. The monolayer could be deposited onto all substrates tested with transfer ratios of 1.0.

So, although all these precursors have the same backbone, the transfer type and quality differ greatly.

As already mentioned in the Introduction, ad/cohesion between layers and the stiffness of the monolayer mainly determine the success of the transfer.

In the literature a high stiffness of the monolayer is sometimes attributed to a high molecular weight.^{5,6,22} These authors argue that due to a high amount of crossovers in high molecular weight polymer monolayers²³ a sort of stiff physical network is formed which declines the transfer. We proved, however, in part 1 that no crossovers are formed. Moreover, the molecular weight of all the precursors is almost equal.¹ Some show a good transfer whereas others do not; thus, high stiffness due to a high molecular weight cannot be the reason for differences in transfer behavior.

The strength of the adhesion and the cohesion is determined by many factors such as the strength of the interactions between the surface groups, the surface roughness,^{24,25} and water penetration into the multilayers during dipping.^{26,27} Other factors such as the T_g of the polymer and the contact angle during transfer^{28,29} might play a role in the transfer process.

Therefore, it is hard to attribute the difference in transfer behavior of the precursors to one parameter

only. However, it is striking that the precursor monolayers with a close packing (prec-BuMePPV, prec-MePPV, and prec-DBuPPV stabilized at 15 mN/m) give a bad transfer, whereas the less closely packed monolayers (prec-MEHPPV and prec-DBuPPV stabilized at 7 mN/m) give a good transfer. The transfer behavior of prec-DMePPV is a borderline case in this series, because only the transfer of the first monolayer is successful.

The cohesive forces between the polymer chains in the monolayer, which have lateral cohesive π - π interactions between the aromatic rings as the most prominent interaction, will be stronger in the more closely packed monolayers. Strong cohesive π - π interactions between the aromatic rings will lead to a stiff monolayer. Therefore, we assume that the monolayers of prec-DBuPPV, stabilized at 15 mN/m, prec-BuMePPV, and prec-MePPV are too stiff to be transferred. Successive dippings with bare substrates at the same position in the monolayer of prec-BuMePPV leads to a decrease in transfer ratio of the first monolayer, meaning that the film is damaged during repeated dippings probably due to a high stiffness. When similar experiments are carried out with prec-DMePPV, the transfer ratio of the first layer is always 1.0. Because subsequent dippings lead to decreasing transfer ratios, we speculate that this is due to lack of cohesion of the applied monolayer with previously transferred layers and not to a high stiffness. Because little drops of water remained on the substrate after deposition, we assume that a high water penetration into the previously transferred monolayers is a possible reason for the bad cohesion.

The transfer of prec-MEHPPV is better than the transfer of prec-DBuPPV stabilized at 7 mN/m. The likely reason for this observation is that prec-MEHPPV is more amphiphilic leading to a real Y-type transfer with strong polar-polar and strong hydrophobic-hydrophobic interactions between layers.

In many cases where the conventional vertical dipping method fails, the Langmuir-Schaefer method is found to be applicable.³⁰ We therefore tried the Langmuir-Schaefer method to transfer monolayers of prec-DMePPV and found that at least 40 monolayers could be transferred onto hydrophobized substrates with an average transfer ratio of 0.8.

Small-Angle X-ray Reflection (SAXR). To determine whether the multilayer films of prec-DBuPPV and prec-MEHPPV have a regular layer structure, they were investigated by means of small-angle X-ray reflection (SAXR). From SAXR experiments the overall thickness of the multilayer assembly, the surface roughness of the film, and the periodicity and quality of the layer structure can be determined.

Figure 3 (solid curve) shows the results of SAXR measurements of a multilayer containing 20 monolayers of prec-MEHPPV (Figure 3A) and of a multilayer containing 16 monolayers of prec-DBuPPV (Figure 3B). Both scattering curves show Kiessig fringes arising from the overall thickness of the multilayer. These reflectivity curves could be fitted well with the theoretical model (see Experimental Section). From these fits (Figure 3, dotted curves) a prec-MEHPPV multilayer thickness of $225 \pm 2\text{ }\text{\AA}$ and a surface roughness of the air-film surface of $5.8 \pm 0.5\text{ }\text{\AA}$ could be determined. The thickness of 16 monolayers of prec-DBuPPV is $104 \pm 3\text{ }\text{\AA}$ with a surface roughness at the air-film surface of $10 \pm 1.5\text{ }\text{\AA}$. Bragg peaks were not observed in the range

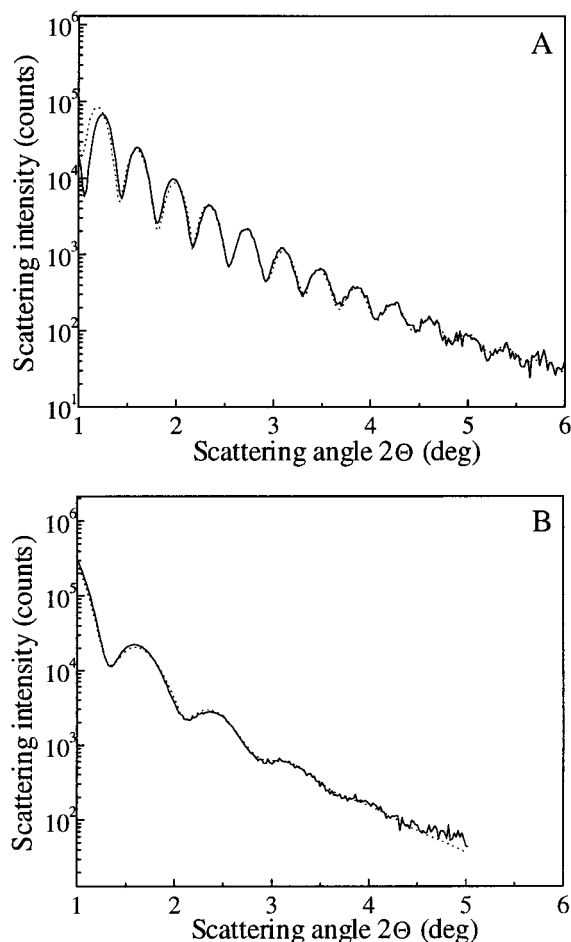


Figure 3. Small-angle X-ray reflection (SAXR) measurement (solid line) and fitted curve (dotted line) of (A) multilayer assembly of 20 monolayers of prec-MEHPPV and (B) multilayer assembly of 16 monolayers of prec-DBuPPV.

(2θ) from 1° to 12° , meaning that no regular layers are present in the film.

FT-IR Transmission and GIR Spectra of the Multilayer Structures. In the preceding paper the orientation of the precursor monolayer at the air–water interface was studied with FT-IR reflection measurements.¹ In summary, it was found for prec-MEHPPV and prec-DMePPV monolayers (both stabilized at 15 mN/m) and for prec-DBuPPV monolayers (stabilized at 7 mN/m) that the aromatic rings are oriented almost perpendicularly to the water surface. With FT-IR spectroscopy measurements on transferred multilayers we investigated to what extent this orientation is preserved after transfer. Therefore, we used both transmission FT-IR spectroscopy (electric field vector parallel to the substrate surface) and grazing incidence reflection FT-IR (GIR) spectroscopy (electric field vector perpendicular to the substrate surface). The transmission spectra contain bands of which the transition dipole moment has a component parallel to the substrate, and the GIR spectra contain bands of which the transition dipole moment has a component perpendicular to the substrate. Spectrum simulations were carried out to elucidate the influence of the optical effects and to make comparison of the transmission and the GIR spectra possible.¹

The results of the transmission FT-IR and GIR experiments with multilayers of prec-DMePPV, prepared by the Langmuir–Schaefer method, are shown

in Figure 4, A and B (solid lines), respectively. The calculated transmission and GIR spectrum of a nonoriented prec-DMePPV film are also shown in Figure 4 (dashed lines). The thickness of a multilayer assembly of 40 monolayers of prec-DMePPV was estimated to be 260 Å. The transmission and GIR spectra of the prec-DBuPPV multilayers transferred by the Langmuir–Blodgett technique at a surface pressure of 7 mN/m are shown in Figure 5, A and B (solid lines), respectively.

The thickness found from the SAXR experiments was used to calculate the nonoriented spectra. When the calculated and measured transmission spectra of prec-DMePPV and prec-DBuPPV (Figure 4A and Figure 5A, respectively) are compared, significant differences can be seen. The largest differences are in the bands at 1502, 1407–1413, and 1201–1204 cm^{-1} , which can be ascribed to phenyl stretch and to aromatic ether stretch vibrations, respectively. (For a detailed band assignment, see Tables 1 and 2 in the preceding paper.) The directions of the transition dipole moments of these absorption bands are lying in the plane of the aromatic rings, and these bands will be called the aromatic ether bands.

The same, but more distinct, differences between the measured and calculated transmission spectra were found by the FT-IR external reflection spectroscopy of prec-DMePPV stabilized at 15 mN/m and prec-DBuPPV stabilized at 7 mN/m at the air–water interface (see part 1, Figure 3c and Figure 4d, respectively). These results can be compared with the results of the transition FT-IR measurements of the multilayer films of Figures 4A and 5A, respectively, because in both cases only groups with a component of the transition dipole moment parallel to the water or substrate surface will absorb IR light. Because the differences in the transmission spectra of the multilayers are less distinct, it means that the aromatic rings of prec-DMePPV and prec-DBuPPV in the multilayers have lost some of their perpendicular orientation but are still predominantly perpendicular to the substrate surface. So, the orientation of the aromatic ring is preserved to a large extent after transfer.

This orientation of the aromatic rings in the multilayers is in correspondence with the results of the grazing incidence spectra of the multilayers. In the GIR measurements of the multilayers only bands with a component of the transition dipole moment perpendicular to the substrate surface absorb. The aromatic ether bands are stronger in the measured GIR spectra than in the calculated GIR spectra, from which it can be concluded that the rings are more perpendicularly oriented to the substrate surface.

The intensities of the prec-DBuPPV bands in the 3000–2800 cm^{-1} region, which can be attributed to the CH stretch vibrations, are the same in the calculated and measured spectra. From this it can be concluded that the butyl chains are not oriented in the multilayer structures. This is not surprising, considering the fact that rather short butyl chains are not expected to crystallize.

Figure 6A shows the measured and calculated GIR spectra of 20 layers of prec-MEHPPV transferred onto gold. For the calculation of the GIR spectra of prec-MEHPPV the thickness of 225 Å found with the SAXR experiments was used. Figure 6B (solid line) shows the measured GIR spectrum of two monolayers of prec-MEHPPV transferred onto gold and the calculated GIR

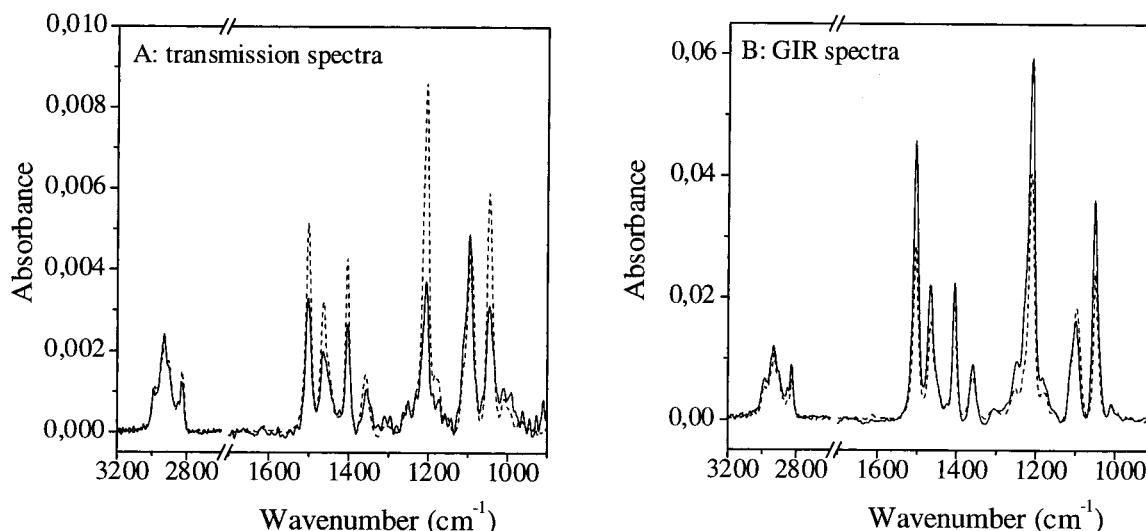


Figure 4. (A) Measured transmission spectrum of 40 monolayers of prec-DMePPV transferred by the Langmuir–Schaefer method onto a Si wafer (solid line). (B) Measured GIR spectrum of 40 LB layers of prec-DMePPV transferred onto gold (solid line). Calculated spectra in dashed lines.

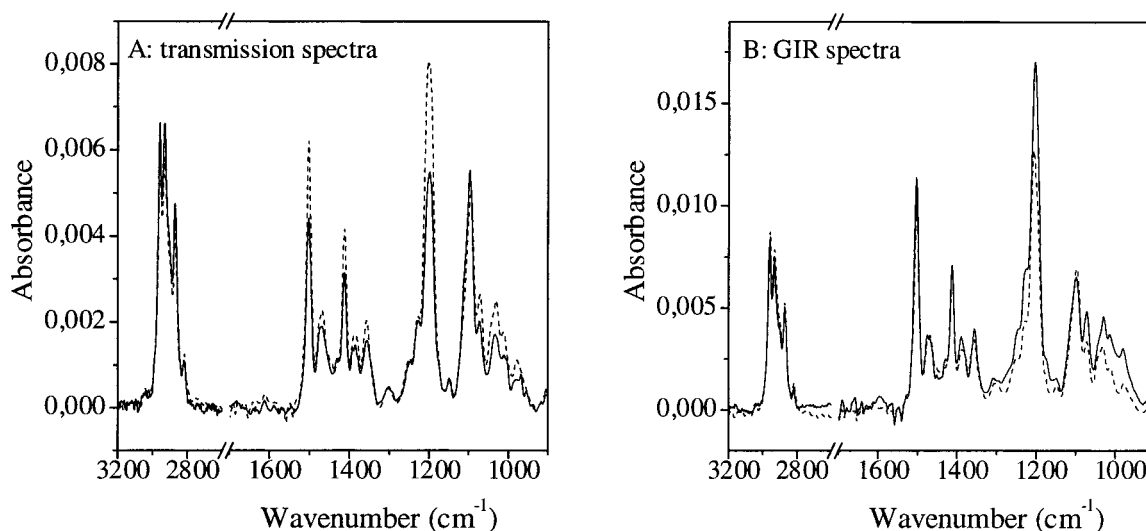


Figure 5. (A) Measured transmission spectrum of 32 monolayers of prec-DBuPPV which were deposited on both sides of a ZnS substrate. (B) Measured GIR spectrum of 16 LB layers of prec-DBuPPV transferred onto gold. Calculated spectra in dashed lines.

spectrum of a nonoriented 22 Å thick prec-MEHPPV film on gold.

Comparing the measured and calculated GIR spectra of 20 monolayers of prec-MEHPPV (Figure 6A, solid and dashed line), it can be seen that these spectra are almost identical. So, there are no indications that the structure of the multilayer deviates from a nonoriented structure. Therefore, it can be concluded that the orientation of the monomeric units in the monolayer of prec-MEHPPV is completely lost after transfer. However, when less than 10 monolayers was transferred, some residual orientation was found with the strongest dichroism found for a film of two monolayers on a gold substrate. The GIR spectra of this film can be seen in Figure 6. Again a more or less perpendicular orientation of the aromatic rings with respect to the substrate is observed.

Thus, the perpendicular orientation of the aromatic ring of the precursor polymers is lost to a major or minor extent in the multilayer assemblies. This is not surprising, because the monolayer loses contact with the water surface after transfer and as a consequence the driving force for the alignment of the monolayer. Since the monolayer is not fixed by any kind of crystalline order,

we can expect that the monolayer structure is subject to relaxation processes.

In the prec-DMePPV case, the orientation is preserved to a large extent. The reason for this might be the rather high T_g of 93 °C of this polymer. Therefore, extensive backbone motions are not possible. Moreover, although the hydration interactions of the ether groups will be lost, the π – π interactions between the aromatic rings can in principle be preserved.

Prec-DBuPPV has, like prec-MEHPPV, a T_g of 27 °C. Nevertheless, in the prec-DBuPPV case, the orientation is preserved to a large extent in a multilayer assembly of many monolayers, whereas in the prec-MEHPPV case the orientation was lost completely after transfer. To explain this, we have to focus on the multilayer architecture of prec-DBuPPV and prec-MEHPPV.

The transfer of prec-DBuPPV was Y-type with transfer ratios 0.5 downstroke and 1.0 upstroke. This results in a multilayer structure as is depicted in Figure 7A. The rough and bad structure of prec-DBuPPV is in agreement with the high surface roughness found from the SAXR experiment (Figure 3B) and the absence of Bragg peaks in this experiment.

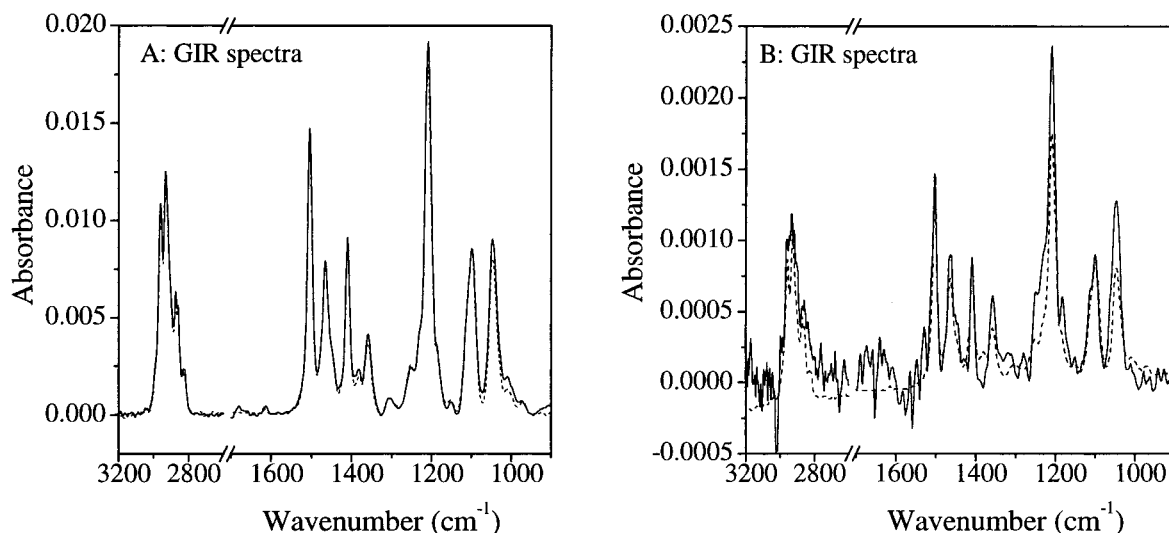


Figure 6. Measured GIR FT-IR spectrum of monolayers of prec-MEHPPV transferred onto a gold substrate (solid line) and calculated GIR spectrum (dashed line) of (A) 20 monolayers and (B) 2 monolayers.

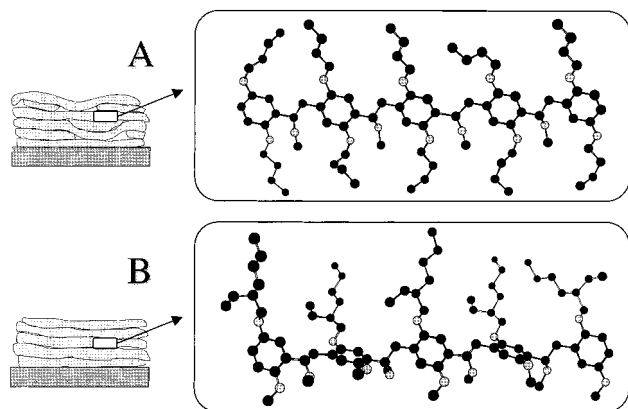


Figure 7. Schematic presentations of the proposed multilayer structure of (A) prec-DBuPPV and (B) prec-MEHPPV. Carbon, black atoms; oxygen, gray atoms. Hydrogen atoms are not shown.

The aromatic ring of prec-DBuPPV is symmetrically substituted, which leads to a pressure-induced orientation of the monolayer of prec-DBuPPV at 7 mN/m (see Figure 7 of part 1).¹ It is very likely that after release of the applied pressure the monomeric units take on a more favorable orientation with π - π interactions between the aromatic rings and London/van der Waals forces between the alkyl chains. This would lead to a decrease in area, but this decrease is probably canceled out because the aromatic rings take on, as was concluded from the IR measurements, a somewhat more planar orientation with respect to the water surface. We thus assume that a prec-DBuPPV chain in the multilayer takes on the conformation depicted in Figure 7A.

Prec-MEHPPV is substituted asymmetrically, and the transfer of prec-MEHPPV is Y-type with transfer ratios of 1.0 leading to a rather smooth surface (Figure 7B). In the thicker films of prec-MEHPPV no dichroism was found. Compared to the butyl side chains of prec-DBuPPV, the side chains of prec-MEHPPV are more bulky. Therefore, we assume that the chains are sterically hindered and that due to this the aromatic rings along the chain are forced to take on a twisted orientation with respect to each other (see Figure 7B). This results in nonoriented monomeric units and a badly defined layer structure, which lacks a Bragg pattern.

Despite this relaxation of the chain, a fully random 3D conformation is not likely because the T_g of prec-MEHPPV is 27 °C, which is above room temperature. At the air-water interface this sterical hindrance is probably canceled out by the strong hydrophilic interactions of the ether groups with the water subphase. In the thinner film some orientation is found, because the well-defined substrate surface can probably provide interactions with the monolayer helping to largely maintain the orientation.

Conclusions

The alkoxy-substituted precursor polymers form stable monolayers at the air-water interface. The less closely packed monolayers, prec-MEHPPV and prec-DBuPPV stabilized at 7 mN/m, could be transferred very well with the Langmuir-Blodgett technique, but 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 of one monolayer of prec-DMePPV onto a bare substrate is good, but deposition of more monolayers is not successful. Multilayers of Prec-DMePPV can be prepared by the Langmuir-Schaefer method.

The orientation in the monolayers of prec-DMePPV and prec-DBuPPV at the air-water interface is preserved to a large extent after transfer. 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 did reveal orientation, but this is probably substrate induced.

References and Notes

- (1) Hagting, J. G.; de Vos, R. E. T. P.; Sinkovics, K.; Vorenkamp, E. J.; Schouten, A. J. *Macromolecules* **1999**, *32*, 3930.
- (2) Crisp, D. J. *J. Colloid Sci.* **1946**, *1*, 49, 161.
- (3) Crisp, D. J. In *Surface Phenomena in Chemistry and Biology*; Danielli, J. F., Pankhurst, K. G. A., Riddiford, A. C., Eds.; Pergamon Press: New York, 1958; p 25.
- (4) Nakahara, H.; Fukuda, K. *J. Colloid. Interface Sci.* **1985**, *104*, 290.
- (5) Schouten, A. J.; Wegner, G. *Makromol. Chem.* **1991**, *192*, 2203.
- (6) Tredgold, R. H.; Winter, C. S. *Thin Solid Films* **1983**, *99*, 81.
- (7) Mumby, S. J.; Swalen, J. D.; Rabolt, J. F. *Macromolecules* **1986**, *19*, 1054.

- (8) Elbert, R.; Laschewsky, A.; Ringsdorf, H. *J. Am. Chem. Soc.* **1985**, *107*, 4134.
- (9) Schneider, J.; Ringsdorf, H.; Rabolt, J. F. *Macromolecules* **1989**, *22*, 205.
- (10) Arndt, T.; Schouten, A. J.; Schmidt, G. F.; Wegner, G. *Makromol. Chem.* **1991**, *192*, 2215.
- (11) Teerenstra, M. N.; Vorenkamp, E. J.; Schouten, A. J. *Thin Solid Films* **1991**, *196*, 153.
- (12) Brinkhuis, R. H. G.; Schouten, A. J. *Macromolecules* **1991**, *24*, 1496.
- (13) Duda, G.; Schouten, A. J.; Arndt, T. A.; Lieser, G.; Schmidt, G. F.; Bubeck, C.; Wegner, G. *Thin Solid Films* **1988**, *159*, 221.
- (14) Embs, F. W.; Wegner, G.; Neher, D.; Albouy, P.; Miller, R. D.; Wilson, C. G.; Schrepp, W. *Macromolecules* **1991**, *24*, 5068.
- (15) Lambeek, G.; Vorenkamp, E. J.; Schouten, A. J. *Macromolecules* **1995**, *28*, 2023.
- (16) Schoondorp, M. A.; Vorenkamp, E. J.; Schouten, A. J. *Thin Solid Films* **1991**, *196*, 121.
- (17) Langmuir, I.; Schaefer, V. J. *J. Am. Chem. Soc.* **1938**, *60*, 1351.
- (18) Waren, B. E. In *X-ray Diffraction*; Addison-Wesley: Reading, 1969.
- (19) Leuthe, A.; Riegler, H. *J. Phys.* **1992**, *25*, 1786.
- (20) Allara, D. L.; Baca, A.; Pryde, C. A. *Macromolecules* **1978**, *11*, 1215.
- (21) *Handbook of Optical Constants of Liquids and Solids*; Palk, E. D., Ed.; Academic Press: New York, 1985.
- (22) Peng, J. B.; Barnes, G. T. *Langmuir* **1991**, *7*, 1749.
- (23) Gaines Jr., G. L. *Langmuir* **1991**, *7*, 834.
- (24) Davies, J. T.; Rideal, E. K. In *Interfacial Phenomena*; Academic Press: New York, 1963.
- (25) Jaycock, M. J.; Parfitt, G. D. In *Chemistry of Interfaces*; Ellis Horwood: Chichester, 1981.
- (26) Maoz, R.; Sagiv, J. *Langmuir* **1987**, *3*, 62.
- (27) Popovitz-Biro, R.; Hill, K.; Landau, E. M.; Lahav, M.; Leiserowitz, L.; Sagiv, J. *J. Am. Chem. Soc.* **1988**, *110*, 2672.
- (28) Langmuir, I. *Science* **1938**, *87*, 493.
- (29) Bikerman, J. J. *Trans. Faraday Soc.* **1940**, *36*, 412.
- (30) Okahata, Y.; Ariga, K.; Tanaka, K. *Thin Solid Films* **1992**, *210/211*, 702.

MA990069V