Experimental report

17/09/2017

Proposal: **9-11-1663** **Council:** 10/2012

Title: Kinetics of the collapse and aggregation behavior of a new thermoresponsive polymer - poly(methoxy diethylene glycol acrylate)

Research area: Soft condensed matter

This proposal is a resubmission of 9-11-1614

Main proposer: **Christine PAPADAKIS**

Experimental team:
Konstantinos KYRIAKOS
Che Hung LIN
Natalya VISHNEVETSKAYA
Martine PHILIPP
Margarita DYAKONOVA

Local contacts: Isabelle GRILLO

Samples: poly(styrene-b-methoxy diethylene glycol acrylate-b-styrene) in D2O

Instrument	Requested days	Allocated days	From	To
D33	2	0		
D22	2	2	22/03/2013	24/03/2013

Abstract:

We wish to investigate new, micelle-forming block copolymers containing a new thermoresponsive block, poly(methoxy diethylene glycol acrylate) (PMDEGA), and polystyrene end blocks. This polymer cannot form hydrogen bonds with itself, in contrast to the often investigated PNIPAM. The focus will be on the kinetics of the collapse and aggregation behavior during a temperature jump across the cloud point (~35-40°C) with the focus on (i) the role of bridging between micelles, (ii) the collapse of the micellar shell and the subsequent aggregation of the collapsed micelles, and (iii) the thermal stability of the micellar core. Real-time SANS with a time resolution of 0.1 s will allow us to characterize these issues and relate them to the peculiar mechanical properties. We will compare the results to the ones obtained by us previously on P(S-b-NIPAM-b-S).

Thermoresponsive polymers are of interest for many applications, such as controllable filters. An important aspect is the kinetics governing the switching behavior of such systems, which comprises the collapse at the cloud point, T_{CP}, and subsequent aggregation. Both have been studied by means of time-resolved small-angle neutron scattering (TR-SANS) [1-3], revealing the complex nature of these processes. The focus of the present project is on a novel thermoresponsive polymer, poly(methoxy diethyleneglycol acrylate) (PMDEGA), which bears similarities to poly(ethylene glycol) [4]. Block copolymers of PMDEGA with a hydrophobic block, in the present case polystyrene (PS) leads in aqueous solution to core-shell micelles with a thermoresponsive block. Recently, studies of such systems regarding their ability to form gels and of the associated structural changes have been carried out [4,5].

Here, we report on TR-SANS experiments on aqueous solutions of various amphiphilic block copolymers from polystyrene (PS), which is hydrophobic, and PMDEGA. They were studied during a rapid change of the temperature across the cloud point, T_{CP}, i.e. temperature jumps. The first question addressed is the influence of the copolymer architecture on the behavior: a diblock copolymer $P((S\text{-}d_8)_{11}\text{-}b\text{-}PMDEGA_{355})$ and two triblock copolymers $P((S\text{-}d_8)_9\text{-}b\text{-}MDEGA_{304}\text{-}b\text{-}(S\text{-}d_8)_9)$ and $((S\text{-}d_8)_9\text{-}b\text{-}MDEGA_{601}\text{-}b\text{-}(S\text{-}d_8)_9)$ were investigated. At this, the PS blocks were fully deuterated to enhance the scattering contrast between the core and the shell, and they were very short compared to the PMDEGA blocks. The second question addresses the influence of the start and the target temperatures. Therefore, various temperature jumps were performed. In all cases, the polymer concentration was 30 mg/ml, and D_2O was chosen to enhance the contrast between the shell and the solvent. All T_{CP} values were determined beforehand by turbidimetry.

TR-SANS experiments were performed at the high-flux SANS instrument D22. The wavelength was $\lambda = 8$ Å, which together with the sample-detector distances of 14 m and 4 m resulted in a q-range of 0.003-0.2 Å^{-1}. The temperature jumps were realized by using a modified stopped-flow SFM-300 by Bio-Logic, coupled with a custom-made external sample cell. The temperature in the sample cell was calibrated before the beamtime. The sample was kept in the reservoir at the start temperature and was injected into the sample cell, which had been carefully preheated to the target temperature. A transistor-transistor logic (TTL) signal started data acquisition, resulting in good reproducibility. 2D SANS images were collected starting with 0.2 s acquisition time for the first image and increasing logarithmically until 303 s and then continued with 15 s per frame for a total measuring time of 1500 s. All temperature jumps were repeated twice for the SDD of 4 m and thrice for 14 m. Since no deviations were observed, they were averaged to increase statistics. Model fitting was carried out using NIST SANS analysis package within the Igor Pro environment.

We discuss here, as an example, the results obtained for the $P((S\text{-}d_8)_9\text{-}b\text{-}MDEGA_{304}\text{-}b\text{-}(S\text{-}d_8)_9)$ triblock copolymer for a temperature jump from 33.5 °C (T_{CP}-3 K) to 38.5 °C (T_{CP}+2 K). T_{CP} is reached after ~25 s. Figure 1a shows the time-dependent SANS curves. Different regimes are distinguished: During the first 20 s, i.e. before T_{CP} is reached, the scattering curve is typical for a solution of swollen micelles, being only weakly correlated (red curves). When crossing T_{CP}, the forward scattering increases (green curves) which reflects that the collapsed micelles form large aggregates. Moreover, the correlation peak increases and shifts with time to higher q-values; i.e., the mutual distance decreases, as expected for bridged collapsed micelles. In this regime, which lasts until ~100 s, the forward scattering increases and then decreases slightly, which is a hint for structural reorganization within the aggregates. In the late stage (blue curves), forward scattering at very small q values is ovserved.

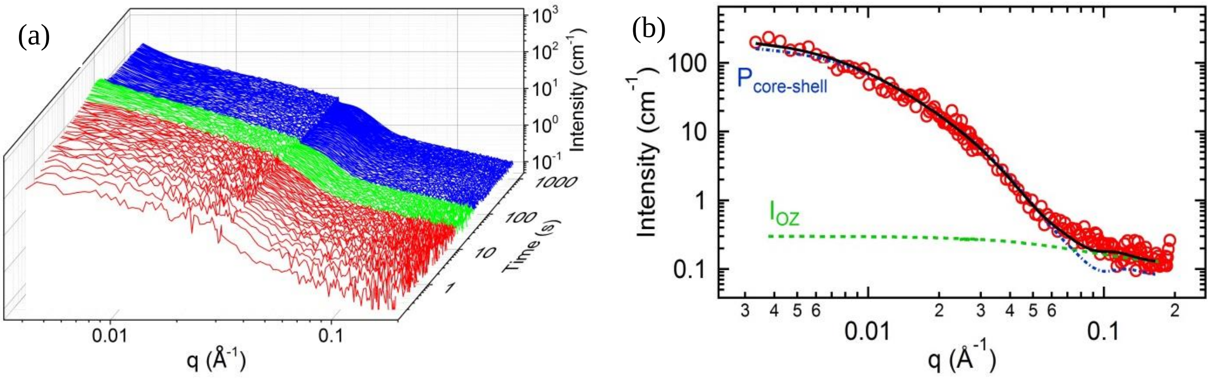

Figure 1. (a) SANS curves of P((S-d_8)$_9$-*b*-MDEGA$_{304}$-*b*-(S-d_8)$_9$) at 30 mg/ml in D_2O in dependence on time after the transfer from 33.5 °C to 38.5 °C. The different colors indicate different regimes. (b) Curve measured 4.3 s after injection (circles) together with model fit (full line). The contributions of the spherical core-shell form factor, $P_{\text{core-shell}}$, (dashed-dotted line) and of the Ornstein-Zernike structure factor, I_{OZ} (dotted line) are given as well.

For the first regime, a model was used which includes the form factor of spherical core-shell micelles and an Ornstein-Zernike term, accounting for concentration fluctuations within the swollen micellar shell was used (Figure 1b). Due to the poor statistics, the coefficients of the Ornstein-Zernike term had to be kept fixed at values known from our previous work on similar micellar systems: The correlation length was kept constant at $\xi = 1.5$ nm and the prefactor I_0 at 0.15-0.25 cm^{-1}.

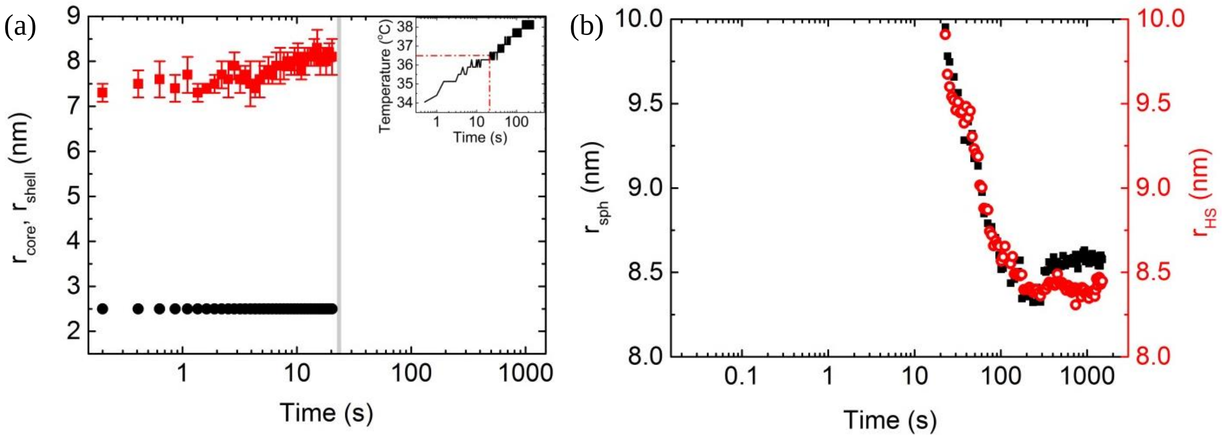

Figure 2. (a) Core and micellar radius, r_{core} and r_{mic}, as a function of the time after the injection. The grey line indicates the time when T_{CP} was passed. The dotted-dashed line shows the CP. The inset shows the temperature profile in the cell. (b) Sphere radius, r_{sph} (left axis), and hard-sphere radius, r_{HS} (right axis), as a function of time.

Figure 2a compiles the fitting results of the form factor. The core radius was determined from fitting of the curves at the end of the first regime to be r_{core} ~2.5 nm and was fixed at this value for all fits. The scattering length densities (SLDs) of the solvent and the core were kept constant at values 6.36×10^{-6} Å^{-2} and 6.30×10^{-6} Å^{-2}, respectively. The SLD of the shell was treated as a free variable and was found in the range of 1.3-1.4$\times10^{-6}$ Å^{-2}, which is slightly higher than the nominal SLD value of 1×10^{-6} Å^{-2} of the pure polymer. This increase is expected for PMDEGA chains hydrated by D_2O. The micellar radius, r_{mic}, is 7.3 nm and increases slightly as T_{CP} is approached. The shell blocks thus stretch, resulting in a thicker shell.

The curves above T_{CP} were fitted using a model consisting of a form factor for homogeneous spheres together with a hard-sphere structure factor. No core-shell structure of the micelles could be distinguished any longer, in spite of the PS blocks being deuterated. A Porod contribution is added to describe the forward scattering due to large aggregates. Figure 2b compiles the fitting results. The size of the spheres, r_{sph}, corresponds to the radius of the collapsed micelles. The hard-sphere radius, r_{HS}, corresponds to half the average distance between the collapsed micelles. Both, r_{sph} and r_{HS}, decrease with time. The collapse of the PMDEGA blocks leads not only to a collapse of the shell, but also to a decrease of the distance between the micelles because the intermicellar PMDEGA bridges collapse as well. Interestingly, this transition is not abrupt, but takes place over a long time. It has been previously observed that the PMDEGA systems exhibit a rather broad transition as a function of temperature, a very different behavior from the well-known PNIPAM.

To summarize, in this very successful experiment, we studied amphiphilic block copolymers of the novel thermoresponsive PMDEGA during the rapid increase of the temperature through the cloud point. We focus on the influence of the architecture and the target temperature. TR-SANS elucidates the structural changes that accompany the collapse transition. We observe these changes to occur over a broad time region, which is a totally different behavior compared to PNIPAM, for instance, in agreement with our previous findings.

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