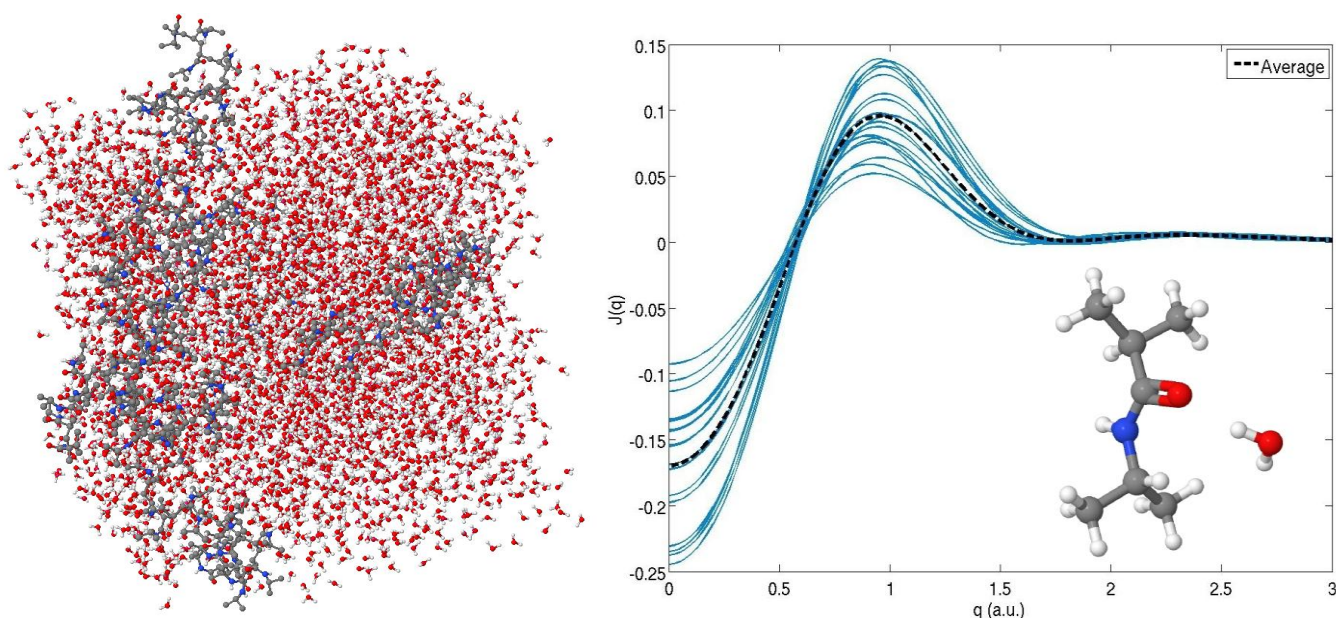
	<b>Experiment title:</b> Phase transition and self-organization of a thermoresponsive polymer	<b>Experiment number:</b> SC 2853
<b>Beamline:</b> ID15B	<b>Date of experiment:</b> from: 28.10.2009 to: 3.11.2009	<b>Date of report:</b> 5.10.2012
<b>Shifts:</b> 18	<b>Local contact(s):</b> Dr. Veijo Honkimäki	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants</b> (* indicates experimentalists): Mikko Hakala, University of Helsinki Iina Juurinen, University of Helsinki* Szabolcs Galambosi, University of Helsinki* Keijo Hämäläinen, University of Helsinki*		

Stimuli-responsive polymers are scientifically and technologically important 'smart' materials, which have the property to react to external conditions, such as temperature, light, pH, the type and ion strength of the solvent. Poly(N-isopropylacrylamide), abbreviated PNIPAM, is a widely studied synthetic thermoresponsive polymer (see e.g. [1-3]). At about 32°C aqueous PNIPAM undergoes a volume phase transition. The transition is very actively studied at both macroscopic and microscopic levels. The scientific question and our objective is the detailed understanding of the influence of the internal microstructure on the thermoresponsive properties. Any increase in this knowledge will improve greatly the design of new functional materials based on PNIPAM. In addition, the knowledge can be straightforwardly used to evaluate the performance of molecular dynamics (MD) simulations methods. The project involves the performed experiment, computational parts and interpretation of the results based on structural models. We carried out the measurements according to the plan outlined in the proposal. Temperature was adjusted above and below the transition temperature (300K and 308K). We used borosilicate glass capillaries in which the aqueous solution of PNIPAM was enclosed. The measurement was done in two concentrations, 0.5% and 5% of PNIPAM in water. In addition, also frozen samples were measured. The analysis of the measured experimental data continues, and preliminary results can be expected within one month. The computational part of the project is divided into various steps. In the first step, classical molecular dynamics calculations were performed for short PNIPAM chains by the Gromacs code. One simulation cell contained multiple chains, in a way that the concentrations used in the experiment were reachable. Figure 1 shows an example simulation cell. From the simulations the pair distribution functions were analyzed

in order to identify the distance of water from the amine group of the polymer. However, we noticed that it may be rather difficult to obtain a representative MD simulation of the real polymer since it contains a large amount of repeated units. Therefore, our plan for the second step of the computational part is to extract from the MD simulations small model systems and perform the Compton profile calculations for them. An example of these calculations is shown in Figure 2, where the effect of the breaking of the hydrogen bond between the oxygen in the side chain of the polymer and water is studied (figure includes as an example a case where the hydrogen bond is intact). Parts of these results have been presented already in conferences [4-6]. The proposed research constitutes the first steps in applying synchrotron inelastic x-ray scattering to understand complex, higher-molecular mass polymers. The project is a new opening towards detecting subtle chemical effects related to polymer topologies and ordering in industrially relevant liquids. Employing the computations, after completing the analysis of the experimental data, we expect to be able to publish the project as a scientific article and as presentations in conferences. The possible journals for reporting the project are Journal of Chemical Physics or Journal of Physical Chemistry.



**Figure 1 (left). Snapshot from the MD simulation of aqueous PNIPAM.**

**Figure 2 (right). Model calculations for Compton profile differences. The curves show how the Compton profiles of isolated PNIPAM and water molecules change when there is a hydrogen bond between the molecules. 20 calculations with the average and an example of the molecular configuration are shown.**

- [1] C. Wu and X. Wang, Phys. Rev. Lett. 80, 4092 (1998). [2] G. Graziano, Int. J. Bio. Macromol. 27, 89 (2000). [3] X.-J. Ju et al., Smart. Mater. Struct. 15, 1767 (2006). [4] I. Juurinen, M. Hakala, S. Galambosi, A. G. Anghelescu-Hakala ja K. Hämäläinen, "Self-assembly of thermoresponsive polymer p(NIPAM)", Physics Days 2010, Jyväskylä, Finland. [5] I. Juurinen, M. Hakala, S. Galambosi and K. Hämäläinen, "Molecular systems in phase transitions", 7th International Conference on Inelastic X-ray Scattering, 2010, Grenoble, France. [6] I. Juurinen, M. Hakala, S. Galambosi ja K. Hämäläinen, "Phase transitions in molecular systems", Hercules 2011, Grenoble, France.