Hydrogels are three-dimensional networks of polymer chains that swell, but do not dissolve in water. With an external stimulus such as temperature or pH, these hydrogels will switch between a collapsed and an extended chain conformation. The collapse transition of polymers with a lower critical solution temperature (LCST) behavior exhibits interesting properties which have a large variety of applications, as drug delivery system [1], valves to control liquid transfer [2]. Recently a very promising new thermo-responsive homopolymer poly-(monomethoxy diethyleneglycol acrylate) (PMDEGA) was successfully synthesized, which exhibits a higher LCST as compared to the frequently investigated thermoresponsive polymer poly(N-isopropylacrylamide) (PNIPAM). PNIPAM has a LCST (at around 32°C) closed to the room temperature, which will limit its use in some tropical countries. In contrast PMDEGA has a higher LCST as compared to PNIPAM, which could be an interesting alternative to the use of PNIPAM. In order to create an internal ordering in the thin hydrogel films of PMDEGA, the homopolymer is replaced by a PMDEGA based tri-block copolymer with polystyrene as end groups, denoted P(S-b-MDEGA-b-S).

It has been known for years that block copolymers can form micelles or aggregates in a selective solvent for one of the blocks as a result of the association of the insoluble blocks. However, most of these studies were focused on polymer solutions. In contrast, our investigation focuses on films. We selected five different solvents (THF, ethanol, 1,4-dioxane, toluene and water) and films were prepared by solution casting on pre-cleaned Kapton foils. In contrast to conventional Si substrates, Kapton foils are flexible substrates and offer the possibility to perform transmission experiments. Aim of the investigation is to understand the influence of the used solvent on the installed morphology of the copolymer containing PS and PMDEGA blocks and to determine the influence on the LCST of the tri-block copolymer films.

Transmission SAXS was performed at the beamline A2 at HASYLAB (DESY). The used wavelength was 0.15 nm and the sample-detector distance was 2.5 m. The polymer films were placed in a small sample cell which was positioned vertically with respect to the direction of the x-ray beam. During the measurement, 0.25 mL D2O was injected into the sample cell and the cell was heated from 30°C to 50°C in steps of 2°C. At every temperature, the sample equilibrated during 10 minutes waiting time followed by 10 minutes counting time to probe the SAXS signal. Due to the small temperature steps 10 minutes equilibration time turned out to be sufficient.

As an example, figure 1 shows the 2D scattering patterns of a P(S-b-MDEGA-b-S) film which was prepared in THF with the temperature increasing from 30°C to 50°C. As expected, all scattering pattern are isotropic. The scattering patterns change strongly in the temperature series due to passing the LCST. The structure of the film changes due to the collapse of PMDEGA chains above LCST. Thus the observed behaviour is very typical for a temperature-sensitive hydrogel.

To get more insights, the 2d SAXS data are radially averaged. Figure 2 shows the comparison of SAXS data of films prepared out of THF (left) and water (right). The phase behavior of these two films shows quite some differences. Because water is a good solvent for PMDEGA, but a poor one for PS, the insoluble PS chains will form the core of the micelles in the water solution, while PMDEGA chains will form the shell of the micelles. In the solution casting of
the aqueous P(S-b-MDEGA-b-S) solution, the structure of the micelles may be frozen-in during the film formation by water evaporation. In contrast, THF is a good solvent for both blocks, PS and PMDEGA chains. As a consequence, no micelle structure is formed. In THF solvent, the LCST region is much broader than in water. In the SAXS data, it can be seen that for both solvents, below LCST the correlation peaks are shifted towards larger values of the scattering vector components $q_z$.

In conclusion, P(S-b-MDEGA-b-S) films prepared out of five different solvents by solution casting were examined with transmission SAXS. For all samples the LCST of the tri-block polymer films is obtained. It turns out that the use of a block-selective solvent will influence the LCST of the film due to the formation of a micelle structure inside the film.

![Figure 1](image1.png)

**Figure 1:** 2D scattering patterns of a P(S-b-MDEGA-b-S) film which is prepared out of THF solvent with the temperature increasing from 30°C to 50°C (passing LCST).

![Figure 2](image2.png)

**Figure 2:** SAXS data of films prepared out of THF (left) and water (right) for temperatures ranging from 30°C to 50°C.

**References**