

Langmuir and Langmuir–Blodgett Films of Side-Chain Liquid-Crystalline Poly(maleic acid-*alt*-1-alkene)s

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Langmuir layers of side-chain liquid-crystalline poly(maleic acid-*alt*-1-alkene)s (SCLCPs) with biphenyl mesogens were studied on water subphases but were also transferred by the use of the Langmuir–Blodgett technique. Brewster angle microscopy showed that the SCLCPs with methoxybiphenyl mesogens strongly aggregate on the water subphase and form islands, which merge upon compression. In contrast, SCLCPs with cyanobiphenyl mesogens spread nicely and compression of these polymers resulted in the formation of triple layers. Langmuir monolayers of SCLCPs with methoxybiphenyl mesogens show Z-type transfer. Atomic force microscopy and X-ray reflectivity measurements of the resulting Langmuir–Blodgett mono- and/or multilayers indicate that the side chains of these polymers are possibly tilted. The multilayers have a double layer periodicity, which requires a reorientation of the side chains during or after transfer. Annealing of these Langmuir–Blodgett films resulted in an increase of the mean film thickness and a more uniform *d* spacing within the multilayer. With atomic force microscopy droplets were observed on top of the multilayer, indicating dewetting of the upper layers.

1. Introduction

The Langmuir–Blodgett (LB) technique consists of successive transfer of a Langmuir monolayer to a substrate and allows the fabrication of ultrathin films with controllable thickness.¹ This well-controlled transfer results in LB-films that are ordered at a molecular level. Therefore, these films have attracted considerable attention in the field of electrooptical and information storage devices.^{2–5} The ordered structure of LB-films also makes these films interesting for model studies of thin films of side-chain liquid-crystalline (SCLC) copolymers.^{6–8} To understand the build-up of this layered structure, detailed analysis of the Langmuir monolayer is necessary.^{9,10}

A class of polymers containing maleic anhydride moieties has been applied successfully in LB technology.^{11–22}

Although a majority of the studied polymers contains alkyl side chains,^{12–15,19–22} some polymers have been reported that have mesogen-containing side chains.^{11,16–18} Recently, novel poly(maleic anhydride-*alt*-1-alkene)s were synthesized with methoxybiphenyl or cyanobiphenyl mesogens in the side chain.²³ Whereas the polymer with cyanobiphenyl mesogens exhibits a nematic mesophase, the polymers with methoxybiphenyl mesogens exhibit smectic A or higher ordered mesophases.²³ Van der Wielen et al.^{24,25} studied the behavior of some of these polymers in spin-coated films on silica. After annealing above the glass transition, they found that the spin-coated film adopts a smectic structure with a *d* spacing comparable to that in

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the bulk. At the polymer–substrate interface the side chains lie flat on the surface.

The present study describes the monolayer behavior on water of several SCLC copolymers with maleic acid moieties in the backbone. The maleic acid moieties in the copolymer are expected to improve the adhesion.^{26–30} The monolayer behavior has been studied by recording surface pressure–area isotherms and Brewster angle microscopy (BAM). In addition, the monolayer behavior of polymers with a doubled mesogen density^{31,32} was studied. Langmuir monolayers of a polymer with methoxybiphenyl mesogens have been transferred to glass and silica substrates. The properties of the resulting Langmuir–Blodgett films (LB films) were studied by X-ray reflectivity and atomic force microscopy (AFM). Finally, the properties of LB films are compared to those of spin-coated films as described by van der Wielen et al.^{24,25}

2. Experimental Section

Materials. The water for the subphase was purified by filtration through a Seralpur Pro C90 purification system. The solvents were commercially available and used without further purification. The synthesis and characterization of the polymers has been described elsewhere.^{23,31,32}

Methods. The surface pressure–area isotherms were recorded on a Lauda FW2 Filmwaage, which was thermostated at 25 °C. The polymers were spread from chloroform/dimethyl sulfoxide (DMSO) solutions (98/2 v/v) (1 mg/mL) onto the aqueous subphase by use of a Hamilton syringe. After spreading, the monolayer was allowed to equilibrate for 10 min before compression started. A compression rate of 2 Å²/(repeating unit min) was used.

Monolayers were transferred onto both hydrophobic and hydrophilic glass and silicon oxide substrates at a constant pressure of 15–20 mN/m for polymer **1-9,0**. The substrates were cleaned with chloroform, treated with 30% H₂O₂/25% NH₃ solution (caution) and ultrapure water (1/1/5 v/v/v) at 50–80 °C for 30 min, washed with ultrapure water, sonified in 5% HCl in water for 15 min, dipped into ultrapure water, sonified in methanol for 15 min, sonified in methanol/chloroform (3/1 v/v) for 15 min, and sonified in chloroform for 15 min. The substrates were stored in methanol. Before use the substrates were dried by purging them with a stream of nitrogen. Some substrates were hydrophobized by leaving them in 1,1,1,3,3,3-hexamethyldisilazane for 24 h.

The Brewster angle microscope was home-built. Technical details on the assembly of this microscope were published elsewhere.³³

The X-ray reflectivity measurements were performed with a two-circle diffractometer using the Cu K α radiation ($\lambda = 0.154$ nm) from a rotating anode as described before.³⁴ The collimation of the beam resulting from a primary (0 0 2) graphite monochromator and the slit setting led to a resolution in q_z direction of $\Delta q_z = 4 \times 10^{-4}$ nm⁻¹. The data were corrected for the sample size effects at small incidence angles as well as for the background scattering and were normalized to unit incident intensity. The data were analyzed according to an iterative matrix formalism

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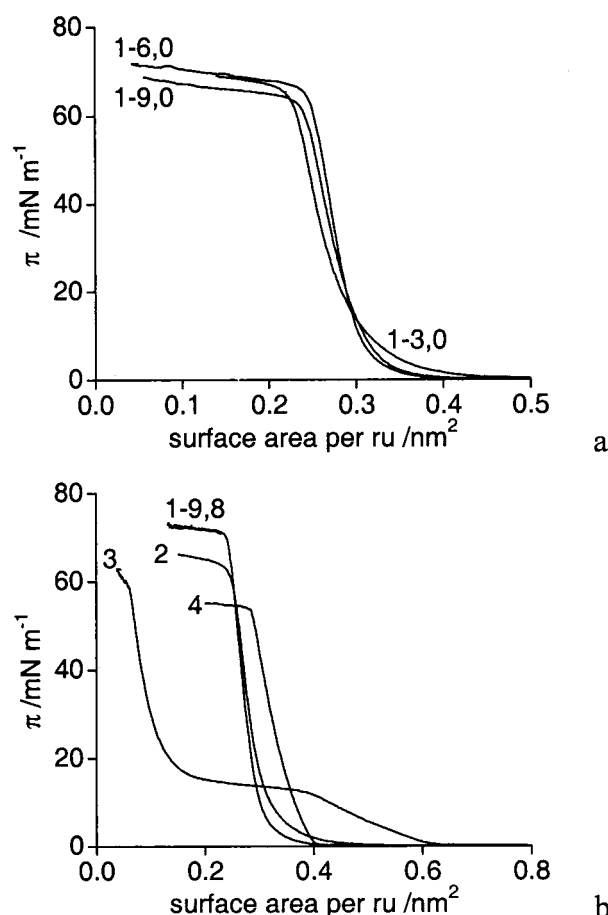


Figure 1. π – A Isotherms of polymers **1-m,0** (a) and **1-9,8** and **2–4** (b).

derived from the Fresnel equations^{35,36} by taking into account the deviation from the ideal decay of the reflectivity for a perfectly smooth surface due to the presence of roughness. In real space the sample surface was imaged by AFM measurements which were executed in the tapping mode with a commercial ND-MDT (Moscow) microscope in ambient air. The lateral and vertical resolution were approximately 10 and 0.02 nm, respectively. Annealing of the LB film was done under nitrogen atmosphere at 135 °C.

Hydrolysis of Polymers. The maleic anhydride moieties in all polymers except polymers **5-m** were hydrolyzed by dissolving 0.2 g of polymer in a tetrahydrofuran/water mixture (95/5 v/v) followed by refluxing during 48 h. The reaction mixture was poured into hexane, which resulted in precipitation of the polymer. The polymer was obtained as a white powder by filtration. Fourier transform infrared (FTIR) spectroscopy showed that all maleic anhydride moieties were ring-opened to maleic acid moieties. This process was characterized by the disappearance of the symmetric and antisymmetric stretching bands at 1861 and 1780 cm⁻¹ typical for an anhydride, and the appearance of the C=O stretching band at 1733 cm⁻¹ characteristic for a carboxyl group.²³ Thin-layer chromatography showed that the ester bonds in polymers **2** and **6** were not cleaved under these conditions.

3. Results and Discussion

3.1. Langmuir Films of Alternating Polymers with Maleic Anhydride Moieties. Figure 1a and b shows the surface pressure vs area (π – A) isotherms of polymers **1-m,p**, **2**, **3**, and **4** (Scheme 1). The corresponding surface

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Scheme 1. Molecular Structure of Polymers 1–4

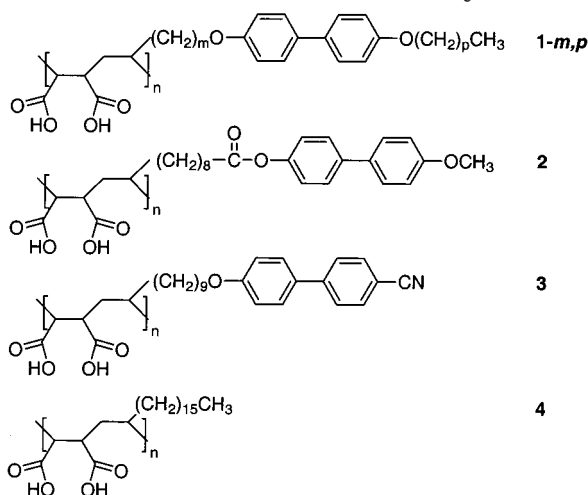


Table 1. Properties of Langmuir Films

polymer	area per repeating unit	
	0 mN/m, nm ² ^a	30 mN/m, nm ²
1-3,0	0.30	0.267
1-6,0	0.31	0.279
1-9,0	0.31	0.276
1-9,8	0.30	0.276
2	0.31	0.285
3	0.61	0.098
4	0.37	0.321
5-3	0.51	0.454
5-6	0.51	0.474
6	0.54	0.472

^a By extrapolation of the linear section of the isotherm to zero pressure.

areas per repeating unit, i.e., per alternating pair of monomer units in the backbone, are summarized in Table 1. The minimal surface areas per repeating unit of compounds **1-*m,p*** and **2** are smaller than the values of 0.39 and 0.37 nm² of poly(maleic acid-*alt*-hexadec-1-ene)¹⁴ and poly(maleic acid-*alt*-octadec-1-ene), i.e., polymer **4**. This may result from the degree of polymerization: low molecular weight polymers are compressed more easily to relatively compact and ordered monolayers than are high molecular weight polymers. Furthermore, the mesogen–mesogen interactions of the side-chain liquid-crystalline poly(maleic acid-*alt*-1-alkene)s may result in more compact aggregates. The degrees of polymerization of poly(maleic acid-*alt*-hexadec-1-ene) and poly(maleic acid-*alt*-octadec-1-ene) are 230 and 64, respectively, whereas the present polymers have degrees of polymerization of about 18.

The minimal surface areas per repeating unit of compounds **1-*m,p***–**4** (Table 1) are much larger than the cross-sectional area of a methylene chain combined with a biphenyl mesogen (approximately 0.26 nm²). This means that the polymer backbone is largely responsible for the minimal area of about 0.3 nm² per repeating unit observed in the isotherms of the polymers. Probably, the hydrophilic headgroups are large and therefore they include both carboxylic acid groups; i.e., both of these groups are in contact with the water surface.

The isotherms shown in Figure 1a are relatively steep with high collapse pressures, suggesting that the compressed films are well ordered. This was confirmed for polymer **1-9,0** by temperature-dependent measurements, which showed that the minimal surface area per repeating unit increased only by about 0.01 nm on going from 11 to

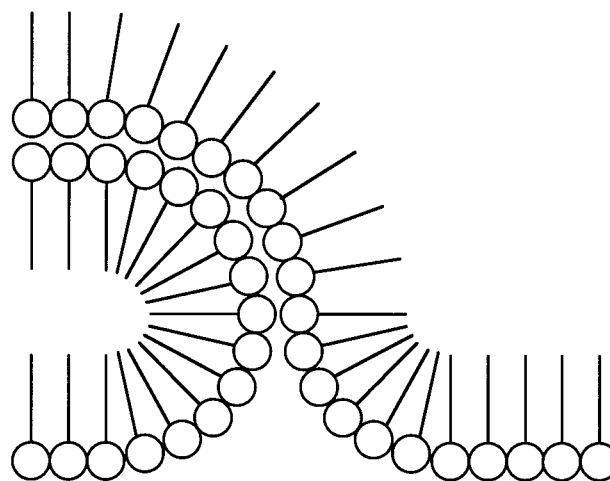


Figure 2. Schematic representation of the transformation of a monolayer into a triple layer.

42 °C. There is an interesting trend in the quality of the isotherms, and presumably the order in the monolayers, as the length of the spacer increases. For nonyl and hexyl spacers, the shape of the isotherms does not differ significantly; the surface area per repeating unit for different surface pressures are similar (Table 1 and Figure 1a). For a propyl spacer, however, the isotherm is less steep and the pressure increases at a higher surface area than for polymers **1-9,0** and **1-6,0**. This indicates that, for longer spacers a more stable monolayer is obtained. This can be expected, because the longer spacer decouples the motions of the polymer backbone from those of the mesogenic groups.³⁷ For shorter spacers, it is more difficult for the mesogenic groups to assume a parallel orientation, hence the slightly less stable monolayer observed for polymer **1-3,0**.

Figure 1b shows that the isotherms of polymers **1-9,8** and **2** have shapes comparable to those of polymers **1-*m,0***. However, the isotherm of polymer **1-9,8** is somewhat steeper and has a lower area per repeating unit at 0 mN/m (Table 1), indicating a higher degree of order in the monolayer. This behavior is comparable to that of the bulk, which showed that the degree of order in the mesophase increased with the length of the mesogenic tail.²³

Polymer **3**, which contains cyanobiphenyl mesogens, has a surface area per repeating unit that is considerably larger than that of polymers with apolar mesogenic substituents. This can be ascribed to interactions between the polar mesogenic tails and the water surface. Everaars et al. observed that double-chained ammonium amphiphiles containing cyanobiphenyl mesogens can adopt a flat orientation of cyanobiphenyl mesogens on the water surface.³⁸ However, for the present polymers a completely flat orientation of cyanobiphenyl mesogens can be ruled out because this situation would require a surface area per repeating unit of more than 0.82 nm² instead of the observed 0.61 nm². Furthermore, this polymer shows a plateau in the $\pi - A$ isotherm. The molecular area at the low area side of this plateau, approximately 0.13 nm²/repeating unit, is too small to accommodate a monolayer. This indicates that a multilayer is formed upon compression, probably a triple layer (Figure 2), as has been observed before for poly(maleic anhydride-*alt*-vinyl ethers) with cyanobiphenyl mesogens.¹¹

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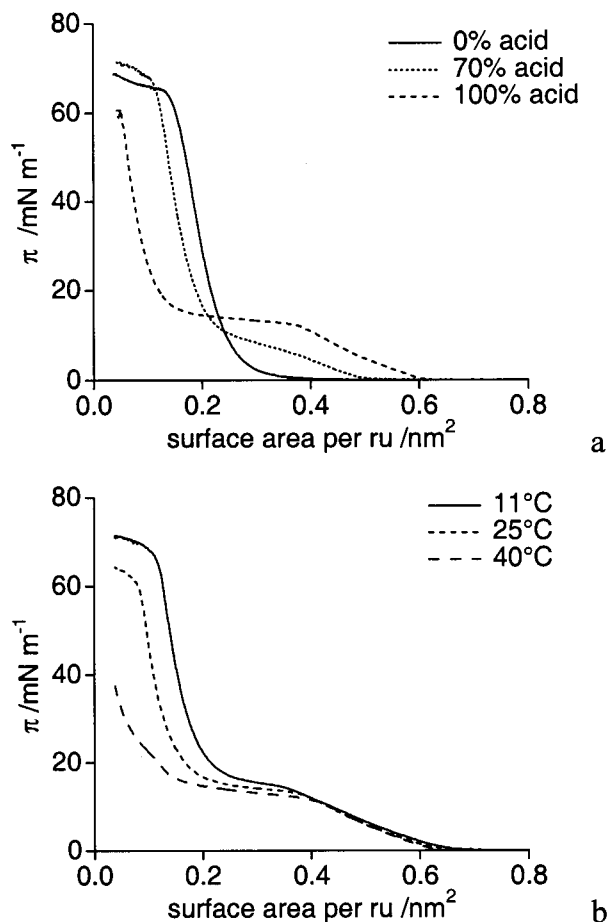


Figure 3. $\pi - A$ Isotherms of polymer **3** (a) for different anhydride contents in the backbone; and (b) at different temperatures.

To study the effect of the backbone flexibility on the interactions between the mesogenic cyano substituents and the water subphase, the isotherms of polymers with different acid contents were recorded (see Figure 3a). When the maleic anhydride moieties are converted into maleic acid moieties the flexibility of the polymer backbone increases. Figure 3a shows that for low acid contents the shape of the isotherms resembles that of polymers **1-m,p**. This may indicate that a stiff polymer backbone prevents the cyano groups from interactions with the water subphase.

Figure 3b shows that with increasing temperature the surface area per repeating unit at 0 mN/m remains constant, but the length of the plateau increases and the collapse pressure decreases. At 25 °C, the molecular area at the low area side equals about one-third of the molecular area at the start of the plateau. This suggests the formation of a triple layer, which has been observed before for some low molecular weight fatty acids³⁹ and compounds with cyanobiphenyl moieties.^{11,40,41} At 11 °C, the monolayer is very rigid and the applied compression speed is probably too high to result in a well-defined triple layer. At 40 °C, the flexibility of the triple layer is high enough so that another small plateau can be observed at the low area side. The surface area at the low area side of this plateau is about one-fifth of the molecular area at the start of the plateau.

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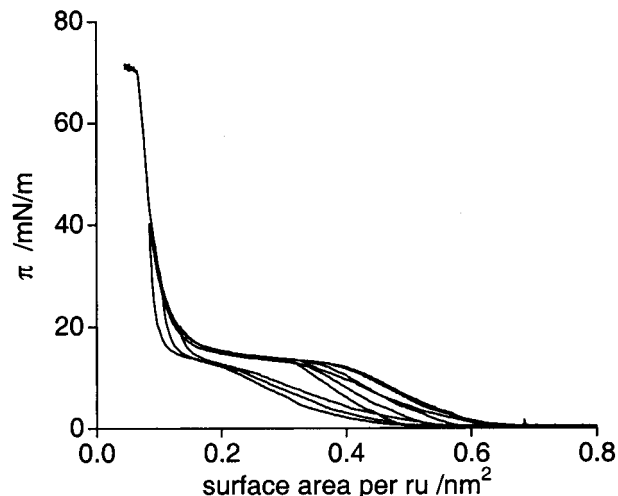


Figure 4. Consecutive compression-expansion cycles for polymer **3** at 25 °C.

The multilayer formation can be attributed to the tendency of cyanobiphenyl mesogens to form antiparallel pairs.^{42,43} At low surface pressure, the interactions of cyanobiphenyl mesogens with water are strong enough to suppress the antiparallel orientation and the polymer is present as a monolayer on the water subphase.¹¹ With an increase of surface pressure the antiparallel orientation is obtained in the multilayer by the cooperative sliding of a bilayer on top of the original monolayer. Polymers with methoxybiphenyl mesogens do not show this behavior because these mesogens do not tend to form antiparallel pairs.⁴²

Consecutive compression-expansion cycles (Figure 4) show that the $\pi - A$ isotherms are reversible after compression before or into the plateau. After compression beyond the plateau, the lift-off area of the following compression cycle shifts to a lower value. Compression beyond the plateau results in a highly condensed and stiff multilayer that does not rapidly return into the monolayer after expansion. Because the surface area of a compressed multilayer does not change for hysteresis cycles above the plateau pressure, it can be concluded that the formation of a triple layer is reversible and no additional layers on top of this triple layer are formed at 25 °C.

The monolayer stability of polymers **1-m,p**, **2**, and **3** was investigated on pure water at 25 °C and different surface pressures. Polymers **1-m,p** and **2** showed stable monolayers at surface pressures of 25 and 15 mN/m after 30–45 min. Polymer **3** showed a stable monolayer below the plateau pressure, i.e., at $\pi = 5$ and 8 mN/m, within 45 min. Thus, the initial area reduction can be attributed to the reorganization of the monolayer and is not due to collapse or dissolution into the subphase. At 30 mN/m, an almost stable multilayer was obtained after 90 min; however, during the following 2 h the area kept reducing slightly. This indicates the formation of a stable triple layer.

BAM was used to visualize the morphology and domain structures of the monolayers of polymers **1-9,0** and **3** on water at 25 °C. Figure 5 shows the micrographs for polymer **1-9,0** at $\pi = 0$ and 50 mN/m. Immediately after spreading, the film consists of polymer islands which merge upon compression (Figure 5a). This behavior has been observed before for poly(siloxane)s with benzoylbiphenyl mesogens,⁹

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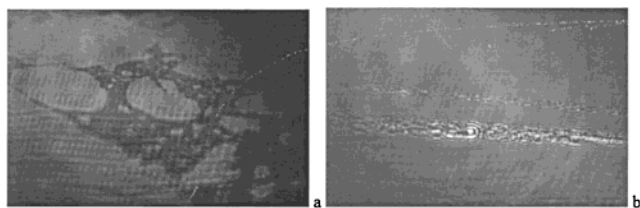


Figure 5. Brewster angle micrographs of polymer **1-9,0** at 0 mN/m (a) and 50 (b) mN/m. Image size approximately $500 \times 500 \mu\text{m}$.

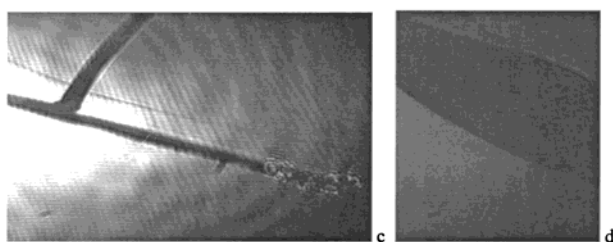
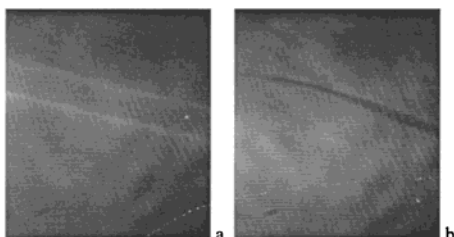


Figure 6. Brewster angle micrographs of polymer **3** at plateau pressure (a and b), 40 mN/m (c), and after expansion of a condensed film (d). Image size approximately $500 \times 300 \mu\text{m}$ (a, b, and d) or $500 \times 500 \mu\text{m}$ (c).

poly(glutamate)s with decyloxybiphenyl mesogens,⁷ and poly(maleimide-*alt*-vinylpyridine)s with cyanoazobenzene mesogens.⁴⁴ At 50 mN/m, the monolayer collapses, as can be seen from the horizontal lines with increased intensity (Figure 5b). Polymer **3** shows similar behavior if all acid moieties are converted into anhydride moieties.

Figure 6 shows the micrographs of polymer **3** at different surface pressures. Immediately after spreading the film is homogeneous. Upon compression in the plateau, straight white and black lines are observed parallel to the barrier (Figure 6a and b), probably resulting from the formation of a triple layer. At the point where the layer folds, the differences in refractive indices result in lighter and darker regions in the micrograph. Further compression of the layer resulted in a lighter color of the Langmuir layer, but no other changes were observed. Above 40 mN/m cracks develop in the triple layer and collapse of the triple layer is observed (Figure 6c). After expansion of a condensed multilayer, small holes are observed in an otherwise homogeneous film (Figure 6d), which confirm the observations of the consecutive hysteresis experiments. Relaxation of this film for several hours yields a homogeneous film without holes.

3.2. Langmuir Films of SCLCPs with Doubled Mesogen Density. So far, the polymers we have discussed contain one mesogen per four atoms in the backbone. The surface area per repeating unit of these polymers is mainly governed by the size of the hydrophilic headgroups. Doubling the mesogen density may result in different monolayer behavior, because the surface area per repeating unit may now be governed by the mesogens. Figure

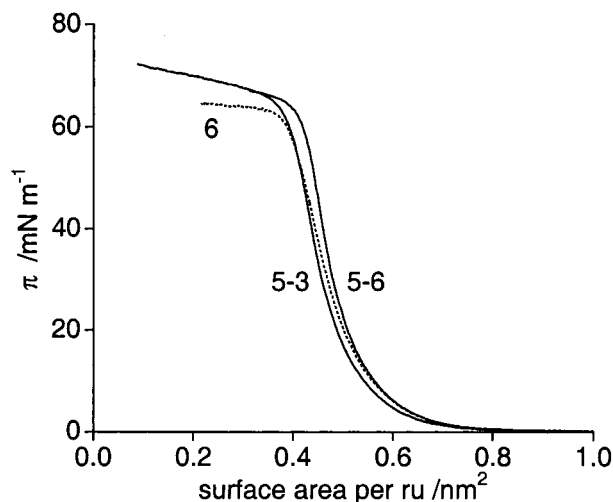
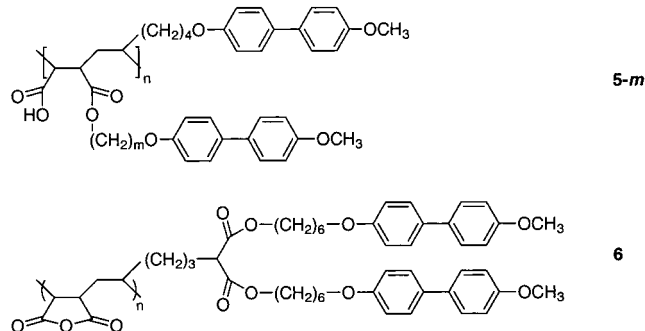


Figure 7. $\pi - A$ Isotherms of polymers **5-*m*** (—) and **6** (···).

Scheme 2. Molecular Structure of Polymers 5-*m* and 6



7 shows the $\pi - A$ isotherms of polymers **5-*m*** and **6** (Scheme 2) that have twice the mesogen density of polymers **1-3**. The corresponding surface areas per repeating unit are summarized in Table 1.

The surface areas per repeating unit for polymers **5-3** and **5-6** are similar (Figure 7). However, polymer **5-6** exhibits a slightly steeper isotherm. From the high surface areas per repeating unit in comparison to that of unmodified polymers, it can be seen that for polymers **5-*m*** the minimal area necessary to accommodate the repeating units is governed by the mesogenic side groups. In a noncrystalline packing of mesogens the cross-sectional area for two mesogens is approximately 53 \AA^2 (calculated from ref 23), which is comparable to the observed surface area per repeating unit for polymers **5-*m***.

Increasing the mesogen density by copolymerizing maleic anhydride and swallow-tailed 1-alkenes with two mesogens yields polymers that show a pressure-area isotherm (Figure 7) that is very similar to that of polymers **5-*m***, although the rise in surface pressure is slightly less steep.

The monolayer stability of polymers **5-*m*** and **6** was investigated on pure water at 25°C and a surface pressure of 25 mN/m. All polymers showed stable monolayers; the time necessary to obtain a stable monolayer was approximately 3 h, which is considerably longer than for polymers with only one mesogen per repeating unit. BAM did not reveal any crystallization during compression.

3.3. Langmuir-Blodgett Films. Monolayers of polymer **1-9,0** could be transferred successfully at 15 and 20 mN/m from the water surface to hydrophobic and hydrophilic glass substrates, respectively, at 25°C . Figure 8 shows that just after the start of the experiment a spontaneous loss of the surface area of the polymer

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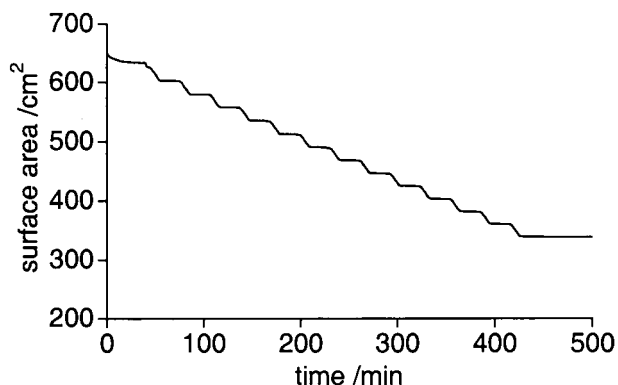


Figure 8. Isobaric measurement of a 1-9,0 monolayer at 15 mN/m and 25 °C during transfer to a hydrophobic surface.

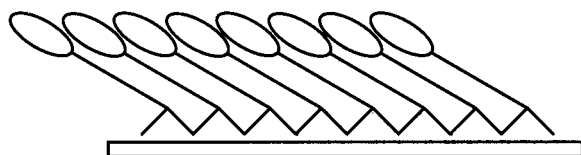


Figure 9. Possible arrangement of side chains in a LB monolayer of polymer 1-9,0.

monolayer occurs. The monolayer becomes stable after 30 min. The initial area reduction can be attributed to a reorganization of the monolayer. After stabilization, substrates were dipped and for both hydrophilic and hydrophobic substrates transfer was observed only during emersion of the substrate from the water subphase (Figure 8), which indicates Z-type transfer. For hydrophobic surfaces, the transfer ratio was $0.85 (\pm 0.05)$ and remained constant up to 13 layers (Figure 8). For hydrophilic surfaces, the transfer ratio was $1.00 (\pm 0.05)$ for the first cycle and leveled off to a value of $0.80 (\pm 0.05)$ for the fifth up to the tenth dipping cycle. The barrier did not move during the waiting cycle prior to the subsequent dipping, which indicates a fast stabilization of the monolayer after the substrate has been pulled out.

Monolayers of polymer 1-9,0 have also been transferred to hydrophilic silicon wafers with a transfer ratio of 0.70. Transfer of multiple monolayers was not successful: after transfer of a monolayer, the resulting LB layer was washed off during the following immersion of the substrate. The washing off could not be prevented by changing the immersion speed. For a micrometer-detail of the surface, AFM revealed that the monolayer of polymer 1-9,0 was smooth and had a thickness of approximately 1.3 ± 0.2 nm, which is significantly smaller than the length of a side chain (2.7 nm).²³ The difference in experimental and theoretical thickness indicates that the side chains lie tilted on the surface, as is schematically depicted in Figure 9. However, there was no proof that the tilt is as regular as is depicted in Figure 9 and is homogeneous throughout the whole sample. The tilt can probably be ascribed to the fact that the side chains are not space-filling, especially at low transfer ratios. Other polymers that have tilted side chains in LB films are poly(maleic anhydride-*alt*-octadec-1-ene)¹⁴ and Schiff base modified poly(maleic anhydride-*alt*-styrene).⁴⁵

Figure 10 shows the X-ray reflectivity curves of a multilayer (10 layers) of polymer 1-9,0 transferred to a hydrophilic glass substrate by the LB technique before and after annealing in the mesophase. In general, X-ray

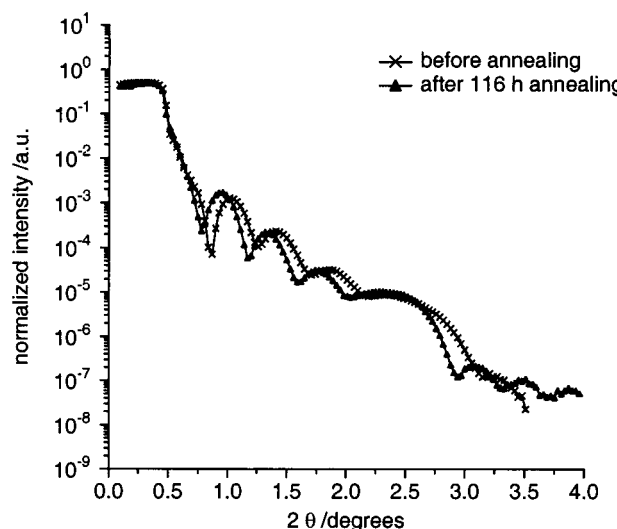


Figure 10. Reflected X-ray intensity as a function of twice the angle of incidence θ for a LB film of polymer 1-9,0 on hydrophilic glass after 10 dipping cycles.

reflectivity is a powerful method to investigate interfacial properties of layered materials. From the specular reflectivity, in which the reflected intensity depends on the wave vector transfer perpendicular to the sample surface, the density profile in the direction perpendicular to the sample surface can be obtained.

The curve marked by crosses in Figure 10 results from the reflectivity measurement before any annealing of the sample. In the reflection pattern so-called Kiessig fringes are visible, indicating a layer on top of the glass substrate with a relatively smooth surface. The Kiessig fringes originate from interference of X-ray beams reflected at the air-polymer interface and at the polymer-substrate interface. Hence, a mean total film thickness of 19.6 nm can be calculated from their period. In addition, a rather broad multilayer Bragg peak can be observed, resulting from a one-dimensional periodicity in the direction perpendicular to the substrate. The position of the Bragg corresponds to a smectic ordering within the LB film with a period of $d = 3.95$ nm.

Successive annealing of the sample in the mesophase (135 °C) combined with X-ray reflectivity measurements showed an additional ordering process of the layers which is very slow. Only after 4 days could a stable situation be achieved. Finally, annealing results in a slight shift of the fringes to a smaller period in the 2θ values, which indicates an increase of the mean total film thickness to 20.5 nm (the second curve in Figure 10). The interface roughness seems to be unchanged, as can be concluded from the very similar slope of both curves. Furthermore, both the Bragg peak and the following fringes sharpen, which indicates an ordering process of the mesogens resulting in a more uniform d spacing within the film.

From the comparison of the d spacing (3.95 nm) and the film thickness (19.6 nm), it follows that the LB film consists of 5 layers. These 5 layers have been obtained by transferring 10 Langmuir monolayers, which indicates that the LB film has a double layer periodicity. The side chains in this double layer will not overlap due to a lack of space, because it was shown that in polymers with a doubled mesogen density, the minimal area to accommodate the repeating units is governed by the mesogenic side chains and not by the polymer backbone. The d spacing of the double layer structure in the LB film (3.95 nm) is significantly smaller than the calculated d spacing of a calculated smectic A2 double layer (S_{A2} ; 5.36 nm). There-

(45) Dhathathreyan, A.; Mary, N. L.; Radhakrishnan, G.; John Collins, S. *Macromolecules* **1996**, *29*, 1827.

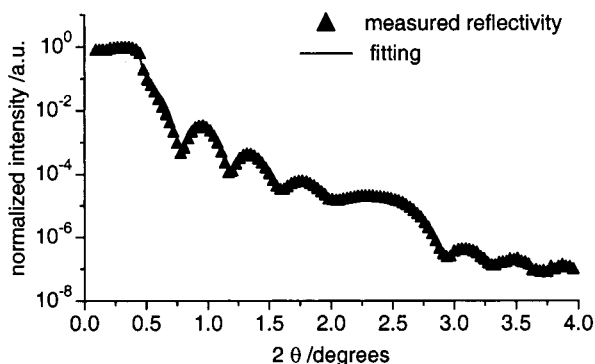


Figure 11. Reflected X-ray intensity as a function of twice the angle of incidence θ for a LB film of polymer **1-9,0** on hydrophilic glass after 10 dipping cycles (crosses) and the model fits (solid line).

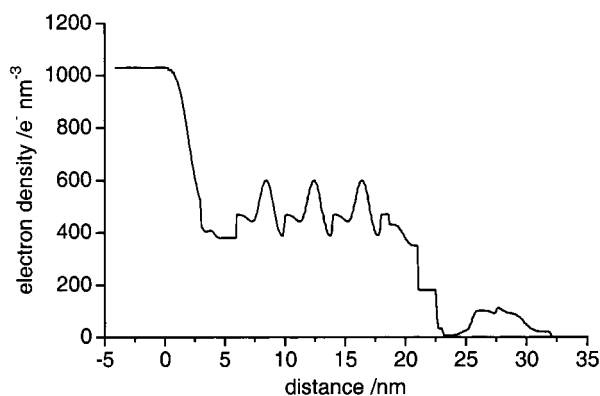


Figure 12. Electron density profile of a LB film of polymer **1-9,0** as given in Figure 9 (after 116 h annealing at 135 °C) as a function of the depth.

fore, we suggest that the side chains may be tilted because the mesogens are not space-filling, i.e., the LB film may have a smectic C2 structure. However, we have no strong evidence that certifies this assumption. Because the isobaric measurement (Figure 8) indicates Z-type transfer, which implicates that the LB film should have a monolayer periodicity (smectic A1 or C1), the double layer periodicity requires a reorientation of side chains during/after transfer of the Langmuir monolayer.

The results of the fitting for the annealed film in Figure 11 agree well with the experimental results. Only at small incidence angles is there some deviation, which can be explained by a lateral inhomogeneity of the sample in the following way: at small angles of incidence the X-ray beam illuminates a rather large sample area (26×6 mm), whereas at larger incidence angles this area is 3 orders of magnitude smaller (0.1×6 mm). Hence, the influence of inhomogeneities and irregularities over which the beam averages at small incidence angles is much larger and masks the signal from well-ordered regions of the sample. However, the existence of the Bragg peak is a clear indication of the presence of these well-ordered regions. The low intensity of the Bragg peak shows that these well-ordered regions are quite small. Indeed, as shown in the electron density profile resulting from the fit (Figure 12), the LB film contains only three periods with a double layer structure. The width of the Bragg peak arises from both a superposition of the Bragg peak with the Keesig fringes at this position and a relatively high degree of roughness.

As described by van der Wielen et al.,²⁴ the different electron densities in the profile can be related to backbone regions, spacer regions, and mesogen regions. Although

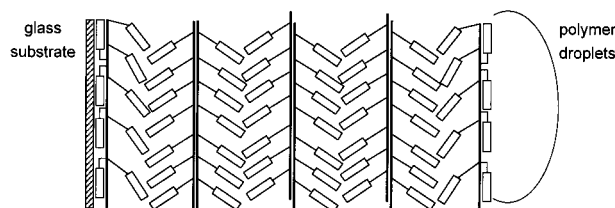


Figure 13. Schematic representation of the proposed layered structure within the annealed LB film of polymer **1-9,0** after annealing at 135 °C for 116 h. The tilt direction of the side chains is arbitrarily chosen and the side chains may tilt randomly.

there is no hard evidence that a certain electron density corresponds to a certain region, there are indications that the assignment as described below is reasonable. However, one must bear in mind that only one sample has been studied and some strange phenomena in this profile cannot be explained.

The region close to the substrate is difficult to interpret. The Z-type transfer and the good adhesion properties of the maleic acid moieties would result in a situation where the polymer backbone is at the glass substrate. In comparison to the "bulk" of the LB film, however, the electron density profile clearly shows a lower electron density at the substrate. This may result from surface roughness and/or may indicate some kind of disordered layer as depicted schematically in Figure 13. One must keep in mind that the picture of the first layer in Figure 13 is rather speculative. The orientation of the mesogens at the substrate–polymer interface (Figure 13) is difficult to explain, because it is expected that the polymer backbone is present at the glass substrate (see above). However, a similar orientation of mesogens was observed before in annealed spin-coated films of polymer **1-9,0**.²⁴ Although Figure 13 shows a situation with only mesogens at the glass substrate, it is possible that also some acid moieties may be in contact with the glass substrate.

The peaks in Figure 12 with the highest electron density in the film can be assigned to the backbone region, because it is expected that this layer has the highest density due to the oxygen atoms in the acid groups. The peaks in Figure 12 with a slightly lower electron density can be assigned to the mesogen layer. The electron density minima between the maxima of the mesogen and backbone regions can be ascribed to the low electron density of the spacers compared to that of the backbone and the mesogens.

The top layer has a lower electron density than the bulk of the film because it may consist of multidomain droplets, which lay on top of an ordered layer. The region of the high electron density plateau in the left of Figure 12 is ascribed to the glass substrate.

To get a more detailed picture of the surface of the annealed LB film, AFM measurements were performed (Figure 14). These measurements clearly showed dewetting of the top layers (Figure 14a). The droplets are on average about 40–50 nm high and between 100 and 200 nm wide. The presence of these droplets explains the disordered profile obtained with X-ray reflection. However, underneath the droplets the complete and relatively smooth polymer film was visible (Figure 14b). A closer look at this film between the droplets allows us to distinguish a typical terracelike surface of a smectic ordered SCLCP with step heights of about 3.7 ± 0.2 nm. This height agrees well with the mean d spacing determined by X-ray reflectivity.

In contrast to the dewetting of ordered spin-coated films, which have an interdigitated layer periodicity,²⁴ the

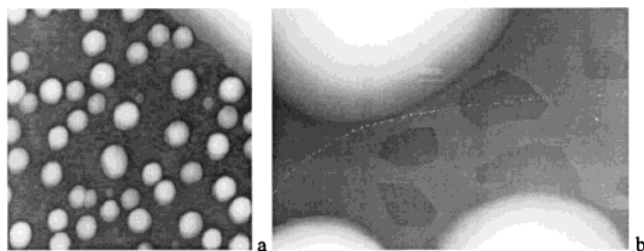


Figure 14. AFM images of the Langmuir–Blodgett film of polymer **1-9,0** after annealing for 116 h in the mesophase at 135 °C: $1.7 \times 1.7 \mu\text{m}$ (a) and $0.17 \times 0.25 \mu\text{m}$ (b).

dewetting in the LB films only seems to occur in the upper layer (Figures 13 and 14). The dewetting in the upper layer arises from the orientation of hydrophilic acid groups at the polymer–air interface, which induces a relatively high surface energy. Dewetting may take place until no hydrophilic groups are present at the polymer–air interface, i.e., the surface energy has reached a minimum. This process may already start immediately after the last Langmuir film has been transferred to the glass substrate and may not necessarily require a thermal treatment. The double layer periodicity probably prevents the film from an almost complete dewetting, as observed in spin-coated films.²⁴

4. Conclusions

SCLCPs with methoxybiphenyl mesogens form stable well-ordered Langmuir films with high collapse pressures. The polymer backbone determines the minimal area necessary to accommodate the repeating units and the interactions between mesogens hardly influence this area. When the mesogen density is doubled, the mesogens determine the minimal area necessary to accommodate the repeating units. BAM experiments show that SCLCPs with methoxybiphenyl mesogens strongly aggregate on the water subphase and form islands. Upon compression these islands merge.

In contrast, for SCLCPs with cyanobiphenyl mesogens, BAM reveals that these polymers spread nicely and no island formation results. The lift-off areas of these polymers suggest an orientation of the cyanobiphenyl mesogens with the cyano groups in contact with the subphase. Because of the tendency of cyanobiphenyl mesogens to form antiparallel pairs, compression results in the formation of a triple layer as confirmed by BAM experiments. Backbones with a higher content of anhydride moieties are more rigid and therefore do not undergo triple layer formation. BAM experiments showed that these polymers form islands that merge upon compression.

Langmuir layers of SCLCPs with methoxybiphenyl mesogens show Z-type transfer with high transfer ratios toward hydrophilic and hydrophobic glass substrates. On hydrophilic silicon, these polymers probably have tilted side chains in the LB monolayer. LB multilayers on hydrophilic glass may also consist of polymers with (randomly) tilted side chains, and X-ray reflectivity measurements show a d spacing of 3.95 nm. This may indicate that the film has a double layer periodicity, e.g., smectic C2. The double layer periodicity requires a reorientation of the side chains during or after transfer.

Annealing of the LB films results in an increase of the mean film thickness and a more uniform d spacing within the film. Fitting of a model to the experimental X-ray reflectivity data indicates that the first layer on the glass substrate is slightly disordered. The following three double layers may be well-ordered, and on top of these three double layers droplets are present as confirmed by AFM measurements. These droplets indicate that dewetting has occurred before or after annealing. The main reason for this dewetting may be the presence of acidic groups at the polymer–air interface, which induces a relatively high surface energy. Therefore, a reorientation of polymer at the polymer–air interface will occur, which decreases the surface energy.

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