	Experiment title: *Characterizing the effect of catalyst-imbued amphiphilic polymeric nanoparticles' structure on the catalytic activity in water.*	**Experiment number:** MX-2477
Beamline: BM29	**Date of experiment**: from: 5 Nov 2022 to: 6 Nove 2022	**Date of report**: 19 Jan 2023
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Report:

Single-chain polymeric nanoparticles (SCPNs) are polymers were the backbone is functionalized with different grafts. Imparting these folded nanoparticles with specific functional groups makes them promising candidates as nanocarriers, bio-orthogonal catalysts, or sensors. Many different approaches exist to fold polymers into SCPNs.[1] In particular for the systems in this experiment, folding in water is achieved through the hydrophobic effect and hydrogen-bonding interactions. Additional conformational stability is obtained through introduction of covalent cross-links. The effect of polymer composition and folding on its size and structure is of great importance to understand the aqueous behavior of these particles. Hence, small-angle X-ray scattering (SAXS) measured at ESRF is important to reveal the shape, size, and structure of SCPNs in water.

Many samples were successfully measured at ESRF. Here, we will focus only on a few samples to highlight the success of the measurements. The polymers (Figure 1) are polyacrylamides with DP = 200 randomly functionalized with side-chains. Benzene-tricarboxamide in red, coumarin as cross-linkable unit in green, and dodecylamine are the hydrophobic grafts, and the relatively bulky Jeffamine@M1000 graft is the hydrophilic moiety. Here, we highlighy three polymers functionalized from the same backbone. **P4** incorporates all different grafts, **P3** lacks coumarin grafts, and **P7**, incorporates exclusively the hydrophilic graft Jeffamine@M1000. The DPs are twice as large as used for previously studies amphiphilic polymers,[2,3] which showed a strong effect on the particle shape. Cross-linking of **P4** into **P4_PW1** occured via dimerization of the coumarin moieties using UV-light ($\lambda = 365$ nm). The polymers are dissolved and subsequently cross-linked in water.

All scattering curves were fitted with a worm-like chain model, which describes the polymers as semi-flexible polymers. The agreement between the model and the obtained data is high, as χ_2 is close to 1 for all models.
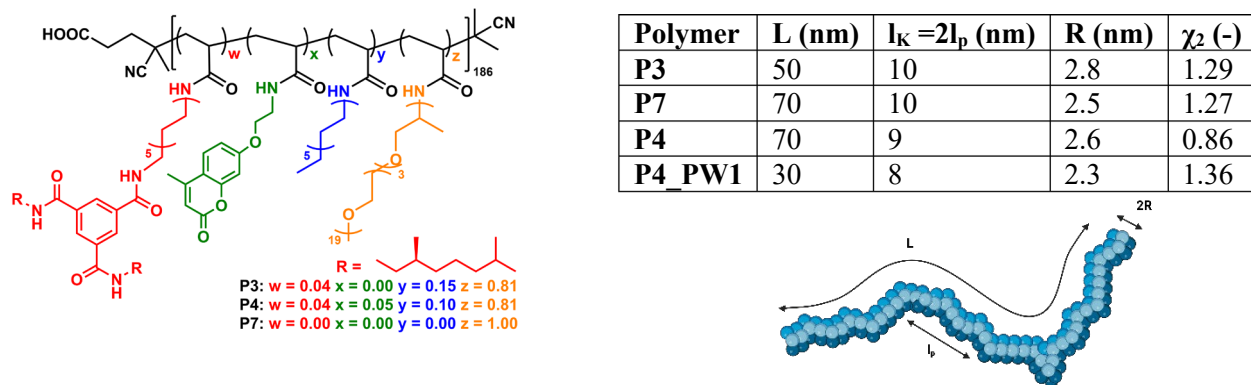
Polymer	L (nm)	$l_K = 2l_p$ (nm)	R (nm)	χ_2 (-)
P3	50	10	2.8	1.29
P7	70	10	2.5	1.27
P4	70	9	2.6	0.86
P4_PW1	30	8	2.3	1.36

P3: w = 0.04 x = 0.00 y = 0.15 z = 0.81
P4: w = 0.04 x = 0.05 y = 0.10 z = 0.81
P7: w = 0.00 x = 0.00 y = 0.00 z = 1.00

Figure 1: *Left) Structures of the random heterograft amphiphilic copolymers **P3**, **P4**, and **P7**. Right) Length L, Kuhn length l_K, radius R, and the fit error χ_2 obtained from the worm-like chain form factor fit in SASview.*
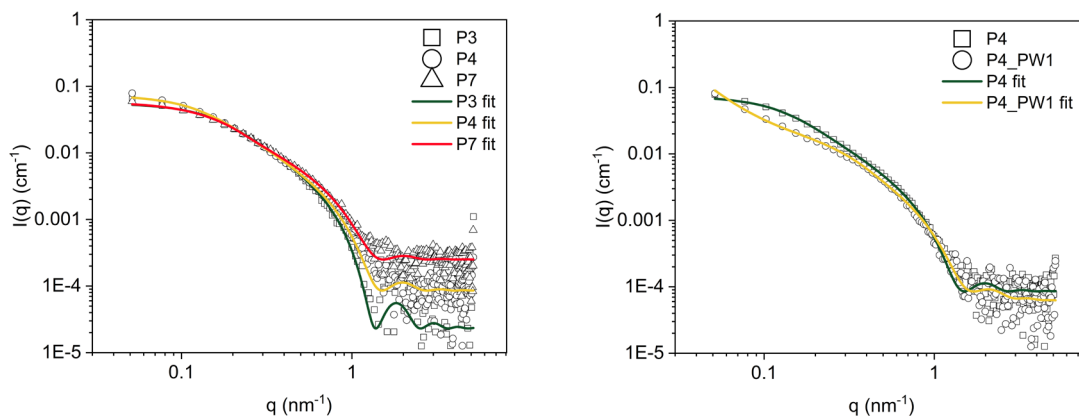

Figure 2: *SAXS scattering curves obtained for **P3**, **P4**, and **P7** in water (left) and form factor fit to the worm-like chain model (left), and for **P4** befare and after cross-linking (**P4_PW1**) (right).*

Spherical, ellipsoidal, or Gaussian coil models can not succesfully fit the obtained SAXS curves. These models were tried by others on similar systems in the past.[2,4] Hence, our polymers behave distinctly different.

The scattering curves of **P3**, **P4**, **P7**, shown in Figure 2 (left), reveals that the length (50 – 70 nm, consistent with polymer contour length), flexibility (l_k = 9 – 10 nm), and radii (2.5 – 2.8 nm), are very comparable between the samples. Hence, the graft composition does not seem to influence the polymer dimensions much. This notion strengthens the idea that the hydrophobic grafts form small, local hydrophobic pockets, but do not result in macroscopic collapse of the polymer chain. Instead, the high incorporation density of bulky Jeffamine@M1000 grafts dictates the shape of the polymer. This could not be determined using other analysis techniques we have used before, such as light scattering. Absolute scale fitting revealed that the polymers are present as single chains in solution.

Coumarin dimerization of **P4** into **P4_PW1** (Figure 2 right) results in a decrease of the chain length and radius, indicating that smaller particles are formed. Additionally, the upturn at low q observed for **P4_PW1** indicates the presence of a small amount of larger aggregates, consistent with previous size exclusion chromatography results, and was fitted using an additive power law model. Whereas the cross-linking is mostly intramolecular in nature, there might be small amounts of intermolecular cross-linking. The presence of aggregates hinders the use of absolute scale fitting to determine the polymer aggregation number. We therefore performed SEC-SAXS, but due to dilution on the column, the signal-to-noise ratio was poor. For future SEC-SAXS experiments, we will have to increase the polymer concentration by three-to-four fold to get satisfactory statistics. Coupled with the UV-detector, this will additionally allow absolute scale fitting of the data for samples containing small amounts of aggregates.

In summary, the current experiment was successful and the high quality data allowed for absolute scale form factor fitting to a worm-like chain model. These new insight will help us rationalize the catalytic activity of the polymers.

Literature

1) G. ter Huurne *et al*., CCS Chem. **2019**, 1, 64. 2) G. ter Huurne *et al*., Macromolecules **2015**, 48, 3949. 3) G. ter Huurne *et al*., Macromolecules **2017**, 50, 8562. 4) P. Stals *et al.,* Macromolecules **2014**, 47, 2947.