Langmuir-Blodgett films of unidirectionally aligned α-helical diblock copolypeptides

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Summary

Ultra-thin films of unidirectionally oriented α-helical polypeptides have drawn enormous attention due to their intriguing electro-optical properties arising from the large degree of polar order they exhibit. In this respect, thin films of hairy-rod polypeptides are of particular interest. Besides the rigid-rod feature, the liquid-like properties of the surrounding amorphous side chains make them attractive as matrices for embedding and orienting dyes, transporting charge carriers in photoconductive devices as well as optical recording and storage materials.

The surface grafting method has been widely used to orient the α-helical chains of polypeptides at interfaces. However, the disadvantage of the surface grafting process is the difficulty in analyzing the grafted polymers.

An alternative way to prepare functional ultra-thin polymer films with controlled directional properties is by combining the Langmuir-Blodgett (LB) technique with the unique properties of polymer brushes. This thesis is devoted to the study of α-helical poly(α-L-glutamic acid)-b-poly(γ-methyl-L-glutamate-ran-γ-stearyl-L-glutamate) with 30 mol% of stearyl substituents (PLGA-b-PMLGSLG) amphiphilic diblock copolymer for the fabrication of α-helical double-brush LB monolayers. These ultra-thin films combine the unique properties arising from the unidirectionally aligned helix macrodipole and the liquid-like features of the side chain mantle of the PMLGSLG block. Such systems are promising for thin film applications requiring incorporation and orientation of bio- and optical molecules.

Scheme 1. Schematic representation of the double-brush structure of the PLGA-b-PMLGSLG monolayer.
In the first chapter of this thesis a brief introduction to polypeptides and block copolymer synthesis as well as approaches to orient polypeptide chains at interfaces is given. Especially the construction and properties of Langmuir and LB films of α-helical polypeptides are emphasized.

Chapter 2 reports on the synthesis of the PLGA-b-PMLGSLG diblock copolymers via a diblock copolymer precursor consisting of poly(γ-tert-butyl-L-glutamate) (PtBuLG) and PMLGSLG blocks, with the tert-butyl group as a mild acid-labile protecting group for the carboxylic acid. The primary amine-initiated N-carboxyanhydride polymerization method was employed. Depending on the nature of the amino acid residue, synthetic polypeptides can be obtained in different conformations (α-helix or β-sheet). The effects of reaction conditions (solvent, monomer concentration, temperature) on the helicity of the diblock copolypeptides were studied. Optimal conditions to successfully synthesize completely α-helical diblock copolypeptides were found. Diblock copolymers of PLGA-b-PMLGSLG with close-to-designed molecular weights and small polydispersities were obtained and characterized in detail.

The monolayer behavior of α-helical PLGA-b-PMLGSLGs at the air-water interface is investigated in Chapter 3. The study of Langmuir monolayers and LB films of these diblock copolymers by surface pressure-area (π-A) isotherms, Brewster angle microscopy, circular dichroism, transmission FT-IR and X-ray reflectivity demonstrated the formation of a stable α-helical double-brush structure, with the helices tilted away from the substrate surface.

Chapter 4 evaluates the surface potentials of the α-helical amphiphilic diblock copolypeptides of PLGA-b-PMLGSLG of various block lengths during monolayer compression at the air-water interface. The effective dipoles and influence of the monolayer helix length vertically aligned at the air-water interface were experimentally assessed for the first time. The reorientation of water molecules on monolayer spreading was found to be significant, resulting in a large initial surface potential of hundreds of mV generated by the water. Upon tilting of the PMLGSLG block away from the water surface during monolayer compression, the cancellation of the dipole moments of water molecules generated upon monolayer spreading and probably a change in local relative permittivities during molecular packing led to a gradual decrease in the derived effective molecular dipole moment of the monolayer. The molecular dipole contributions, dependent on the conformation and orientation of the polar groups (peptide groups and ester and terminal methyl groups in the side chains) are not readily distinguished and can change significantly during the compression of the monolayer. Nevertheless, the results showed that while the peptide dipoles of the α-helical hydrophilic block immersed in the sub-phase were effectively screened by the water, the screening effects on the peptide dipoles of the α-helical hydrophobic block appeared to be negligible. The effective
dipoles of the α-helical hydrophobic block tilted away from the water surface were significantly maintained and increased with increasing hydrophobic block length.

Chapter 5 deals with the analysis of the average helix tilt angles, estimated separately for the two blocks, of the PLGA-b-PMLGSLG diblock copolymers in Langmuir and LB monolayers using different methods, including π-A isotherms, transmission FT-IR and X-ray reflectivity. In particular, the effect of chain length on the helix orientation of α-helical diblock copolypeptides of PLGA-b-PMLGSLG in Langmuir and LB monolayers is reported for the first time. Monolayers of PLGA-b-PMLGSLGs of various block lengths were deposited onto silicon substrates at maximum transfer pressures. The hydrophobic block length was found to strongly affect the helix orientation of the diblock copolypeptides. Increasing the degree of polymerization of the hydrophobic block (DP_{PMLGSLG}) resulted in an increase in the average tilt angle between the helices and the surface normal. The observed effect might tentatively be attributed to the interactions of the off-axis components of the unscreened peptide dipoles between the parallel aligned α-helices. In addition, the results might also suggest that for small values of DP_{PMLGSLG} (≤ 39), monolayers of PLGA-b-PMLGSLGs exhibit a smectic C-like phase already at the beginning of and throughout the double-brush formation regime (after the immersion of the hydrophilic block in the water sub-phase). For larger values of DP_{PMLGSLG}, the PMLGSLG helices are tentatively oriented isotropically around the water surface normal with an average helix tilt angle and undergo a transition to a smectic C-like phase upon compression to high surface pressures. In particular, when DP_{PMLGSLG} is very small (i.e.11), the α-helices of the PMLGSLG block are oriented nearly perpendicular to the interface and the long alkyl side chains are partially expelled from the brush layer.

Interestingly, we observed strong effects of in-plane anisotropy produced by the transfer process in the LB monolayers of the PLGA-b-PMLGSLG diblock copolymers. The azimuthal helix orientation of PLGA-b-PMLGSLGs in LB monolayers and the influence of dipping conditions were investigated using polarized transmission FT-IR in Chapter 6. Particularly, by manipulating the dipping position relative to the previous transfer, an azimuthal alignment of the α-helices in the transferred films either parallel to or tilted by an angle of 45° with respect to the dipping direction can be obtained. This observed phenomenon originates from the flow history retained in the compressed monolayer and arises mainly from the deformation of the PMLGSLG top brush layer upon transfer.

In Chapter 7, the helix orientation in the LB monolayers of PLGA-b-PMLGSLGs was further manipulated by annealing, taking advantage of the PLGA block containing the side chain carboxylic acid groups capable of forming hydrogen bonds and the mobility of the side chain mantle of the PMLGSLG block. Due to the increased interactions between the carboxylic groups of the PLGA segments upon annealing, the surface shrinkage of the films occurred with an
increase in both film thickness and density. As a result of the side chain melting and surface constraint, the PMLGSLG block helices became less tilted to the substrate-normal.

In summary, the results presented in this thesis have demonstrated the successful fabrication of double-brush ultra-thin films of diblock copolypeptides with a high degree of polar order. Different physico-chemical phenomena concerning fabrication and manipulation of the molecular orientation of these films have been explored in order to fully understand and control the film structure and properties. The directional properties and the liquid-like matrix provided by the amorphous stearyl side chain make these films suitable for functionalization with various bio- and optical molecules. The work of this thesis paves the way for further studies of the system as functional materials.