Rheo-NR to study the ordering of soft polymer crystals at the solid-liquid interface

Tim GÜNTER[1], Franz ADLMANN[1], Ayan SAMANTA[2], Judith HOUSTON[3], Sarah ROGERS[4], Masako YAMADA[5], Apostolos VAGIAS[6], Philipp GUTFREUND[6], Max WOLFF[1]

[1] Department of Physics and Astronomy, Uppsala University, Sweden
[2] Department of Chemistry, Uppsala University, Sweden
[3] European Spallation Source ESS, Lund, Sweden
[4] ISIS Neutron and Muon Source, Didcot, UK
[5]J-PARC Center, KEK, Tōkai, Japan
[6]Institut Laue-Langevin (ILL), Grenoble, France

Soft crystalline structures are of great importance in many applications that improve human life on a day-to-day basis. Some examples include engineering of human tissue constructs [1]. They are particularly suitable in this environment because of their good biocompatibility and low toxicity as well as their tunable viscoelastic properties. The exact formulation can be varied by variables, such as temperature or ionic strength, to achieve desired properties. Soft crystals have a complex microstructure; therefore, a detailed understanding of how molecular and crystalline structure influence their viscoelasticity is of large interest. One example for polymers forming soft crystals in solution are polyethylene-glycol(PEG)-polypropylene-glycol(PPG)-PEG triblock copolymers, which can self-assemble into micelles in aqueous solution. The bulk properties of such systems have been extensively studied by rheology and scattering experiments, most notably by Small-Angle Neutron Scattering (SANS) [2]. However, close to an interface the structure differs from the bulk, which is less well studied.

In this work we employ in situ-Rheo-Neutron Reflectometry (Rheo-NR) to get insights into the effect of shear on the near surface structure of micellar crystals close to solid substrates [3]. We systematically study the ordering process of the triblock polymer Pluronic F127 in aqueous solution. Rheological parameters, such as shear rate, are found to have a decisive impact on the specular scattering intensity of the 111-Bragg peak as well as the off-specular scattering. A low shear rate seems to support alignment of the lattice planes along the interface, whereas high shear rates result in melting of the crystal. For temperatures near the thermo-gelling point and low shear rates, a coexistence of cubic close packing and hexagonal close packing could be observed, which disappears with higher shear rates. Apart from shear we study the influence of surface energy and temperature on the near surface order. A highly hydrophobic surface and a highly hydrophobic surface cause better alignment, whereas a surface of intermediate hydrophobicity shows worse alignment.

[1] H.-W. Kang et. al., Nature Biotechnology, 34 (3), 312 (2015)
[2] C. R. López-Barrón et. al., Physical Review Letters, 108, 258301 (2012)
[3] M. Wolff et. al., Langmuir, 24, 11331-11333 (2008)

E-mail of the corresponding author: tim.gunter@physics.uu.se