![ESRF logo]	**Experiment title:** Interactions between PEGylated particles under marginal/poor solvent conditions	**Experiment number**: SC4053
Beamline:	**Date of experiment**: (3 shifts) from: March 13, 2015 to: March 15, 2015	**Date of report**: 2016-09-05
Shifts: 4	**Local contact(s)**: G. Lotze/T. Narayanan	*Received at ESRF:*

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Report:
The experiments, conducted at ID02 in March 13-15 of 2015, were aimed at gaining an improved understanding of interactions between colloidal particles bearing grafted poly(ethylene glycol) (PEG) using USAXS measurements.

Results: In the present experiments, while the aim was on salt effects on interactions, it was also necessary to characterize the in-house-synthesized dispersions regarding size and size distribution. In Fig. 1 the scattering is shown from dilute samples of three batches of pHFBMA particles, all with grafted PEG480 but produced with varying ratio between PEG macromonomer and fluorinated monomer. This ratio needs to be optimized so as to yield a low polydispersity without sacrificing the stability against salt addition. The analysis of the experiments shows that the size dsitribution exhibits a slight bimodality in general. It also shows that the lower the ratio is, the smaller the degree of size bimodality. As will be seen later (cf. Fig. 3) the LP5 batch in Fig. 1 exhibits also an extreme stability against the salting-out carbonate anion.
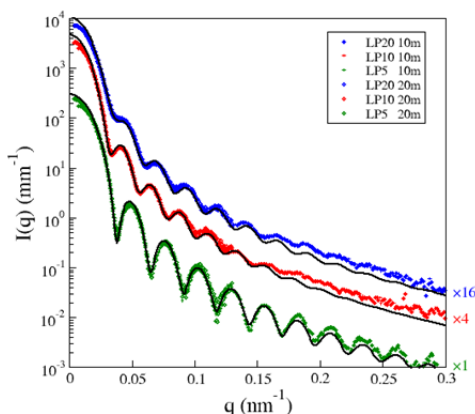

Fig. 1: Form factors recorded at 10 and 20 m detector distances of three synthesized batches of pHFBMA-PEG particles as a function of the molar ratio between PEG macromonomer and HFBMA monomer. The solid curves are least squares fits to theory based on a bimodal size distribution.

Turning to the effect of salt, which, in the case of sodium carbonate, worsens the solvent conditions for the PEG graft, this was investigated at constant particle concentration. As can be seen in figure 2, adding sufficient amount of Na_2CO_3 to the system results in attractions

between particles. When the surface-graft consists of PEG2000 these attractions set in when the carbonate concentration exceeds 0.5 M. However, when the graft is shorter as for the particles in Fig. 3 with PEG480, not even 1 M Na_2CO_3 is enough to bring about any signs of attractions.
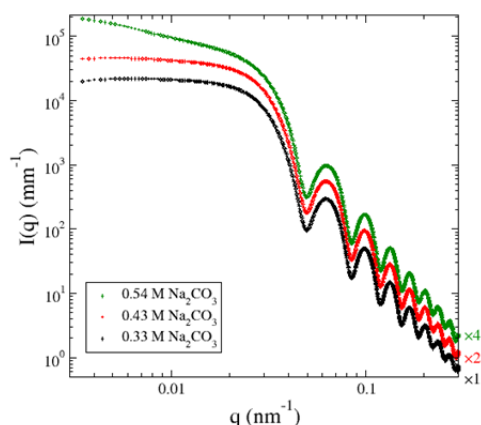

Fig. 2: Scattering intensity as a function of q for a constant particle concentration but with varying concentration of sodium carbonate, as labeled. The particles carry a PEG graft of 2000 g/mol molecular weight.
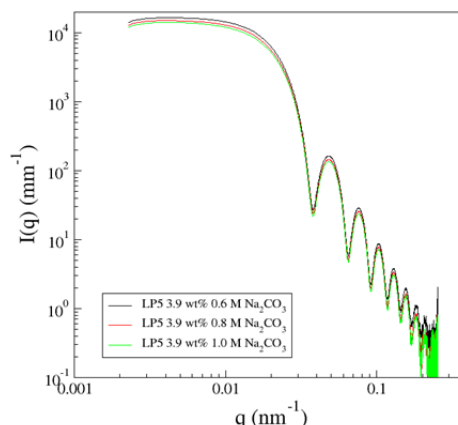

Fig. 3: Scattering intensity as a function of q for a constant particle concentration but with varying concentration of sodium carbonate, as labeled. The particles carry a PEG graft of 480 g/mol molecular weight.

Particles were also transferred into ethanol in order to correlate the stability of the dispersions with the behavior of bulk PEG solutions. Ethanolic PEG solutions exhibit crystallization at temperatures below ~35°C. As shown in Fig. 5, on transferring PEG-grafted particles into ethanol, fractal aggregates result indicative of non-equilibrium aggregation due to strong attractions among particles. This behavior can be contrasted with the salting-out of aqueous dispersions, for which attractions gradually strengthen as salt is added. Raising the temperature above 35°C did not redisperse the particles in ethanol as anticipated based on the behavior of bulk PEG polymer solutions.
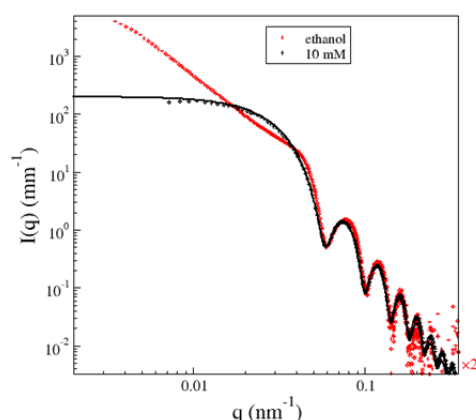

Fig. 5: Scattering intensity from aqueous and ethanolic dispersions of the same pHFBMA-PEG particles. The agreement at high q point to particles maintaining their integrity on transfer into ethanol but the low-q scattering indicates that fractal aggregates form.

Conclusion: The fluorinated particles used in this study are nearly refractive index matched to the solvent (both for aqueous and ethanolic dispersions), which means that the der Waals interactions between particle cores are weak. Thus, the attractions observed in the scattering here must derive from polymer-solvent-polymer interactions.

Publication: Several results of the SAXS and USAXS measurements have now been published as part of an article, J. Ulama, M. Z. Oskolkova, and J. Bergenholtz, "Polymer-graft-mediated interactions between colloidal spheres", *Langmuir* **32**, 2882-2890 (2016).