Formation of an Optically Active Helical Polyisocyanide Langmuir–Blodgett Film

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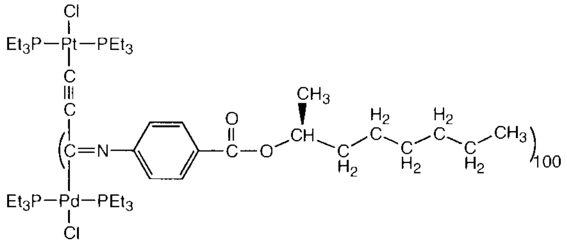
(Received May 1, 2001; CL-010398)

An optically active helical polyisocyanide synthesized with a screw-sense-selective living polymerization formed a condensed monolayer on the water surface and was transferred onto a solid support as Y-type LB film with an ordered orientation.

The helical structures found in DNA and protein are one of the main factors of molecular function. Macromolecular asymmetry originated from the helical structure of a polymer backbone has attracted a great deal of interest.[1] Recently, helical polymers which can form monolayer on the water surface and give ordered LB film have been investigated.[2,3] Here we would like to report an optically active helical polymer Langmuir–Blodgett film constructed from polyisocyanide. Discussion on the molecular orientation of the helical polymer in the LB film with polarized UV absorption and CD spectra were described.

Poly((*S*)-2-octyloxycarbonylphenyl isocyanide) with a polymerization degree of 100 (see below) was synthesized with a screw-sense-selective living polymerization[4,5] from the isocyanide using chiral organotransition metal μ-ethynediyl Pd–Pt dinuclear complex as a catalyst.[6] The helical polymer was spread from a chloroform solution on a water surface to measure the surface pressure (π)–area (A) isotherms at 15, 20 and 25 °C (Figure 1). A steep rise in surface pressure can be seen, and no significant dependence on temperature was observed. Clearly this polymer forms a stable and condensed monolayer on the water surface. The limiting surface area per monomer unit of the polymer is determined to be 0.24 nm^2. It is known that poly(isocynide)s have a 4/1 helical structure,[7–9] thus the average area per helical unit on the water surface is calculated $0.24 \times 4 = 0.96$ nm^2.



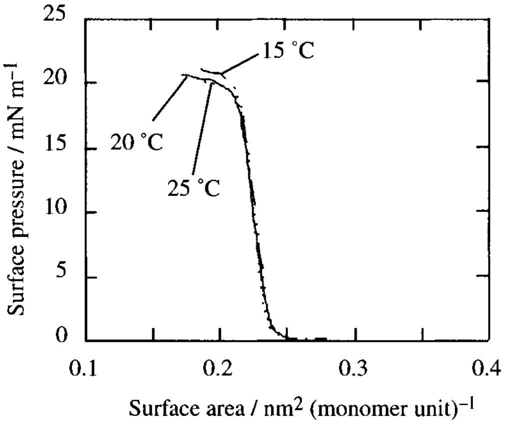


Figure 1. Surface pressure (π)–area (A) isotherms of polymer at various subphase temperatures.

The monolayer on the water surface can be transferred onto a hydrophobic glass plate treated by dichlorodimethylsilane by a vertical dipping method under a surface pressure of 14 mN m^{-1} in up- and downward strokes with a transfer ratio of 1.0. The UV absorption spectra in LB films with various deposited layers are shown in Figure 2. The spectrum of the LB film is resemble to that in chloroform solution. It means that there are no special aggregation and stacking of the conjugated unit between the adjacent layers and in the same layer in the LB films. The absorbance at 199 nm and 254 nm in the LB films increases linearly with increasing number of deposited layers. A linear relationship between the absorbance and the number of layers indicates regular deposition of the monolayer onto solid support.

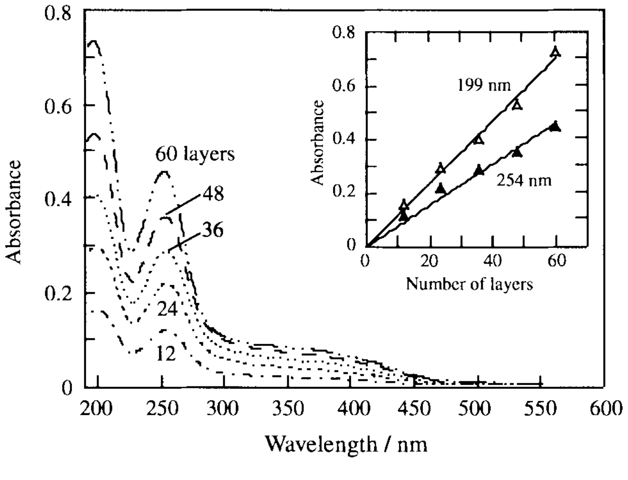
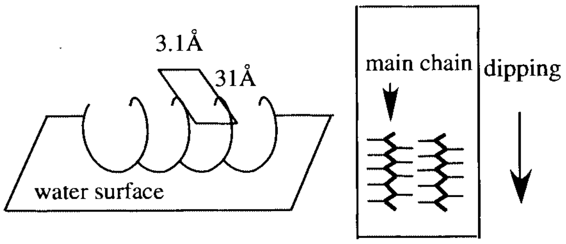


Figure 2. UV absorption spectra of polyisocyanide LB films as a function of deposited layers.

The X-ray diffraction spectrum (XRD) of the LB films consisting of well-defined Kiessig fringes and Bragg peaks indicates the layer structure with a spacing of 31 Å, which corresponds to the diameter of the helix. These results agree with the film thickness estimated from the CPK model, where the side chain is oriented perpendicular to the main axis of the helical cylinder and assuming slight interdigitation of the side chains.

Considering that the section area of one helical unit determined from the π–A isotherm is 96 Å^2 and the diameter of the helix determined from the X-ray diffraction is 31 Å, we can calculate the pitch of the helix as 3.1 Å. This data is smaller than that (4.2Å) in the powder of poly(phenethyl isocynide).[5] We think that this polyisocyanide takes more condensed monolayer on the water surface by compression and keeps the same form in the LB film.



In order to obtain an information about the orientation of polymer backbone in the LB films, the absorption dichroism measurement was carried out for the LB film with 60 layers deposited on a hydrophobic quartz glass. The absorption spectra were measured by using polarized light parallel or perpendicular to the direction of dipping (Figure 3). The absorbance of the perpendicular polarized light was stronger than that of parallel polarized light. Considering the structure of helical polymer, the side chain extends at the peripheral position of the helix core when the main chain roll up as a helix. The absorbance at 199 nm and 254 nm can be assigned to –C=N and phenyl group and the transition moment is perpendicular to the axis of helical cylinder. We can say that the side chain of the helical polymer is almost perpendicular to the direction of dipping as shown above, and the axis of helical cylinder is laid in the direction parallel to the dipping direction. This orientation is caused by flow orientation of the rigid polymer monolayer on the water surface at the deposition onto solid support.

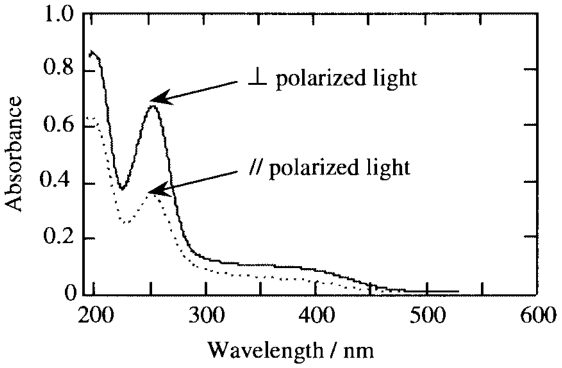


Figure 3. UV absorption spectra of poly(isocyanide) LB film (60 layers) with parallel and perpendicular polarized light as an incident light.

The formation of optically active LB films based on helical polyisocyanide is confirmed by CD (circular dichroism) spectral measurement (Figure 4). The film exhibited a unique curve and a large Cotton effect which arises from the helical chirality of polymer skeleton. We can see that the chirality is maintained well in LB films.

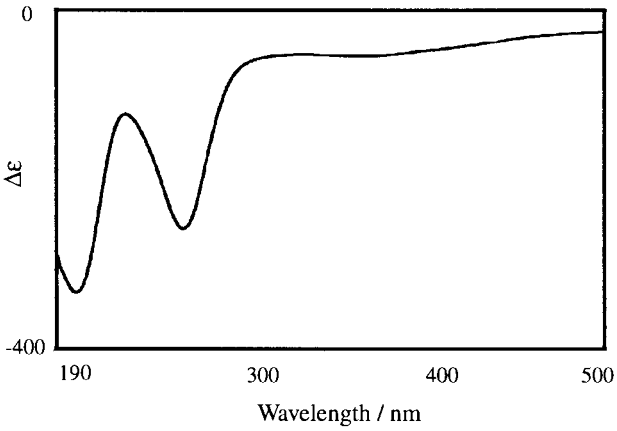


Figure 4. CD spectrum of polyisocyanide LB films with 30 layers.

In conclusion, the optically active helical polyisocyanide forms a stable and condensed monolayer on the water surface, and it can be transferred onto solid supports in both up- and downward strokes with unity ratios. The helical backbone of polymer orients with the helical axis parallel to the direction of the dipping.

References and Notes

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