# Experimental report

08/02/2016

**Proposal:** **9-11-1752** **Council:** 4/2015

**Title:** Swelling and switching of doubly thermo-responsive diblock copolymer films

**Research area:** Soft condensed matter

**This proposal is a new proposal**

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**Samples:** poly(N-ispropylacrylamide)-block-4-((3-methacrylamidopropyl)dimethylammonio)butane-1-sulfonate)

| Instrument | Requested days | Allocated days | From | To |
|---|---|---|---|---|
| D17 | 4 | 3 | 09/11/2015 | 12/11/2015 |

## Abstract:

In a set of recent experiments we have investigated the swelling and switching of thermo-responsive homopolymer and copolymer films, which exhibit a lower critical solution temperature (LCST) type phase transition from a swollen to a collapsed chain conformation. Such films are nano-scale sensors. The thermal response of these sensor films to e.g. a temperature change from below LCST (23 °C) to above LCST (45 °C) showed an unexpected behavior, which has been related to the chain collapse and water release, relaxation and reswelling. In the proposed experiment we want to increase the complexity of the thermos-responsive films by using doubly responsive films instead of the previously addressed singly responsive films. The novel diblock copolymer has a LCST and an UCST type block and undergoes two phase transitions with increasing temperature. At the instrument D17 we are able to follow the kinetic of the transition from a swollen to a collapsed hydrogel film with neutron reflectivity with a time resolution of 10 seconds! Deuterated water (D2O) is used to achieve a high contrast.

# Swelling and switching of doubly thermo-responsive diblock copolymer films (9-11-1752)

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The collapse transition of polymers with a lower critical solution temperature (LCST) in aqueous environment is of great interest for a number of purposes where a strong change of volume is needed when a small change of a given stimulus, like the temperature or the ionic strength, occurs. Such thermo-responsive polymers are of huge importance for applications in thin films, such as nano-sensors, artificial muscles, valves, light modulation systems and optical switches. In this context, the polymer, which received most attention so far, is poly(*N*-isopropylacrylamide), PNIPAM [1-4]. It exhibits an LCST of about 32 °C. Combining this LCST switching behavior with another stimuli-responsiveness, such as an upper critical solution temperature (UCST) behavior, can significantly increase the richness of the thermal response of the polymer, due to the presence of two phase transitions. Our collaboration partners have recently proven that such doubly thermo-responsiveness is achieved in diblock copolymers for which a PNIPAM block is combined with a poly(sulfobetaine) block [5]. For such polymers, different states of fully swollen, partially collapsed and partially dehydrated chains, as well as fully collapsed chains can be observed in aqueous solution in dependence of temperature.

For our neutron reflectivity (NR) investigations, we prepared thin films of $PSBP_{78}$-*b*-$PNIPAM_{400}$ on silicon substrates, where PSBP stands for 4-((3-methacrylamidopropyl) dimethylammonio) butane-1-sulfonate. Thin films were prepared out of trifluoroethanol on pre-cleaned silicon supports [6]. The NR measurements were performed at the instrument D17 at ILL. With the two dimensional neutron detector of the D17 reflectometer both, the specular and the off-specular intensity were recorded. As a consequence, the key parameters such as film thickness, film roughness and solvent penetration were obtained [2-4]. The NR curves were recorded during the kinetics of swelling, collapse and rehydration of the thin films with a very high time resolution between successive reflectivity measurements of down to 5 s. One fixed incident angle and TOF mode were used in these kinetic studies.

The measurement protocol for the $PSBP_{78}$-*b*-$PNIPAM_{400}$ films was as follows: First, the initial sample was characterized with a static NR curve (at two incident angles with good statistics). Afterwards, deuterated water was injected in the reservoir of the chamber, so that a humid atmosphere was installed in the chamber, which was kept at 20°C. The swelling of the hydrophilic polymer film was followed with kinetic NR measurements for 4 hours at optimized fixed instrument settings (for recording the kinetics). In order to be able to resolve the initial changes in the film, an extremely high time resolution of 5 s could be chosen for the first 5 minutes. Afterwards it was increased to 10 s in order to achieve better statistics. As the film did not necessarily fully equilibrate after 4 h of swelling, no static NR measurement was performed afterwards. Instead, the temperature was increased from 20°C to 40°C to induce the film switching, and the response of the film was followed with kinetic NR measurements. The same instrument settings were used and the time resolution was again 5 s for the first 5 minutes, and afterwards increased to 10 s. After the film switching the new state was probed with a static NR measurement. This allows characterizing the details of the state in which the switched film had been (film thickness, $D_2O$ enrichment layers in the film, $D_2O$ concentration in the individual layers, surface and interface roughness) after a first temperature jump.

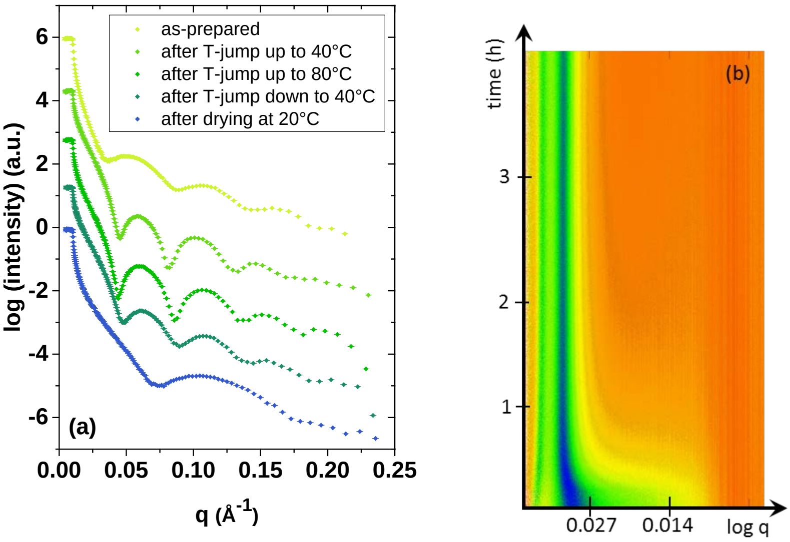

***FIGURE 1:*** *(a) Static NR curves measured for the PSBP$_{78}$-b-PNIPAM$_{400}$ film at the individual points of the switching protocol (curves shifted vertically for clarity). (b) Evolution of the NR curves versus time during the isothermal swelling kinetics at 20°C.*

Immediately afterwards, the temperature was increased to 80°C and the response of the doubly thermo-responsive film (kinetics and statics) was recorded with kinetic NR measurements, according to the protocol as described for the 20°C to 40°C temperature jump. The same holds true for the subsequent jumps to lower temperatures, first back to 40°C and then back to 20°C. The only difference is that here slightly different instrument settings needed to be chosen in order to avoid an oversaturation of the 2D detector because of the $D_2O$ that condensates on the film’s surface. In the last step, the deuterated water was sucked out of the reservoir inside the vapor chamber and the vapor chamber was evacuated in order to remove the remaining deuterated water from the chamber. The influence of this drying, or dehydration, on the structural evolution of the thin film was as well followed with time resolved NR measurements. The whole swelling and switching experiment was finished by recording a final “static” NR curve.

Figure 1 shows examples from the dataset for the $PSBP_{78}$-*b*-$PNIPAM_{400}$ film. Figure 1a depicts the different static NR curves measured for this film. At 40°C, it is expected that the PNIPAM block is collapsed, whereas the PSBP block is swollen (temperature lies above the LCST of the PNIPAM block, and below the UCST of the sulfobetaine block). In agreement, the thickness of this film is larger than for the as-prepared, almost dry film. As expected, the film collapses when heated to 80°C, as the UCST of the sulfobetaine block is passed through. The film properties visibly depend on the history of the sample: both curves recorded at 40°C, once after heating the film to this temperature, once after cooling it to this temperature, do not coincide. It seems that on the one hand the film thickness differs; on the other hand, the film roughness or the water distribution have changed after the whole protocol since then the fringes are less pronounced. After dehydrating the film at 20°C, a much thinner film than the original one remains on the silicon substrate.

Figure 1b depicts one representative dataset recorded during the time-dependent changes of the films, namely that of the isothermal swelling of the as-prepared film at 20°C. The uptake of $D_2O$ by the film is most pronounced during the first hour of the experiment. Indeed, a clear shift of the critical edge occurs, which is more and more determined by that of deuterated water in the course of the experiment. Meanwhile the $D_2O$ does not only occupy available free volume within the film, but also leads to an increase of its thickness, as demonstrated by the slight shift of the fringes to lower q-values.

A detailed data analysis of the whole datasets of the very successful beamtime is currently ongoing, in order to get more quantitative insights into the changes in thickness, $D_2O$ diffusion, and roughness of the doubly thermo-responsive films.

**References:**

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