

PLL-g-PEG monolayers on SiO₂: investigation of layer thickness and water content

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Poly(L-lysine)-graft-poly(ethylene glycol), PLL-g-PEG, a polymer able to render metal oxide surfaces protein-resistant when adsorbed with sufficiently high surface coverage, has been measured in the adsorbed state on SiO₂ by in situ neutron reflectometry. Information about polymer layer thickness and water content of these layers has been obtained. However, the investigation of such thin layers (< 5 nm) reaches the limit of the technique and interpretation of the results should be done with care.

Non-specific protein adsorption is undesirable in implant and biosensor applications since it can lead to implant rejection or impede the sensitive detection of specific molecules in the latter case. Thus the production of protein-resistant surfaces is of considerable interest. Poly(L-lysine)-g-poly(ethylene glycol) (PLL-g-PEG) is a recently developed co-polymer that adsorbs on negatively charged surfaces through the amine groups in its backbone. The possibility to synthesize polymers with different architectures by varying the molecular weight of both components (PLL and PEG) as well as the grafting density offers the advantage of having a variety of polymers with different types of interactions with biological surroundings. The investigation of the triangle "polymer architecture – polymer conformation – water content in the polymer layer" is an attempt to get a clearer picture of the protein repellence mechanisms.

Co-polymers consisting of a PLL backbone (20 resp. 300 kDa) and PEG chains (2 resp. 5 kDa) grafted to the backbone were used. Grafting densities were varied between 2.1 and 3.5 lysine monomers per PEG chain. Adsorption on a 1 cm thick Si block was performed in HEPES buffer solution of defined ionic strength (1 resp. 10 mM NaCl). After half an hour adsorption followed by thorough rinsing with D₂O, measurements were performed in a D₂O (1 resp. 10 mM NaCl).

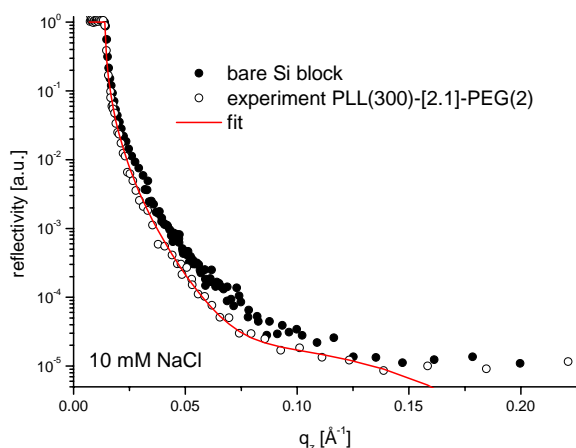


Figure 1: Reflectivity curve of PLL(300)-[2.1]-PEG(2), 10 mM NaCl, model fit and bare Si as reference.

The oxide layer thickness of the bare Si surface was determined to be 0.87 nm. Analysis of the total reflection edge at low q_z values when polymer was adsorbed indicated the presence of about 5 vol-% of H₂O in the bulk solvent.

This is attributed to H₂O that is strongly bound to the PEG chains. As a consequence, the scattering length density (SLD) for the solvent was corrected from the pure D₂O value to $6.02 \cdot 10^{-6} \text{ \AA}^{-2}$. The polymeric layer was modeled by fitting for its thickness and SLD, the latter quantity allowing the estimation of hydration by interpolating the SLD's of pure PEG and pure solvent. A typical fitting curve is shown in Fig. 1. The background in the spectra is around 10^{-5} , which explains the deviation seen between fit and experiment for q_z -values $> 0.14 \text{ \AA}^{-1}$. Fitting results are summarized in Tab. 1.

Table 1: Thickness d and hydration of PLL-g-PEG layers adsorbed on SiO₂.

Polymers	salt [mM]	d [Å]	SLD [Å ⁻²]	hydration [vol.-%]	χ^2 -
PLL(20)-[3.5]-PEG(2)	10	38.6	5.05E-06	82	0.053
PLL(20)-[3.5]-PEG(2)	1	39.7	5.48E-06	90	0.052
PLL(300)-[2.1]-PEG(2)	10	46.3	5.33E-06	87	0.062
PLL(300)-[3.2]-PEG(2)	10	49.1	5.56E-06	91	0.060
PLL(300)-[3.2]-PEG(2)	1	50.6	5.59E-06	92	0.082
PLL(300)-[2.1]-PEG(5)	10	38.2	5.44E-06	89	0.068

There is a distinct difference in layer thickness between PLL(20) and PLL(300) co-polymers of similar architecture. The higher values for long PLL may be explained by an inhomogeneous distribution of the PLL segments perpendicular to the surface, whereas the PLL(20) polymers are supposed to lay flat on the surface. The polymer PLL(300)-[2.1]-PEG(5) is known to adsorb differently due to steric effects (combination of long PEG chains and high grafting densities), which explains the rather small thickness values despite high PEG molecular weight. Ionic strength effects are only seen for the PLL(20) polymer, where hydration is larger at low salt, probably due to a more open structure of the PEG chains. For the PLL(300) polymers, no salt effect is seen since the inhomogeneous adsorption of these polymers seems to be the dominating effect.

Generally it must be noted that by investigating of such thin polymeric layers, one reaches the limits of this technique. Thus, results should be backed up by other techniques and interpreted with care.

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