LANGMUIR–BLODGETT MONO- AND MULTILAYERS OF POLY(ISOCYANIDE)S WITH DIFFERENT SIDECHAINS

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In this study poly(isocyanide)s, [R—N=CC=], with different sidechains R are used as spreading material to form LB monolayers at the water–air interface. Poly(isocyanide)s are rigid-rod polymers with a stable, helical conformation. One of the aims of this study was to ascertain whether this rigid conformation is sufficient to enable the formation of a stable monolayer on the water surface. We find that different poly(isocyanide)s with non-polar aliphatic substituents are unable to form such stable monolayers. On the other hand, poly((S)-1-acetoxy methylethyl-isocyanide), a polymer which has polar substituents, does form a stable monolayer. This monolayer can be transferred onto all kinds of substrates by Z-type transfer. Multilayer formation is possible with transfer ratios remaining constant up to at least 40 layers. From IR measurements it follows that the polymer helices are preferentially oriented with their main axis parallel to the transfer direction.

1. INTRODUCTION

Langmuir–Blodgett (LB) films of preformed polymers are of interest because it is expected that these polymeric films may have a better thermal and mechanical stability than LB films of low molecular weight materials. Different types of polymer have been used as starting materials and the conditions for stable monolayer formation and for transfer of monolayers onto substrates have been studied in detail. It appears that two types of polymer molecule can form stable monolayers. The first type possesses a molecular structure quite analogous to that of low molecular weight amphiphiles, while the second type has a rigid main-chain structure. In the latter case a new phenomenon in the LB process was observed, which was already known from classic polymer science: during the polymer transfer process a flow-induced orientation of the polymer molecules, along the dipping direction of the substrate, takes place.

At this moment it is not clear which factors are responsible for the stability of...
the monolayer on the water surface, when this monolayer consists of rigid polymer molecules. In some cases it has been proposed that the stiffness of the polymer chains is the determining factor; it is not necessary to assume a specific interaction with the water to explain the experimental results. In other cases, however, such a specific interaction with the water might occur.

\[
\begin{align*}
&\text{R} - N - C - N - C - C - N - C - \ldots \\
&\text{C} - \text{N} - \text{C} - \text{N} - \text{C} - \text{C} - \text{N} - \text{C} - \ldots \\
&\text{R} - N - C - N - C - C - N - C - \ldots
\end{align*}
\]

Fig. 1. Helical structure of a poly(isocyanide) molecule. Repeat unit \( C^3 \) is behind \( C^1 \), \( C^6 \) is behind \( C^2 \), etc.

It is the aim of the present work to study the effect of different sidechains on the stability of monolayers formed from polymers of isocyanides, \([R-N=C]_n\). Polymers of isocyanides are very rigid polymers when their sidechains \( R \), contain an \( \alpha \)-substituent. Without an \( \alpha \)-substituent the polymer chains are flexible coils. The polymer has a 4/1 helical backbone with a pitch of 4.2 Å (see Fig. 1). Monolayers at the air-water interface were studied by their pressure-area diagrams at different temperatures. Stability experiments were carried out by measuring the surface area as a function of time at different pressures and temperatures. Orientational effects in the multilayers were studied by means of transmission- (TM) and grazing incidence reflection (GIR) FT-IR spectroscopy as well as ellipsometry.

2. EXPERIMENTAL DETAILS

Poly(isocyanides) 1–5 (Table I), were synthesized in accordance with known procedures. Starting materials were the corresponding amines, which were formylated with ethylformate or with the mixed anhydride of formic acid and acetic acid. Dehydration of the formamides with phosphorus oxychloride and base provided the isocyanides which were polymerized using nickel(II) chloride as the catalyst. \( N \)-formyl-2-butylamine was converted into the isocyanide by the method of Casanova but at a lower pressure (0.5 mmHg) than recommended. The physical properties of the polymers as determined by IR, proton nuclear magnetic resonance (\(^1\)H-NMR) and elemental analyses were in accordance with literature data.

Monolayer properties were studied by measuring pressure-area isotherms on a computer-controlled Lauda Filmbalance (FW 2) with water, purified by a Milli-Q filtration system, as the subphase. Polymers were dissolved in chloroform (spectroscopic quality), max. 0.1 wt.%, and isotherms were recorded at a speed of 5 Å\(^2\) (repeating unit)\(^{-1}\) min\(^{-1}\) at different temperatures. Glass slides and silicon wafers,
TABLE 1
POLY(ISOCYANIDE)S USED FOR LANGMUIR–BLODGETT FILM FORMATION

<table>
<thead>
<tr>
<th>Polymer</th>
<th>( -[C(=N-R)]_x-[C=N-R']_y )</th>
<th>( 10^{-3} \times \bar{M}_n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>R</td>
<td>R'</td>
<td>x</td>
</tr>
<tr>
<td>1 -CH(CH\textsubscript{3})CH\textsubscript{2}CH\textsubscript{3}</td>
<td>-n-C\textsubscript{16}H\textsubscript{33}</td>
<td>0.86</td>
</tr>
<tr>
<td>2 -CH(CH\textsubscript{3})CH\textsubscript{2}CH\textsubscript{3}</td>
<td>-n-C\textsubscript{16}H\textsubscript{33}</td>
<td>0.87</td>
</tr>
<tr>
<td>3 -CH(CH\textsubscript{3})CH\textsubscript{2}CH\textsubscript{3}</td>
<td>-CH(CH\textsubscript{3})CH\textsubscript{2}CH\textsubscript{3}</td>
<td>0.40</td>
</tr>
<tr>
<td>4 -CH(CH\textsubscript{3})(CH\textsubscript{2})\textsubscript{5}CH\textsubscript{3}</td>
<td></td>
<td>1.00</td>
</tr>
<tr>
<td>5 -CH(CH\textsubscript{3})CH\textsubscript{2}O(C\textsubscript{2}H\textsubscript{5})CH\textsubscript{3}</td>
<td></td>
<td>1.00</td>
</tr>
</tbody>
</table>

\(^*\) Vapour-pressure osmometry in toluene at 70 °C.
\(^b\) Membrane osmometry in chloroform at 34 °C.

used as substrates, were cleaned ultrasonically with chloroform, treated with concentrated sulfochromic acid at 80 °C for 2 h, washed several times with Milli-Q water, cleaned again ultrasonically in acetone and in chloroform and finally stored in methanol. Before use the substrate was rinsed with 2-propanol and with chloroform, partially hydrophobized by treatment with a mixture of chloroform and hexamethyldisilazane at 50 °C and finally rinsed with chloroform. Gold substrates were obtained by sputtering a gold layer 500 Å thick onto the cleaned glass slides.

IR measurements were carried out with a Bruker IFS-88 FT–IR spectrometer at 4 cm\(^{-1}\) resolution. The substrates were partly covered with a LB multilayer and the uncovered surface was used as a reference. The FT–IR spectra were recorded by
Fig. 3. Film area as a function of time upon stabilization of polymer 2 (curve A), polymer 3 (curve B) and polymer 4 (curve C). In all cases an equal amount of polymer (base mol.) was applied and the surface pressure was 4 mN m$^{-1}$. The temperature in all cases was 15°C.

the method of Arndt$^{19}$; cycles of 200 scans were used. Film thicknesses were measured using a Gaertner L117 production ellipsometer.

3. RESULTS AND DISCUSSION

Poly(2-butylisocyanide) is too insoluble to be studied by the LB technique. Copolymers of 2-butylisocyanide and long-chain alkylisocyanides (Table I), however, are soluble and can be studied. Figure 2 shows the isotherms of two copolymers (1 and 2) of 2-butylisocyanide and n-hexadecylisocyanide. For both copolymers a gradual, slow increase of the surface pressure upon compression is observed. Determination of the occupied area per repeating unit by extrapolation to zero pressure was not possible. Stabilization experiments gave no positive results (Fig. 3, curve A). It can be concluded that polymers 1 and 2 are not able to form stable monolayers and transfer experiments cannot be performed. Figure 4 shows the isotherms of the copolymer of 2-butylisocyanide and 2-octylisocyanide (3) and the homopolymer of 2-octylisocyanide (4) at different temperatures. When these isotherms are compared with the isotherms of polymers 1 and 2 (Fig. 2) marked
differences can be observed. Surface pressure starts to increase at a much larger area per repeating unit and the appearance of a transition is evident. If one calculates the area per isocyanide molecule in the polymer helix shown in Fig. 1, using a helix-pitch of 4.2 Å, one obtains a value of 12 Å$^2$ for the homopolymer of 2-butylisocyanide. This could correspond quite well with the first rise of the surface pressure around 15 Å$^2$ for these polymers (Fig. 4). Figure 4 thus gives the impression that before the first transition the polymer molecules are well spread and that the monolayer is stable. However, stability experiments showed that this is not the case (Fig. 3, curves B and C). We must conclude therefore, that a high degree of stiffness of the polymer backbone is not a sufficient condition for the formation of stable polymer monolayers at the water-air interface. Additional groups which can improve the interaction with the water surface have to be present in the polymer. Such groups are present in polymer 5 in the form of ester functions. Figure 5 shows the isotherms of this polymer at different temperatures. Again a transition is visible, as in the case of the copolymers, but now at a much higher surface pressure ($\pm 25$ mN m$^{-1}$). In contrast with polymers 3 and 4, polymer 5 forms very stable monolayers below this transition (Fig. 6). From Fig. 5 the dimension of the molecular unit in polymer 5 can be calculated to be 16.6 Å$^2$ (repeating unit)$^{-1}$. This value is in good agreement with that obtained from molecular models.

The molecular area of the phase formed initially is independent of temperature. After the transition we observed a temperature dependence and also kinetic effects. Moreover, at high pressures the polymer film is not stable, as can be seen in Fig. 6.
probably a collapse process takes place. Stabilization of a monolayer of polymer 5 is completed within 15 mins at temperatures below 30 °C and pressures up to 25 mN m⁻¹. Constant Z-type transfer of up to at least 40 deposited layers could be achieved in the case of polymer 5, onto all substrates at a dipping speed up to 10 mm min⁻¹. The transfer ratio amounted to 1.0.

3.1. FT-IR spectroscopy

Multilayers were built on silicon and gold substrates for TM and GIR FT-IR measurements, respectively. The spectra were compared with those of films cast from chloroform solutions onto KBr disks (Fig. 7). Large effects due to orientation are observed. The GIR spectrum (Fig. 7, spectrum B) (E perpendicular to substrate) corresponds to the TM spectrum with E perpendicular to t (Fig. 7, spectrum C). This can be explained if the helical polymer is oriented with its main axis parallel to the transfer direction t because only then is the electrical vector E perpendicular to the helical axis in both cases. The difference between the TM spectra with two polarizations of the IR light (E⊥ - E∥ dipping direction, Fig. 8) shows a positive absorbance attributable to the C=N stretching vibration at 1636 cm⁻¹. The carbon–nitrogen bond is oriented perpendicular to the polymer main-chain helical axis, as is known from the structure of poly(isocyanide)ₖ. So from these experiments too it follows that the helices are preferentially oriented parallel to the transfer direction. For a substituted rigid-rod phthalocyaninato-polysiloxane, Bubeck et al. also found an orientation of the polymer rods parallel to the transfer direction. The negative absorbance of the C=O stretching vibration at 1749 cm⁻¹
indicates that this group is mainly oriented parallel to the polymer helix, which is not in contradiction with molecular models. Assuming that the conformation in the LB multilayer resembles the conformation on the water surface, the lone-pairs of the C=O group would point towards the water surface facilitating the formation of hydrogen-bonds, resulting in a stronger interaction with the subphase. The results of the IR experiments are presented in Table II.

**TABLE II**

<table>
<thead>
<tr>
<th>Frequency (cm⁻¹)</th>
<th>Assignment</th>
<th>Orientation</th>
</tr>
</thead>
<tbody>
<tr>
<td>2981</td>
<td>( \nu(C-H) )</td>
<td>( \parallel ) helix</td>
</tr>
<tr>
<td>2940</td>
<td>( \nu(C-H) )</td>
<td>( \perp ) helix</td>
</tr>
<tr>
<td>2900</td>
<td>( \nu(C-H) )</td>
<td>( \parallel ) helix</td>
</tr>
<tr>
<td>1749</td>
<td>( \nu(C=O) )</td>
<td>( \parallel ) helix</td>
</tr>
<tr>
<td>1636</td>
<td>( \nu(C=\equiv N) )</td>
<td>( \perp ) helix</td>
</tr>
<tr>
<td>1389</td>
<td>( \delta(CH_3) )</td>
<td>( \perp ) helix</td>
</tr>
<tr>
<td>1373</td>
<td>( \delta(CH_3) )</td>
<td>( \parallel ) helix</td>
</tr>
<tr>
<td>1252</td>
<td>( \nu(C=O) )</td>
<td>( \perp ) helix</td>
</tr>
<tr>
<td>1047</td>
<td>( \nu(C=O-C) )</td>
<td>( \perp ) helix</td>
</tr>
<tr>
<td>864</td>
<td>( \nu(C-N) )</td>
<td>( \parallel ) helix</td>
</tr>
</tbody>
</table>
It is evident that strong orientational effects are also present in other vibrational modes, probably because the polymer has a rigid conformation. Calculations of the orientation of groups and the main axis of the helical polymer in the LB multilayers are the subject of current investigations.

3.2. Ellipsometry

LB multilayers of polymer 5 were made on silicon and the thickness of the film

Fig. 7. IR spectra of polymer 5: film cast on a KBr disk (curve A), G1R (curve B), TM with polarization perpendicular (curve C) and parallel (curve D) to the transfer direction. Curve B, 18 layers transferred at 20 mN m\(^{-1}\) and 25 °C, curves C and D: same sample with 40 layers on each side of the silicon substrate transferred at 20 mN m\(^{-1}\) and 20 °C.
Fig. 8. Difference spectrum of the two TM spectra with different polarization, spectra C and D of Fig. 7. Plotted is spectrum C minus spectrum D.

Fig. 9. Thickness of an LB multilayer of polymer 5 vs. the number of layers deposited at 20 mN m$^{-1}$ and 15 °C.
was measured by means of ellipsometry. In Fig. 9 the film thickness is plotted vs. the number of layers deposited. The slope of the line amounts to 13.1 Å per layer. At the transfer conditions (σ = 20 mN m⁻¹ and T = 25 °C) the molecular unit occupies 14.0 Å² (Fig. 5) so the diameter of the helix at these conditions is (14.0 × 4/4.2) = 13.3 Å (the pitch of the helix is 4.2 Å, and there are four units in each turn). It can be concluded that the polymer molecules are cylinders because the spacing of the layers is approximately the same as the diameter of the polymer helices.

4. CONCLUSIONS

From the experiments presented here we may conclude that rigidity of the polymer backbone alone is not a sufficient factor for obtaining stable films on the water–air interface. Polar functions, which can interact with the water surface may be required as well.

FT–IR measurements showed preferred orientation of the rigid polymer helices parallel to the transfer direction.

REFERENCES