Langmuir–Blodgett films of poly(isocyanide)s with different sidechains. 2. poly(3-cholesteryl-6-isocyanohexanoate)*

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Abstract

A poly(isocyanide), $[R \cdot N\text{-}C <]_n$, with pendant cholesterol side groups forms stable Langmuir Blodgett (LB) monolayers at the air-water interface. At high surface pressures, the monolayers are spontaneously transformed into bilayer structures. The monolayer was transferred onto various solid substrates to form LB multilayers. FT-IR, ellipsometry and SAXS indicate that in these multilayers the polymer side chains are oriented perpendicular to the substrate surface.

1. Introduction

Polymers can form stable monolayers at the air-water interface if they have a structure analogous to low molecular weight amphiphiles [1–4] or if they contain a polar moiety which can interact sufficiently with the water layer [5–7]. This polar moiety prevents the polymer monolayer collapsing at low pressures. Poly(isocyanide)s, $[R \cdot N\text{-}C <]_n$, are rigid-rod polymer molecules with a stable 4/1-helical conformation [8, 9]. The four repeating units per turn are stacked parallel with respect to the helical backbone, leaving a pitch of 4.2 Å. A Langmuir–Blodgett study on different polymers and co-polymers of n-alkyl-isocyanides and α-methyl-alkyl isocyanides showed that the polymer helices can be oriented parallel to the air-water interface. These polymers failed, however, to form stable monolayers and they were not transferable to solid substrates [10].

It was found that incorporation of an ester group in the polymer side-chains R, as in poly((S)-1-acetoxymethylethylisocyanide) [11], $[>C\text{-}N\text{-}CH(CH_3) \, CH_2OC(O)CH_3]$ (PAMEIC), leads to stable and transferable monolayers. Apparently, the ester group facilitates the interaction with the water subphase. This observation indicates (as we reported previously [10]) that rigidity in itself is not a sufficient factor for obtaining stable monolayers at the air-water interface. In the present paper we extend our studies and present new

data on a poly(isocyanide) with pendant cholesterol groups, namely poly(3-cholesteryl-6-isocyanohexanoate) (PCIH).

2. Experimental

The synthesis of PCIH is described elsewhere [12]. The cleaning procedures of the substrates and the preparation of the gold plated glass slides have been reported previously [10]. Monolayers were studied by their pressure area isotherms using a computer controlled Lauda Filmbalance (FW-2). The subphase was water, purified by a reversed-osmosis system (Elgastat spectrum SC30) and subsequent filtration through a Milli-Q purification system. Polymers were spread from chloroform or toluene solutions (max. 0.1 wt.%). Isotherms were recorded at different temperatures and at different speeds of compression. After stabilization of the layer on the water surface, multilayers were deposited on silicon wafers, ZnS plates (Cleartran Spectra-Tech) and on gold plated glass slides at a constant temperature and pressure with a deposition speed of 4 mm/min. IR spectra were obtained with a Bruker IFS-88 FT-IR spectrometer equipped with a MCT-A detector (D-313) to a resolution of 4 cm⁻¹. A germanium Brewster angle IR polarizer was used for both grazing incidence reflection (GIR) and transmission (TM) experiments. Spectra were recorded by the method of Arndt [13]; cycles of 200 scans were used.

*For Part I in this series see ref. 10.

3. Results and discussion

3.1. Monolayer properties

Polymer PCIH, spread from chloroform solution, displayed isotherms as shown in Fig. 1, curve A. The average area per repeating unit is lower than expected, which suggests that the polymer forms aggregate in chloroform solution. Changing the solvent to toluene resulted in markedly different isotherms (see Fig. 1, curves B–E). The first pressure rise is observed at 34 Å^2 per repeating unit. It is ascribed to an arrangement of the polymer side chains as depicted in Fig. 2a. In this arrangement the cholesterol groups are oriented more or less perpendicular to the surface. Thickness and width of the cholesterol group are 5.1–5.7 Å and 6.5–7 Å, respectively. The cross section area, therefore, is expected to be 31–39 Å^2, which suggests that the side-groups are stacked as in conventional monolayers of low molecular weight amphiphiles. This is possible because of the C_5-spacer which is present in the polymer side chain and the fact that the helix is not as rigid as in the case of PAMEIC which contains an additional α-substituent next to the –N=C< backbone. Above surface pressures of 20 mN/m a transition occurs which becomes more visible at higher temperatures. We propose that at this transition the monolayer is transformed into a bilayer with an area per repeating unit, amounting to one-third of the original value of the monolayer. The proposed structure of the bilayer is
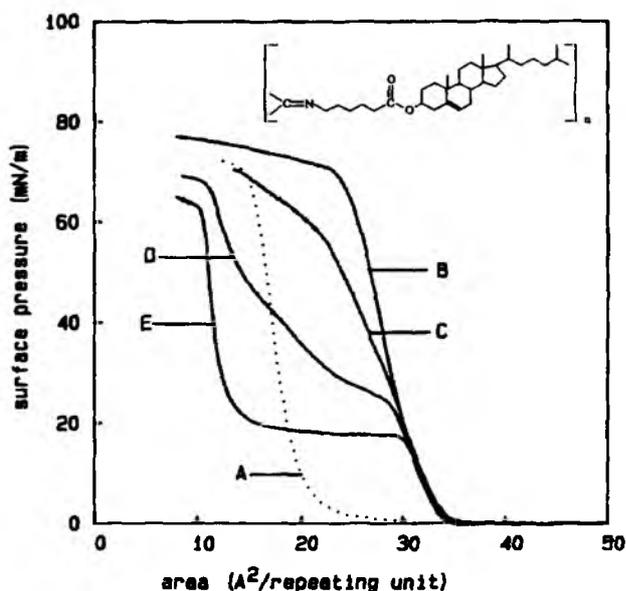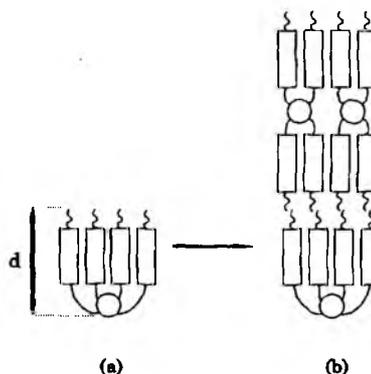
Fig. 2. Schematic visualization of a monolayer (A) of PCIH, which is transformed into a bilayer (B) at higher pressures.

depicted in Fig. 2b. The top layer resembles the liquid-crystalline bulk structure as proposed by van Walree et al. [12].

3.2. Stabilization and transfer

The ester functions in PCIH seem to have enough interaction with the subphase to form stable layers despite the presence of the large hydrophobic cholesterol groups. However, during stabilization of a layer of PCIH at constant pressure of 12 mN/m, the film area was observed to increase. This was not only the case if a pressure was applied. Recording an isotherm after leaving the applied film for 16 h at an area of 160 Å^2/repeating unit before film compression is commenced, also showed a shift to a larger area per repeating unit. Diluting the spreading solution from 0.85 mg/ml to 0.085 mg/ml also led to higher areas. A control experiment using the same amount of pure solvent, did not show any pressure build up after waiting for 16 h. It is not clear yet what factors are responsible for this unexpected thin film behaviour. Despite all this, the layers could be transferred to all kinds of substrates with constant Y-type transfer (transfer ratios: up 1.0 and down 0.7). A stable state is also found after the transition, at $T = 48$ °C, and for example at $\pi = 40$ mN/m. Deposition from this state onto various solid substrates failed, however, probably because the layer is too rigid.

3.3. Infrared spectroscopy

Multilayers were built on substrates for TM and GIR FT-IR measurements. The in-plane linear dichroism, measured from a ZnS plate coated on two sides with 40 layers of PCIH ($\pi = 12$ mN/m; $T = 20$ °C), revealed an alignment of the polymer molecules. Figure 3 shows the difference of two transmission spectra in which the polarization of the IR light is parallel and perpendicular to the dipping direction, respectively. The C=N

Fig. 1. Pressure-area isotherms of PCIH. Spreading solvent chloroform; 19.9 °C curve A. Spreading solvent toluene; 10.8 °C curve B; 20.0 °C curve C; 33.0 °C curve D; and 48.0 °C curve E. Speed of compression is 5 Å^2/(repeating unit min) in all cases.
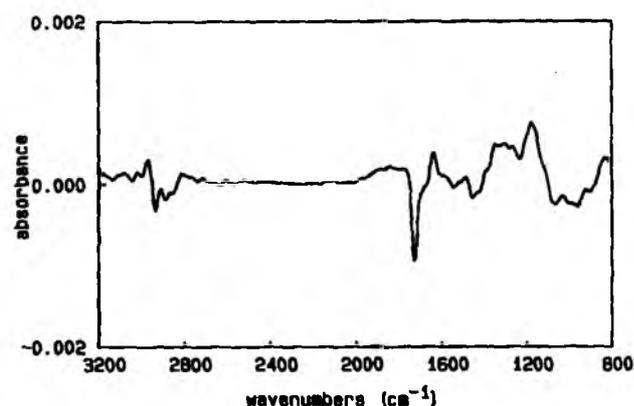
Fig. 3. Difference of the transmission spectra with different directions of polarization of the IR light. Plotted is the absorbance of light polarized perpendicular to the dipping direction of the substrate minus the absorbance of light polarized parallel to this direction. Sample: ZnS deposited on two sides with 40 layers of PCIH.
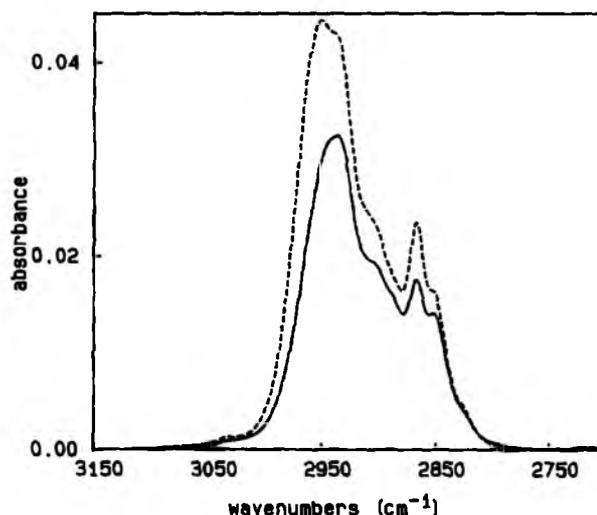

Fig. 4. Infrared spectra of PCIH. Transmission spectrum (———) of a sample, deposited on two sides with 40 layers on ZnS, with the polarization direction of the IR light perpendicular to the transfer direction. GIR spectrum (----------) of 40 layers of PCIH deposited on gold (p-polarization).

bonds have an orientation perpendicular to the polymer main helix. The observed positive absorption at 1637 cm^{-1} (ν(C=N)) in this case indicates that the polymer rods have a preferred orientation which is parallel to the dipping direction. The dichroic ratio is not as high as in the case of PAMEIC. This is probably due to the fact that the two polymers have different aspect ratios. The length, L, of the polymer helix is determined by the degree of polymerization which is 240 and 61 for PAMEIC and PCIH, respectively. The lower degree of polymerization and the more bulky side group of PCIH results in a smaller aspect ratio of $L/D \cong 1-3$ as compared to $L/D \cong 14$ in the case of PAMEIC. Thus, strong orientation effects during the transfer process are not to be expected for PCIH.

The carbonyl stretching vibration at 1735 cm^{-1}, ν(C=O), is oriented preferentially parallel to the main helix. The same orientation of this group was found in PAMEIC [10].

The CH$_3$ groups of cholesterol have a more or less fixed position which is mainly perpendicular to the ring system. The interacting dipole moment of the asymmetric CH$_3$-stretching vibration therefore, is in plane with the cholesterol group. The GIR spectrum of PCIH (40 layers on gold) shows a large CH$_3$ stretching vibration at 2952 cm^{-1}, ν_a(CH$_3$), which is reduced to a shoulder in the transmission spectra (see Fig. 4). This indicates that the cholesterol group has an orientation which is perpendicular to the substrate. The symmetric CH$_2$-stretching vibration at 2853 cm^{-1} is more pronounced in the transmission spectra than in the GIR spectra, which indicates that the corresponding dipole is oriented in the plane of the film. The CH$_2$ groups are mainly located in the C$_5$-spacer groups and in the

tail-groups which suggests that these groups have an orientation perpendicular to the substrate.

3.4. Ellipsometry and SAXS

LB multilayers of PCIH were made on silicon substrates and the thickness of the deposited films was measured by means of ellipsometry. The film thickness appeared to be a linear function of the number of layers deposited. The layer thickness amounted to 25.5 Å per layer, which is in good agreement with the SAXS results of van Walree et al. [12]. They found a spacing of 43.5 Å for two units with interdigitating tails. This corresponds to approximately 25 Å per unit as shown in Fig. 2a.

Small angle X-ray scattering on a 40 layer PCIH coated glass slide revealed a spacing of 45.8 Å which is in line with a Y-type double layer with scattering originating from the electron rich parts, i.e. the double bonds in the ester and isocyano groups.

4. Conclusions

From the experiments presented here we may conclude that a LB monolayer of PCIH molecules exhibits a structure as depicted in Fig. 2a, with the pendant cholesterol groups oriented perpendicular to the subphase. When the surface pressure is increased, a rearrangement of the polymer molecules takes place, probably from a monolayer to a bilayer structure (Fig.

2b). Transfer of the monolayer is possible to different types of substrates. The polymer helices are only slightly oriented parallel to the dipping direction due to the rather small apsect ratio of the molecules.

Acknowledgments

References

1 P. Hodge, E. Khoshdel, R. H. Tredgold, A. J. Vickers and C. S. Winter, *Br. Polym. J.*, *17* (1985) 368.

2 R. Elbert, A. Laschewsky and H. Ringsdorf, *J. Am. Chem. Soc.*, *107* (1985) 4134.

3 S. J. Mumby, J. D. Swalen and J. F. Rabolt, *Macromolecules, 19* (1986) 1054.

4 M. Puggelli and G. Gabrielli, *J. Colloid Interface Sci., 61* (1977) 420.

5 E. Orthmann and G. Wegner, *Angew. Chem., Int. Ed. Engl., 25* (1986) 1105.

6 R. H. G. Brinkhuis and A. J. Schouten, *Macromolecules, 24* (1991) 1487.

7 M. A. Schoondorp, E. J. Vorenkamp and A. J. Schouten, *Thin Solid Films, 196* (1991) 121.

8 W. Drenth and R. J. M. Nolte, *Acc. Chem. Res., 12* (1979) 30.

9 F. Millich, *Adv. Polym. Sci., 19* (1975) 117.

10 M. N. Teerenstra, E. J. Vorenkamp, R. J. M. Nolte and A. J. Schouten, *Thin Solid Films, 196* (1991) 153.

11 M. M. Green, R. A. Gross, F. C. Schilling, K. Zero and C. Crosby, *Macromolecules, 21* (1988) 1839.

12 C. A. van Walree, J. F. van der Pol and J. W. Zwikker, *Recl. Trav. Chim. Pays-Bas, 109* (1990) 561.

13 T. Arndt, C. Bubeck, A. J. Schouten and G. Wegner, *Mikrochim. Acta, 2* (1988) 7.

14 A. J. M. van Beijnen, R. J. M. Nolte, A. J. Naaktgeboren, J. W. Zwikker, W. Drenth and A. M. F. Hezemans, *Macromolecules, 16* (1983) 1679.