Study of the gelation process of a thermoreversible gel with rheo-SAXS

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Tri-block polymer are useful as biocompatible materials for biomedical applications. The most and widely studied ampiphilic block copolymers consist of a poly-propylene oxide (PPO) center block and two identical poly-ethylene oxide (PEO) end blocks. These polymers have a high solubility in water at low temperatures and are commercially available by their BASF trade name Pluoronics. With these triblock copolymers, it is possible to make concentrated solutions at low temperatures, when the polymers form coil-like conformations. As the temperatures increases the middle PPO block becomes increasingly hydrophobic, which drives the formation of micelles that can be spherical, cylindrical or wormlike. By varying the gelator composition, molar mass as well as the gelator concentration, the visco-elastic properties can be tuned for the different applications. One of the advantages is that the gelation process can be easily repeated just by changing the temperature, which makes them suitable for drug-release delivery systems.

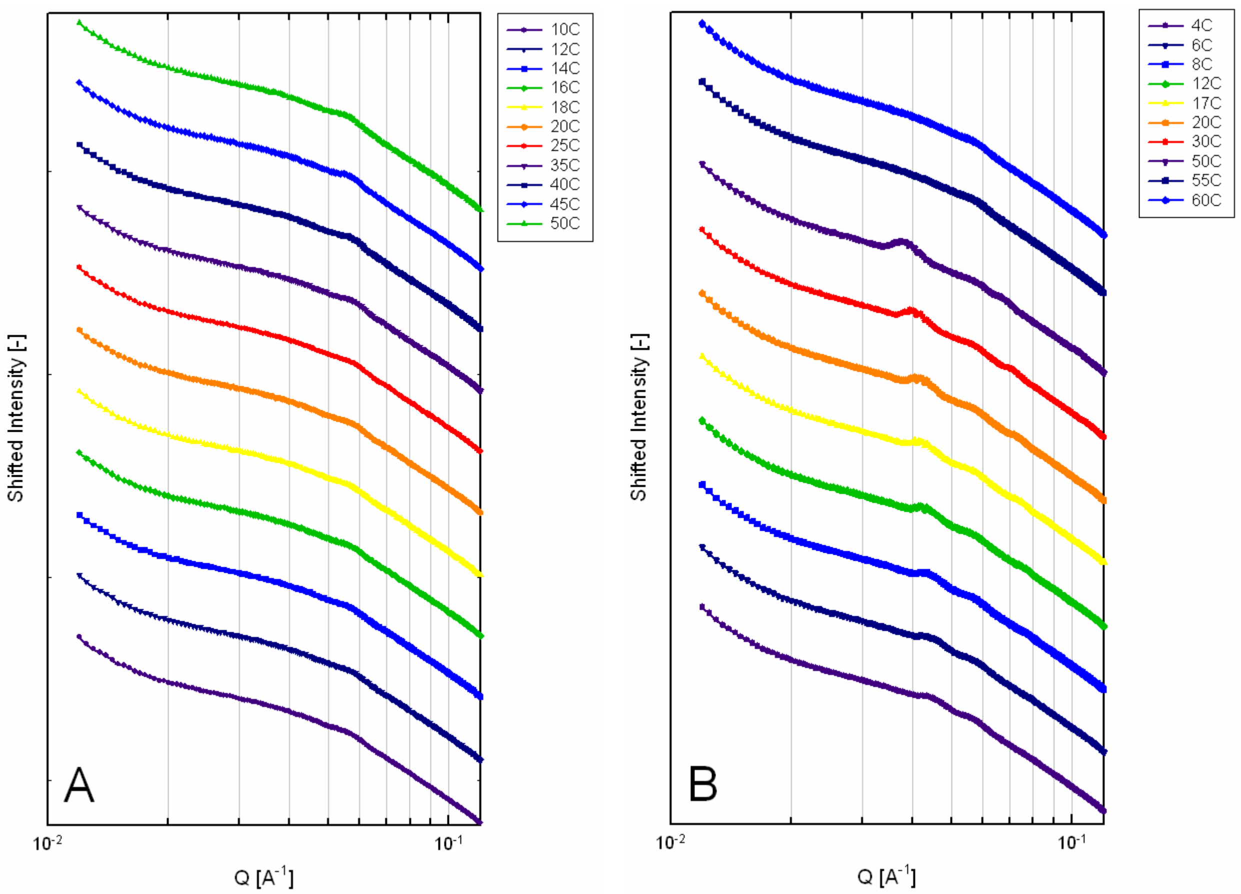

Figure 1: Averaged scattering intensities of P123 in water at different temperatures of 28 wt% gelator concentration (A) and with 42wt % of gelator (B).

By using small angle X-ray scattering in combination with a rheometer the structure can be monitored at the same time with the rheological properties. Starting at low temperature and slowly increasing the temperature the gelation process, and hence how the network is built (see fig 1), can be monitored. We are interested in studying the influence of the gelator concentration on the net structure and in the following step we will add a magnetic content via a magnetic liquid and compare the gelation process with and without magnetic content. The structure and rheology of the net gel have been studied before [1, 2], therefore the phase diagram of the Pluoronics P123, we used in this experiment, is well known [2]. Compared to the other study we are able to measure vertically through the plate-plate rheometer set-up. This has the advantage that the sample can be measured perpendicular to the applied shear deformation.

In this experiment, the X-ray beam with a wavelength of 9.85 keV and was reflected at a diamond crystal [004], which reflects the beam in a 90° angle in vertical position. Afterwards the X-ray beam goes through the plate-plate geometry of the rheometer (purchased and rebuild by Haake). The plate-plate geometery was placed in a chamber with a Peltier system installed on the top of the upper plate, which can control the temperature from 2 to 65 °C with a nitrogen flow. A Pilatus detector was used and placed 1.16 m above the sample.

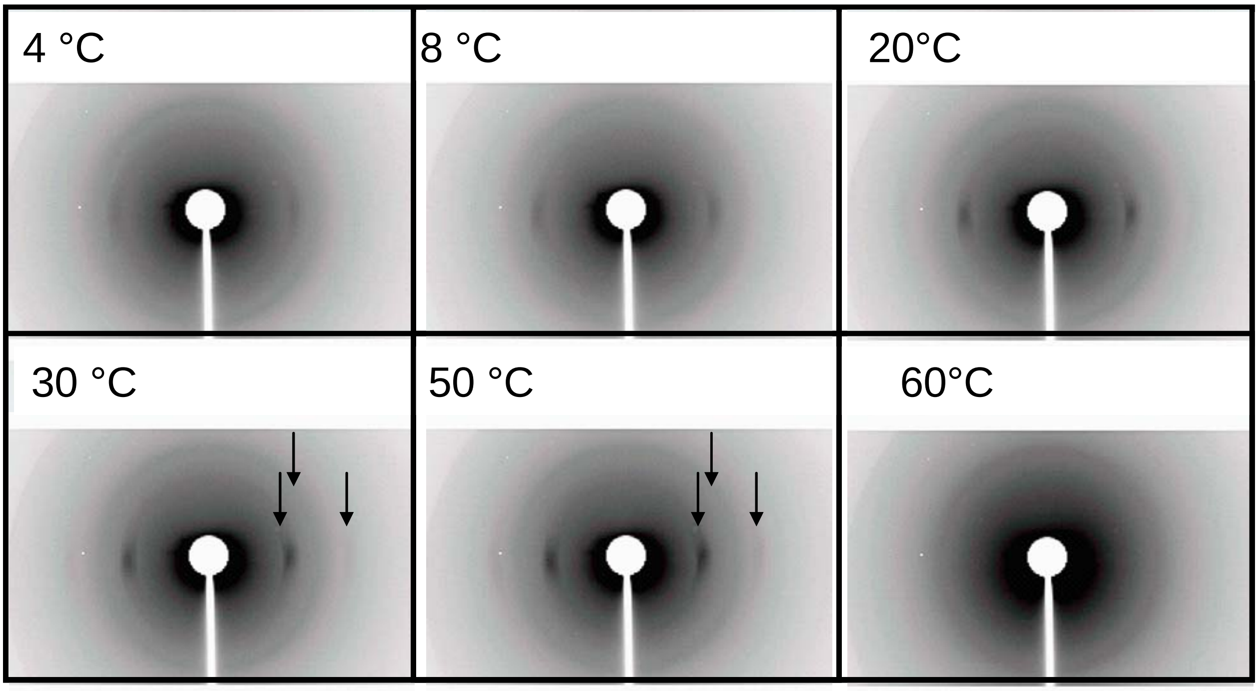

Figure 2: Scattering image of P123 in water with 42wt % of gelator at different temperatures.

Here, we present primarily results of a hydrogel of about 28 and 42 wt% Pluorincs P123 (fig. 1), which was measured at different temperatures from 4 °C till 60 °C. Above 33 wt% the hydrogel forms crystalline structure. Therefore in case of 28 wt% P123 almost no change in the structure is visible (fig 1A), whereas a light shift in the peaks is visible at 42 wt% P123. This shift of the first maximum indicates the change in the size of the micelles (fig. 1B) and above 55 °C a phase transition of the gel. The difference in the micelle formation is also clearly visible on the complete SAXS picture, where the reflex are clearly visible at 30 °C and 50 °C, but vanishes again at higher temperatures (fig. 2).

References

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[2] G. E. Newby, I. W. Hamley, S. M. King, C.M. Martin, and N. J. Terrill, J. Col. Int. Sci. **329**, 54 (2009).