# Experimental report

04/09/2023

**Proposal:** 9-10-1735 **Council:** 10/2022

**Title:** Role of inter-micellar bridging onthe dynamics of thermoresponsive polymer micelles

**Research area:** Soft condensed matter

**This proposal is a new proposal**


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**Samples:** PS-PNIPAM block copolymers in D2O

| Instrument | Requested days | Allocated days | From | To |
|---|---|---|---|---|
| IN15 | 6 | 3 | 07/06/2023 | 10/06/2023 |
| D33 | 2 | 1 | 07/03/2023 | 08/03/2023 |


## Abstract:

We propose to investigate the dynamics of thermoresponsive micelles based on polystyrene (PS) and poly-N-isopropylacrylamide (PNIPAM) in water. Stable, low-polydisperse micelles formed by PS-b-PNIPAM di- and PS-b-PNIPAM-b-PS triblock copolymers will be investigated to clarify the role of bridges on their structure and dynamics. This important question has been never addressed before on the microscopic level and leads to new and controlled macroscopic behavior of thermoresponsive polymers. By means of neutron spin echo (NSE) and exploring partially deuterated polymers, we aim at selectively studying the core and shell dynamics of the micelles. Different diblock/triblock mixtures will be investigated to systematically tune the amount of bridges between micelles. Measurements at different temperatures will address how bridges influence the thermoresponsive behaviour of the micelles. NSE would be suitably complemented by small-angle neutron scattering (SANS) to obtain information on the micellar structure. Taking into account measurements at different contrasts (core or shell deuterated), concentrations, and temperatures, we ask for 6 days of NSE and 2 days of SANS beamtime.

## Experimental report – proposal no. 9-10-1735

In this experiment, the structural and dynamical properties of diblock and triblock copolymers based on polystyrene (PS) and poly-N-isopropylacrilamide (PNIPAM) blocks have been investigated.
For the experiment, 1 day of beamtime and 3 days of beamtime have been allocated at D33 (SANS) and IN15 (NSE) respectively.

### *1. SANS experiment (D33), 07.03.2023-08.03.2023*

| **Sample** | **Polymer concentration [wt%]** |
|---|---|
| dPS-*b*-hPNIPAM 10 kg/mol (short) | 0.1, 0.5, 1, 5, 10 |
| dPS-*b*-hPNIPAM 30 kg/mol (long) | 0.1, 0.5, 1, 5, 10 |
| dPS-*b*-hPNIPAM-dPS 70 kg/mol | 0.1, 0.5, 1, 5, 10 |
| dPS-*b*-h,dPNIPAM short:dPS-*b*-hPNIPAM-*b*-dPS 20:80 | 10 |
| dPS-*b*-h,dPNIPAM short:dPS-*b*-hPNIPAM-*b*-dPS 50:50 | 10 |
| D2O | |
| 20/80 D2O/H2O | |

*Tab.1:list of samples measured at D33.*

An incident wavelength of λ = 4.62 Å has been used, together with the following setting:

- source-to-sample distance: 12.8 m;
- front detectors: 1.5 m;
- rear detectors: 13.3 m;

resulting in an available Q-range between $Q_{min}$=0.034 $nm^{-1}$ and $Q_{max}$=4.98 $nm^{-1}$.
For each sample, up to 5 different concentrations have been measured. The concentration series is shown in two exemplary cases in Fig.1. All samples have been measured in $D_2O$ where the dPS is contrast-matched. For each block copolymer, the shell-matched condition has been measured in a 20/80 D2O/H2O mixture at a fixed concentration of 1wt%. The measuring time was around 15 minutes for the higher concentrations (5-10 wt%) and around 40 minutes for the lower concentrations.

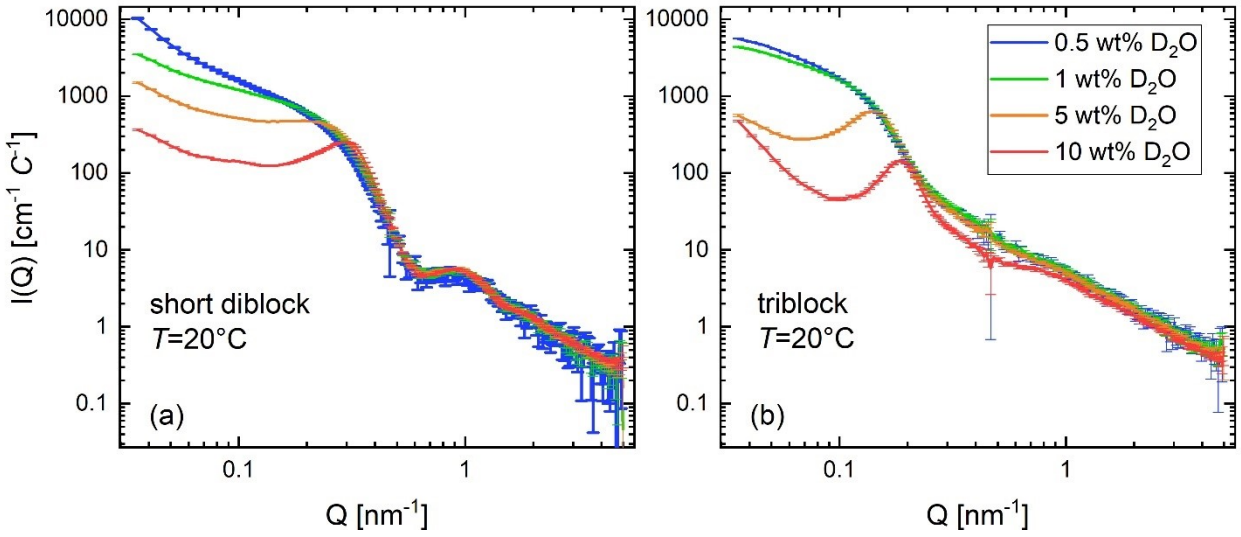


*Fig.1: Scattering patterns for (a) dPS-b-hPNIPAM short and (b) dPS-b-hPNIPAM-b-dPS at different polymer concentrations.*

Samples at all concentrations have been measured at T=20 °C, i.e. below the lower critical solution temperature (LCST) of PNIPAM (LCST ≈ 33 °C). Selected concentrations have been measured also at T=40 °C to investigate the effect of the PNIPAM chains collapse on the micellar structure (see Fig.2).

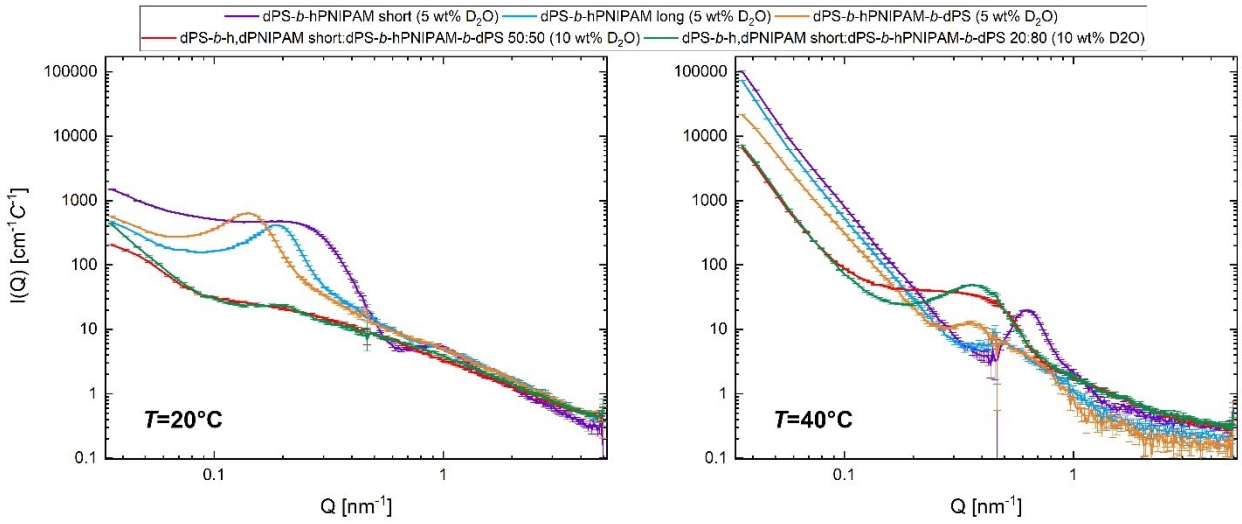


*Fig.2: SANS curves collected at T=20°C (left) and T=40°C (right).*

## *2. NSE experiment (IN15) 07-10.06.2023*

| **Sample** | **Concentration [polymer wt%]** |
|---|---|
| dPS-*b*-hPNIPAM 10 kg/mol (short) | 10 |
| dPS-*b*-hPNIPAM 30 kg/mol (long) | 10 |
| dPS-*b*-hPNIPAM-dPS 70 kg/mol | 5, 10 |
| dPS-*b*-h,dPNIPAM short:dPS-*b*-hPNIPAM-*b*-dPS 20:80 | 10 |
| dPS-*b*-h,dPNIPAM short:dPS-*b*-hPNIPAM-*b*-dPS 50:50 | 10 |
| dPS-*b*-h,dPNIPAM short:dPS-*b*-hPNIPAM-*b*-dPS 80:20 | 10 |
| dPS-*b*-h,dPNIPAM short:dPS-*b*-hPNIPAM-*b*-dPS 90:10 | 10 |
| D2O | |

*Tab. 2: list of samples measured at IN15.*

Data have been collected with the following setup parameters:

$\lambda$ = 13.5 Å: Q = 0.03 Å$^{-1}$, 0.05 Å$^{-1}$, 0.077 Å$^{-1}$ Fourier time up to 500 ns
$\lambda$ = 10 Å: Q = 0.096 Å$^{-1}$ Fourier time up to 300 ns
$\lambda$ = 8 Å: Q = 0.13 Å$^{-1}$, 0.15 Å$^{-1}$ Fourier time up to 200 ns
$\lambda$ = 6 Å: Q = 0.2 Å$^{-1}$, Fourier time up to 50 ns

An average time of ≈8 hrs was required to measure each sample with such scheme. For each sample, a diffraction scan has been performed at the same Q values used for the spin echo experiment (Fig. 3). All the data have been collected at T=20°C. In Fig. 4 the scattering functions of samples with different relative amounts of diblock and triblock copolymers are reported at selected Qs.

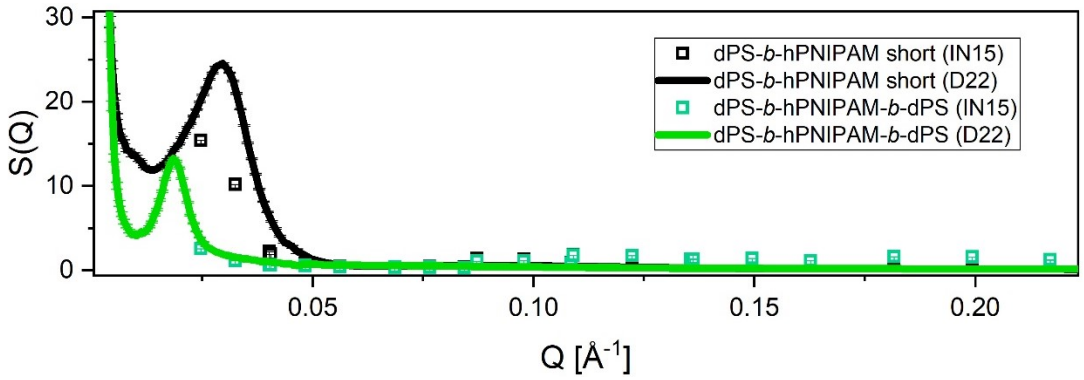


Fig.3: Diffraction pattern for two selected samples, i.e. the short diblock (black) and triblock (green) samples at 10 wt%. For comparison, data acquired on D33 on the same samples are plotted as well.

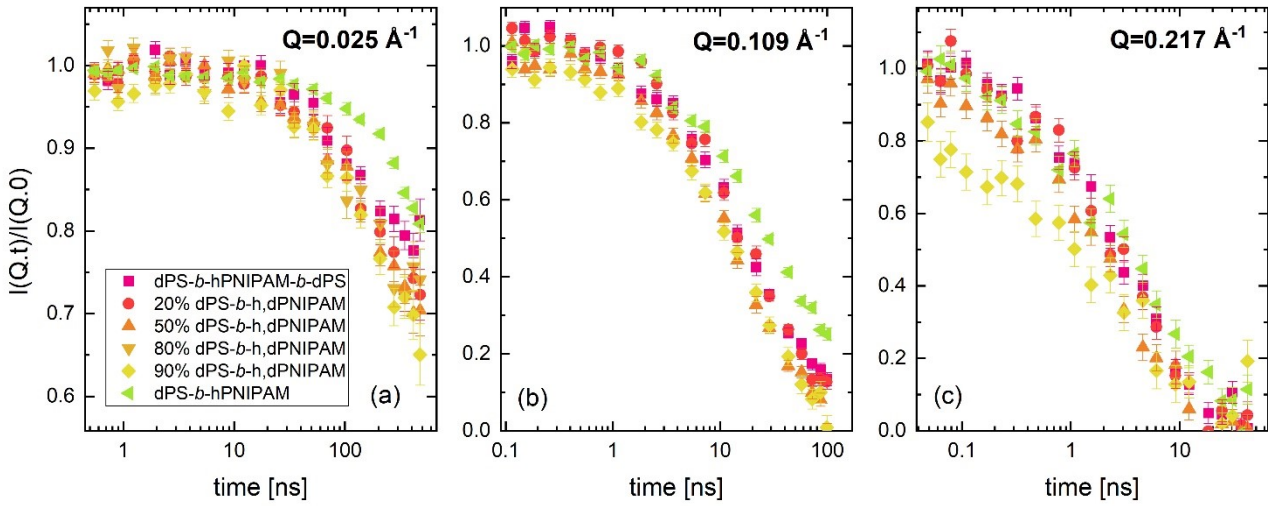


*Fig.4: Scattering functions at selected Q values, namely (a) Q=0.025 Å-1, Q=0.109 , Q=0.217, for samples at a fixed total polymer concentration of 10 wt% with different relative amount of diblock and triblock copolymers.*