# Experimental report

23/01/2017

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| **Proposal:** | **9-11-1731** | **Council:** | 10/2014 |
| **Title:** | Small Ag-PA Aggregates in Re-entrant Phase | | |
| **Research area:** | Soft condensed matter | | |

**This proposal is a new proposal**

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| **Local contacts:** | Ralf SCHWEINS |

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|---|---|
| **Samples:** | D2O<br>Sodium polyacrylate<br>AgNO3<br>NaNO3 |

| Instrument | Requested days | Allocated days | From | To |
|---|---|---|---|---|
| D11 | 3 | 3 | 16/10/2015 | 19/10/2015 |

## Abstract:

Cations interacting specifically with anionic polyacrylates (PA) typically cause precipitation thresholds at stoichiometric amounts of cations per anionic residue. Contrary to this, Ag+ cations generate a much more complex phase behavior, where a regime of aggregation sets in at extremely low Ag+ contents and where a re-entrant phase with stable Ag-PA entities, 25-50 nm in size, occurs at intermediate Ag+ contents in between the aggregation regime and the precipitation threshold. The present proposal focusses on the structural analysis of these small stable entities, which may play an important role if applied in assisted Ag-nanoparticle formation.

Experimental Report 9-11-1731

# Small Ag-PA Aggregates in Re-entrant Phase

**Aim** Although $Ag^+$ is “only” a monovalent cation, it interacts even stronger with polyacrylate (PA) than bivalent alkaline earth cations do.[1,2] The present work focusses on AgPA in dilute aqueous solution. $Ag^+$ ions induce aggregation of PA coils without considerable coil shrinking at ratios of $[Ag^+]/[COO^-]$ as low as 1/1000 leading to homogeneous low density (hld) aggregates. With increasing $[Ag^+]/[COO^-]$ the aggregates undergo shrinking and further aggregation thus forming dense unstable (du) aggregates. Beyond $[Ag^+]/[COO^-]$~0.3 dense stable (ds) aggregates form (**Fig.1**). The stable solution state of the ds-aggregates (**Fig.1**) borders precipitation at ratios of [Ag+]/[COO-]>2. Ag-PA complexes are highly relevant for the preparation and stabilization of Ag-nanoparticles by UV-light.[2,3] If du-aggregates or ds-aggregates are exposed to UV-light, they form and host Ag nanoparticles. Exposure of du-aggregates to UV-light does not only induce Ag-nanoparticle formation, but stops further aggregation.[2] The present work tries to answer the following questions: are ds-particles collapsed single chains establishing a re-entrant phase or compact stable aggregates of chains (not accessible due to an unknown influence of $Ag^+$ and Ag on the scattering contrast in light scattering)? What is the morphology of du-aggregates after exposure to UV-light and of ds-aggregates before and after exposure to UV-light?

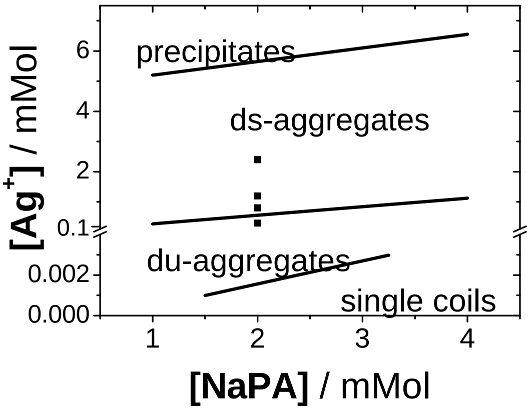

**Fig. 1**. Phase diagram of the $Ag^+$-PA in [+] = $[AgNO_3]+[NaNO_3]$ = 0.01 M. Symbols indicate SANS-experiments performed in the present experiment.

**Description of Experiment** Two PA standard polymers with different molecular weights from PSS (Mainz, Germany) were used. One sample denoted as PA-800 had a molecular weight of 450 kD and the other sample, PA-1200 had a molecular weight of 2440 kD. The solvent was $D_2O$ at a pH = 9 set by the use of NaPA. All solutions had an ionic strength, adjusted with $NaNO_3$ and $AgNO_3$ to [+] = $[NaNO_3]$ + $[AgNO_3]$ = 0.01 M. Seven samples shown in the **Table** were prepared with polymer PA-800. All samples had a concentration of $[COO^-]$=0.1875 g/L (2 mM) at variable content of $Ag^+$. The ratio $[Ag^+]/[COO^-]$ is incorporated into the sample names as leading number. One sample was measured in the absence of $Ag^+$ (0-800) in order to establish a proper reference curve of the NaPA coil. One sample was located in the regime of du-aggregates (01.5-800) and three samples (04-800, 06-800 and 12-800) were located in the regime of ds-aggregates. Directly after preparation of a sample it was split with one part being filled into a Hellma cell for the SANS experiment and the other part being filtered into a light scattering cuvette. Light scattering (LS) was used to scrutinize for compatibility of the sample properties with the state of the art[1,2]. If the results were in accordance with expectations, the part in the Hellma cell was measured by SANS. During that SANS experiment, the light scattering sample was repeatedly analysed by LS for stability. Samples 04-800 and 06-800 were prepared a second time and exposed to UV light for 4 minutes directly after preparation. Subsequently an undiluted portion of each exposed sample was transferred to a Hellma cell and measured by SANS, while a second portion of 0.2 ml was diluted by 1 ml of 0.01 M $NaNO_3$ and analyzed by LS. Finally a third portion also diluted by a factor of 0.2/1.2 was used to demonstrate Ag-nanoparticle formation by UV-vis spectroscopy. With polymer PA-1200 five samples have been prepared. Sample preparation and LS revealed that sample PA-1200 did not behave in accordance with Refs.[1,2] as for instance no Ag-nanoparticles could be induced upon exposure to UV-light with this sample. Hence data from sample PA-1200 shall not be considered any further.

| Sample | [$Ag^+$] / mM | technique | t of experim. | $R_g$ / nm | I(q=0) | $R_h$ nm |
|---|---|---|---|---|---|---|
| 0-800 | 0 | LS | - | 74.1 | 2.97 E5 g/mol | 67.5 |
| 01.5-800-UV | 0.3 | LS | 17:56<br>18:13 | 54.4<br>76.2 | 7.87 E8 g/mol<br>1.07 E9 g/mol | 70.3<br>88.7 |
| 01.5-800-UV | 0.3 | LS | 19:24<br>20:30 | 37.6<br>50.9 | 4.17 E8 g/mol<br>5.35 E8 g/mol | 39.5<br>47.8 |
| 04-800 | 0.8 | LS | 10:59<br>13:21 | 33.4<br>34.6 | 6.78 E7 g/mol<br>6.96 E7 g/mol | 62.2<br>63.5 |
| 04-800 | 0.8 | SANS | 09:52-23:56 | 31.6 | 0.903 | |
| 04-800-UV | 0.8 | LS | 02:12<br>10:55 | 41.7<br>103.2 | 1.16 E9 g/mol<br>3.07 E9 g/mol | 38.5<br>105.1 |
| 04-800-UV | 0.8 | SANS | 01:11-08:36 | 43.3 | 5.012 | |
| 06-800 | 1.2 | LS | 22:59<br>11:53 | 33.9<br>34.3 | 5.86 E7 g/mol<br>6.02 E7 g/mol | 52.4<br>53.0 |
| 06-800 | 1.2 | SANS | 22:38-08:15 | 31.0 | 0.924 | |
| 06-800-UV | 1.2 | LS | 16:55<br>21:21<br>23:48 | 43.2<br>36.9<br>30.1 | 1.58 E9 g/mol<br>2.16 E9 g/mol<br>2.10 E9 g/mol | 38.1<br>33.3<br>32.9 |
| 06-800-UV | 1.2 | SANS | 15:12-33:22 | 37.6 | 3.867 | |
| 12-800 | 2.4 | LS | 13:57<br>19:59 | 32.8<br>35.5 | 3.58 E7 g/mol<br>3.90 E7 g/mol | 40.3<br>39.9 |
| 12-800 | 2.4 | SANS | 12:27-39:04 | 32.1 | 0.768 | - |

Each solution, the solvent and an empty cell were analysed by SANS at a wavelength of 0.6 nm at four distances (1.2 m, 5 m, 8 m and 34 m) respectively. $D_2O$ with 0.01 M of $NaNO_3$ was used as solvent. Only after the experiment was finished, it turned out that the cell with solvent showed an unexpectedly high scattering signal at very low angles caused by air bubbles. We hence applied two different modes of data reduction: (i) we subtracted from a scattering curve of the solution the scattering pattern of the empty cell (at each distance separately). The resulting scattering curves were adjusted to the respective solution curve recorded at 5 m distance by applying appropriate shift factors. Finally a background of $d\Sigma/d\Omega = 0.058\ cm^{-1}$ determined from the high q-regime of the scattering signal of the solvent was subtracted from the as merged solution curves; (ii) we subtracted at each distance from the scattering curve of the solution the scattering signal of respective the solvent cell. The resulting scattering curves of the solute in solution were adjusted to the respective curve recorded at 5 m distance by applying appropriate shift factors. Although differing quantitatively at very low q, the two reductions gave the same trends and discussion shall be restricted to data from mode (i), except for sample 0-800.

**Results and Discussion** One sample denoted as 01.5-800-UV was located in the du-regime of the phase diagram, where aggregation is expected to be stopped by exposure to UV-light. Unfortunately, aggregation reappeared an hour after induction of Ag-nanoparticle formation by UV-light and we had to abstain from a SANS experiment with sample 01.5-800-UV. Three more samples were located in the ds-regime of the phase diagram. All three samples turned out to be stable before exposure to UV-light. LS revealed radii of gyration in the range of 30 nm < $R_g$ < 36 nm and hydrodynamic radii $R_h$ larger by a factor of 2 and 1.5 in case of 04-800 and 06-800, being typical for spherical objects with a low density shell and a factor of 1.4 in case of sample 12-800 characteristic for homogeneous spheres. The resulting SANS curves are shown in **Figure 2a**, in comparison to the curve recorded for the same NaPA coils in the absence of $Ag^+$ cations. The Kratky–plots measured in the presence of $Ag^+$ located in the ds-regime have comparable trends and reveal maxima characteristic for dense particles like spheres or microgels. The samples with $Ag^+$ cations also show a much larger signal than in the sample without $Ag^+$, proofing that ds-particles are aggregates of NaPA chains connected by a large amount of $Ag^+$ cations.

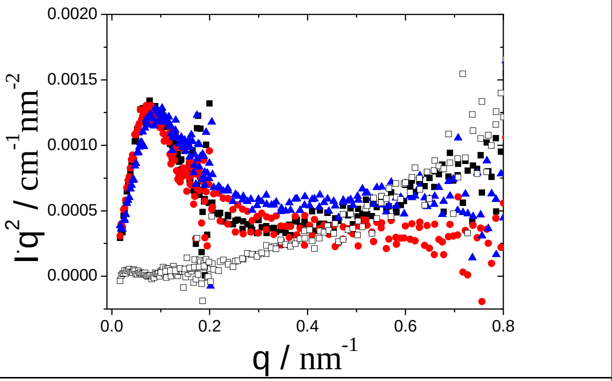

**Fig.2a**. Kratky-Plots of SANS curves for samples 04-800 (■), 06-800 (●) and 12-800 (▲) in the presence of $Ag^+$ in comparison to 0-800 (□) in the absence of $Ag^+$.

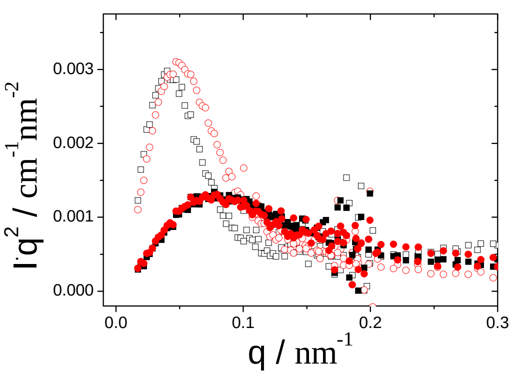

**Fig.2b**. Kratky-Plots of SANS curves for samples 04-800 (■), 06-800 (●) before and 04-800-UV (□), 06-800-UV (○) after exposure to UV-light.

Two of the ds-samples were exposed to UV-light and analysed by LS and SANS. Sample 04-800-UV showed an increase in size by LS. Unfortunately, LS required dilution by a factor of 0.2/1.2. Since this sample was closest to the phase boundary between du and ds-aggregates, dilution may have induced aggregation. However, the initial $R_g$ from LS agreed with time averaged $R_g$ from the SANS measurement. Sample 06-800 turned out to remain stable also after exposure to UV-light. Both exposed samples gained in mass inferred from an increase of the intercepts of the SANS curves by more than a factor of ten if compared to the state before exposure to UV-light. Along with the increase in mass $R_g$ slightly increased whereas $R_h$ decreased, which may be caused by density fluctuations induced by Ag-nanoparticles in the domains of the aggregates. In qualitative agreement with the LS-experiments, exposure to UV-light caused an increase of particle mass (from intercepts) by a factor of five (**Table**). The steeper decay observed in the central range of the scattering curves further supported the transformation to more compact homogeneous particles. The same features can be highlighted with Kratky-plots of the scattering curves (**Figure 2b**), where stronger peaks of the curves recorded after exposure to UV-light stress the evolution of more compact and denser particles due to the formation of silver nanoparticles. Most likely those silver nanoparticles are not only formed from the $Ag^+$ cations already hosted by the PA-aggregates but by incorporation of further $Ag^+$ cations from solution.

## References

[1] Ezhova, A.; Huber, K. Macromolecules 2014, 47, 8002-8011
[2] Ezhova, A. PhD-Thesis, University of Paderborn, 2014
[3] Huber, K.; Hollmann, J.; Witte, T.; Keuker-Baumann, S. J. Am. Chem. Soc. 2007, 129, 1089-1094