Experimental report

13/09/2019

Proposal: **9-10-1554** **Council:** 4/2018

Title: PEO-PLA and Cn-PEO-PLA block copolymers as building units for soft patchy colloids

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: PEOn-PLAm
C28-PEOn-PLAm

Instrument	Requested days	Allocated days	From	To
D11	3	2	23/10/2018	25/10/2018

Abstract:

We plan to use spontaneous self-assembly of tailor-made amphiphilic diblock and asymmetric triblock copolymers to form soft patchy colloids following a theoretical approach of Cappone et al. We aim at mixed micelles of PEO-PLA diblock and Cn-PEO-PLA triblock copolymers by exploiting the difference between the hydrophobic blocks Cn and PLA in entropic and enthalpic contributions to the free energy of micellisation.
We will investigate the association behaviour of the individual components as well as perform first exploratory runs with mixed micelles using SANS at D11.

Scientific background:

We plan to exploit spontaneous self-assembly of tailor-made amphiphilic diblock and asymmetric triblock copolymers to form mixed micelles acting as soft patchy colloids [1] following a theoretical approach of Cappone et al. [2]. The "patchiness" can be achieved by a variety of underlying functional molecular structures, but the common principle of patch formation directly originates from its soft polymeric backbone. Therefore, patch number, size, and strength can be precisely tuned. Using these soft patchy colloids as building blocks we can further control and tailor the formation of supramolecular structures to improve a wide range of polymeric functional materials by "intelligent bonding". Moreover, soft patchy colloids can be viewed as model systems for biological systems where patch formation is ubiquitous.

Aim:

PEO-PLA diblock and C_n-PEO-PLA triblock copolymers should be used as building blocks for soft patchy colloids. By exploiting the difference between the hydrophobic blocks C_n and PLA in entropic and enthalpic contributions to the free energy of micellisation, we can expect that PLA always enters into the micellar core due to its crystallinity and stereocomplex formation, whereas, dependent on the length of the alkane block, C_n can either enter the micellar core ("flower-like" micelles) or stay in solution at the outer surface of the corona. These "dissolved" C_n-blocks will re-arrange to form patches depending on the flexibility (length of the PEO block) and the driving force (length of the C_n-block). The key is to find the correct balance between control parameters but anionic polymerization allow precise tailoring of the individual blocks.

Previous work:

At MLZ we screened PEO-PLA and C_{28}-PEO-PLA block copolymers using USANS/SANS and characterized the individual micellar structures of di- and triblock copolymers separately.

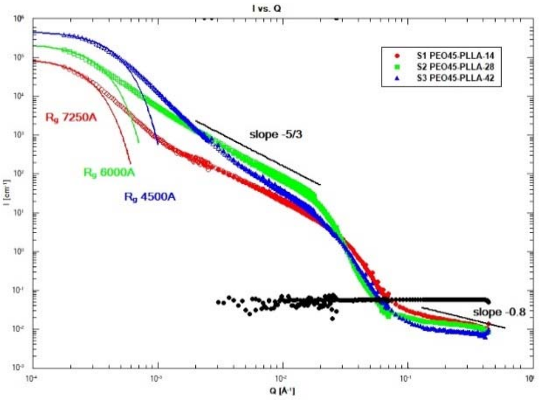

Figure 1: With increasing PLA block length the micellar R_g decreases; data obtained using KWS1/KWS3 at MLZ.

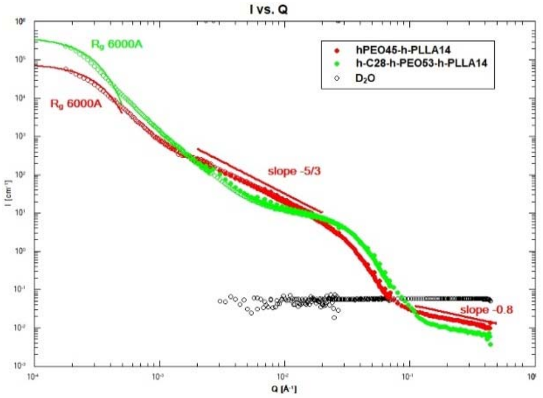

Figure 2: The short C_n-sequence induces profound changes in the overall micellar structure; data obtained using KWS1/KWS3 at MLZ.

We found micellar structures with an overall size in the µm-range so that only the use of the USANS instrument KWS3 reveals the Guinier regime. For PEO_n-PLA_m diblock copolymers with fixed PEO, $n_{PEO}=45$, and increasing PLA block length, $n_{PLA}=14$, 28 and 42, model-free Guinier analysis reveals a decreasing micellar size with increasing PLA block length. Qualitatively all form factors show the typical features of worm-like micelles, i.e. a power law regime with $I \sim Q^{-5/3}$ at intermediate and a second with $I \sim Q^{-1}$at higher Q-vectors.

We observed profound changes in micellar structure on introducing the short C_n-sequence. Although di- and triblock with nearly identical PEO-PLA block ratio show the same overall dimension, e.g. a radius of gyration $R_g \approx 6000$Å, the diblock shows evidence of worm-like chain structure, whereas as the corresponding triblock shows that of spherical aggregates with two characteristic length scales.

Experimental difficulties arose from the bad solubility of samples with long PLA-blocks due to the (partial) crystallinity of the PLA. At 1% volume fraction samples had to be dispersed in D_2O using ultra-sonification at 50-60°C which might affected the stability of the PEO-block. Therefore, alternative ways of micelle equilibration and reducing the block copolymer concentration was the aim of the present D11 experiment.

Present results:

In detail, we focussed on two points to achieve equilibrium micelles:

i.) Effect of co-solvent tetrahydrofuran (THF) on self-assembly and resulting equilibration.
ii.) Effect of temperature ($T=60°C > T_{m,PLA}$) on self-assembly and resulting equilibration.

All solutions were prepared at 0.1% volume fraction. Following Sun et al. [3] we used a solvent mixture of D_2O and THF (80:20 w/w, $\rho=5.11\text{x}10^{10}$ cm^2) to achieve solubility during micelle formation. After measuring samples in the solvent mixture, the THF, which has a much higher vapour pressure than D_2O, was evaporated at ambient temperature and finally D_2O refilled to maintain a constant polymer concentration (since we used h-THF, the actual remaining amount of THF can be extrapolated from the incoherent background, 0.378 cm^{-1} for THF instead of 0.011cm^{-1} for D_2O). Samples directly prepared in D_2O ($\rho=6.36\text{x}10^{10}$ cm^2) were used as reference samples.

Even at a detector distance D=39.5m the Q-range of D11 does not cover the Guinier regime of most samples. At low Q-vectors a power law scattering dominates with a slope dependent on sample (block ratio, solvent composition, temperature). The physical origin of the observed power laws is either the structure of the individual micelle or, rather a drawback, clustering resulting from non-properly dissolved polymer crystallites. In the following we focus on the high Q-regime, therefore all given Radii are internal characteristic lengths of the micellar structures.

Whereas for PLA-PEO diblock polymers the co-solvent has a profound effect on internal R_c (80Å → 40Å → 65Å) as well as on the onset of the high-Q power law ($1/Q^* \approx 17$Å → 10Å → 13Å) , for C_{28}-PEO-PLA triblock polymer this effect is less pronounced ($R_c \approx$ const. = 55 Å and $1/Q^* \approx$ const. = 7Å), see Figure 3.

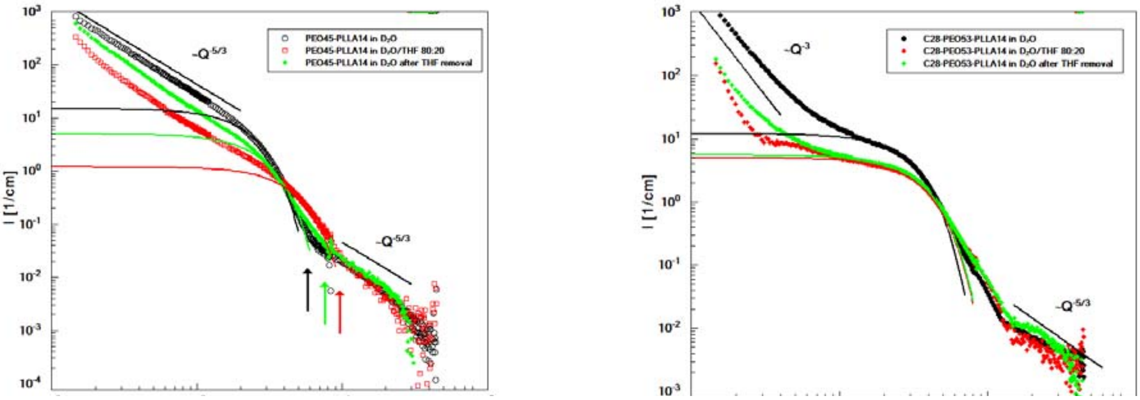

Figure 3: Effect of solvent composition on diblock (left) or triblock (right) copolymer micelles. Solid lines either indicate power law scattering $I(Q) \sim Q^{-b}$ or Guinier form factor $I(Q) \sim e^{-Q^2 R_c^2/3}$. Arrows indicate onset of internal power law scattering resulting from the micellar corona.

The same holds for changing T, but here the effect for C_{28}-PEO-PLA is rather marginal. For PLA-PEO diblock polymers the temperature has only a small effect on internal R_c (80Å → 70Å) but a stronger effect on the onset of the high-Q power law (1/Q* ≈ 14Å → 10Å), see Figure 4. Moreover, in the Q-range 4×10^{-2} Å^{-1} – 1×10^{-2} Å^{-1} there is a substantial change in the scattering profile, which needs further analysis that is more sophisticated.

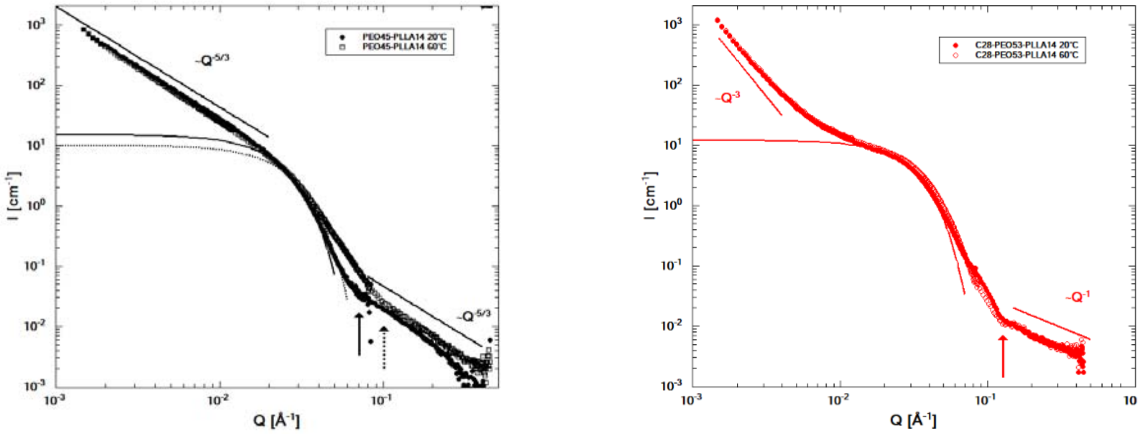

Figure 4: Effect of temperature on diblock (left) or triblock (right) copolymer micelles. Solid lines either indicate power law scattering $I(Q) \sim Q^{-b}$ or Guinier form factor $I(Q) \sim e^{-Q^2 R_c^2/3}$. Arrows indicate onset of internal power law scattering resulting from the micellar corona.

As a first test, we used the Worm-like Chain form factor following Pedersen and Schurtenberger [4] to analyse combined MLZ and ILL data. However, this model does not allows a reasonable description of the low Q-regime. A quantitative modelling in terms of different form factors is in progress.

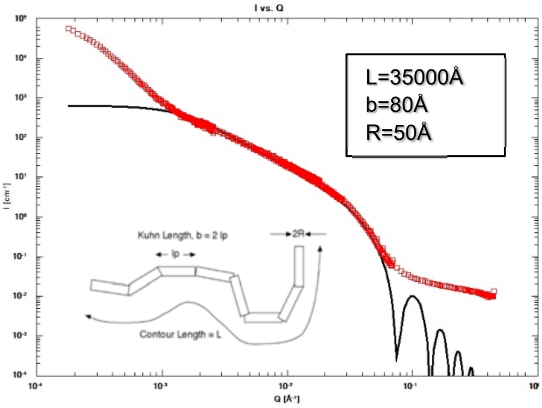

Figure 5: Fit using the worm-like chain form factor for combined USANS/SANS data for PEO45-PLLA14.

Conclusions:

First USANS/SANS results indicates a rich micellisation behaviour of C_n-PEO-PLLA triblock copolymers depending on block ratio, solvent composition and temperature. However, at the moment the main drawback of this system is the difficulty to obtain equilibrium micelles due to the (partial) crystallinity of PLLA, which complicates sample preparation. Therefore, there is still a long way to go before “soft patchy colloids” can be achieved by simple self-assembly.

[1] F. Sciortino et al. Phys Rev. Lett. **97** 168301 (2006)

[2] B. Cappone et al. Phys. Rev. Lett. **109** 238301 (2012)

[3] L. Sun et al., Nature Communications, **5**, 5746 (2014)

[4] J. S. Pedersen and P. Schurtenberger, Macromolecules **29** 7602 (1996)