GISAXS and x-ray reflectivity of DNA-surfactant films

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DNA is a negatively charged polymer and it has the ability to interact with many molecules through its charged phophate groups and its base pairs. Therefore it might be used as a template for selfassembled nanostructures [1]. The structure of a complex introduced by mixing of double stranded NaDNA ($M_W \approx 1.3 \cdot 10^6$ from salmon testes) with didodecyldimethyl ammonium bromide in water (1:1 ratio) was studied at the beamline W1.1 using grazing-incidence small-angle x-ray scattering (GISAXS) and x-ray reflectivity. The DNA-surfactant films were made by dissolving the washed and vacuum dried complex into ethanol after which the solution was spin coated on a Si (100) surface. The films are insoluble in water.

The GISAXS intensity was measured at photon energy of 8048 eV obtained using a Si (111) double crystal monochromator. The beam size was 0.5×0.1 mm^2 at the sample position. A Molecular Dynamics image plate was used as the detector at a distance 31 cm from the sample. The used incident angle $\alpha = 0.155°$ was larger than the critical angle. Reflectivity measurements were made with a scintillation detector with beam size 1×0.1 mm^2. To reduce air scattering the sample chamber was filled with helium and the beam stop was placed inside the chamber. The films were moisturized with de-ionized water for a few minutes and the excess water was poured away just before measuring. During the measurements the chamber moisture content was kept as close to 100% as possible.

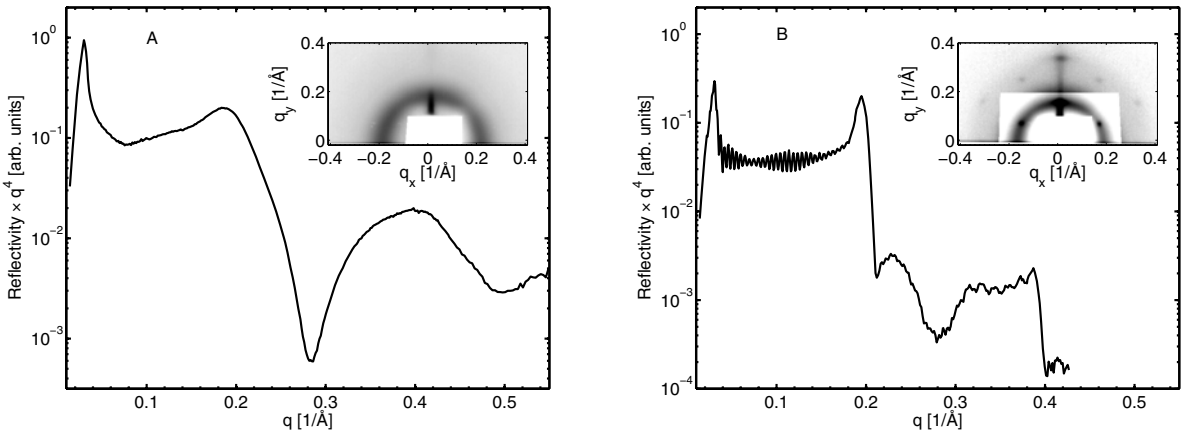

Figure 1: Reflectivity on dry (A) and moisturized (B) DNA-surfactant films (not from same sample). The inserts show the GISAXS patterns of corresponding samples. Length of scattering vector is defined $q = 4\pi \sin\theta/\lambda$. In B the most intensive center part of the GISAXS pattern is multiplied by a factor of 0.2 in order to show more clearly the reflections at higher q.

From reflectivity curves it was possible to determine the film thickness (100 – 200 nm), packing of structural units, and the form factor of the structural units. From the GISAXS patterns it was possible to determine the packing and orientation of the structural units. A clear difference was found in the orientation of the structures in a dry film and a moisturized film. With GISAXS the structure of the DNA-surfactant complex in dry state was found to be unoriented and for example lamellar or hexagonal packing could not be determined from the pattern (Fig. 1, A). Reflectivity revealed that the sample contained cylinders of about 1.3 nm in radius, which is the radius of DNA in A-form.

In the moisturized DNA-surfactant films a hexagonal packing of cylinders was observed, but still an unoriented halo remained in the pattern (Fig. 1, B). Probably there are entangled chains that were not oriented in spin coating due to the thickness of the films and the large molecular weight of the used DNA. Reflectivity in Fig. 1 (B) of the moisturized film is very similar to that observed for hexagonally packed surfactant templated silica thin films [2]. From the minima of the cylinder form factor the moisturized DNA-surfactant film was deduced to contain cylinders of radius 1.7 nm while the lattice parameter of the hexagonal packing was 3.7 nm. This leaves a space of 0.3 nm between the cylinders. The radius of the cylinders indicate that the structure could be reversed hexagonal. For the moment it is unclear whether the minimum at about 0.28 Å^{-1} is due to non-moisturized part of the film or not. Another explanation would be for example incomplete complexation of the DNA-surfactant complex.

The lack of orientation and ordering of the DNA cylinders in the dry DNA-surfactant film indicates that water is an essential part in the ordering in this system. The entanglement of the DNA-molecule in dry state will most likely induce partial denaturation and breaking of the hydrogen bonds between DNA base pairs. This might limit the possible applications of DNA-surfactant thin films in dry state if perfect intercalation of molecules between the base pairs is needed.

References

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