ESRF	**Experiment title:** Control of vesicle structure, stability, and formation process by means of admixing amphiphilic copolymers - a stopped-flow SAXS study	**Experiment number**: SC 2983
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Names and affiliations of applicants (* indicates experimentalists):

Prof. Michael Gradzielski*, Katharina Bressel*, Peggy Heunemann*, Sylvain Prevost*, Paula Malo de Molina*

Stranski-Laboratorium, TU Berlin, Straße des 17. Juni 124, 10623 Berlin

Report:

Vesicles have been studied extensively in the past[1,2,4]. Nevertheless the mechanism of vesicle formation is not yet fully understood. Recent studies have shown that vesicle formation often passes through an intermediate state of disc-like micelles that grow to a maximum size and then close to form vesicles.[1-4] The stability of the discs is controlled by the line tension of the disc-rim. Since the transition between the disc-like aggregates and the vesicles is mostly controlled by the balance between the line tension of the disc-rim and the bending energy of the vesicle membrane a possibility to influences the stability of those transitional aggregates is to add a hydrophobically modified water soluble polymer. These polymers might most likely accumulate at the disc-rim and therefore decrease the line tension, which should lead to larger disc-like micelles and therefore larger vesicles. Another possibility to stabilize or destabilize the aggregates would be by varying the charges of the aggregates or by screening the charges.

In our experiments we used the Pilatus Detector as well as the Frelon Detector. For the Frelon Detector two instrumental set-ups were used with a sample to detector distance of 2m and 8m to cover a large q-range. The Pilatus Detector was set to a constant sample to detector distance of 2m. To ensure the reproducibility of the experiment and to achieve a good time-resolution of the process the scattering of every mixture was monitored over a short time range of a few seconds with a high time resolution and then the mixing was monitored again over a a time range of 20 minutes with a lower time resolution.

In the first part of the experiment we used the Pilatus Detector, which has a very fast read-out time, to monitor the fast aggregation process in mixtures of tetradecyldimethyl amine oxide (TDMAO) and lithium perfluorooctanoate (LiPFO) varying the charges of the aggregates by replacing the TDMAO with the cationic tetradecyltrimetylammonium bromide (TTABr). In addition we investigated the aggregational processes in mixtures of TDMAO and lithium perfluorooctanesulfonate (LiPFOS) in the presence of additional LiBr or LiCl salt to determine the influence of the screening.

In the second part we used the Frelon Detector to monitor the slower vesicle formation in the presence of different amphiphilic polymers of the PEO_n-PPO_m-PEO_n-type varying the length of the hydrophobic or hydrophilic part (Pluronic L35, Pluronic F38, Pluronic P65, Pluronic P104 and Pluronic P123). It could be observed that even a very low polymer concentration of 0.14mM leads to a significantly slower vesicle formation. The characteristic time for the vesicle formation as well as the size of the initially formed vesicles are dependent on the concentration of the polymer. The higher the polymer concentration is the slower is the vesicle formation and the larger are the initially formed vesicles. That supports the proposed mechanism.

In addition we investigated the vesicle formation at different temperatures and could see that the vesicle formation is the faster the higher the temperature is and that the polydispersity increases with the temperature.

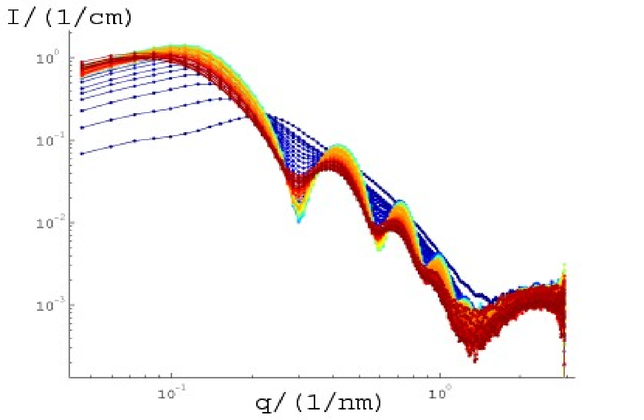

Fig. 1: *Radial averaged SAXS diffraction pattern for TDMAO:LiPFOS (5.5:4.5), ctot=50m*

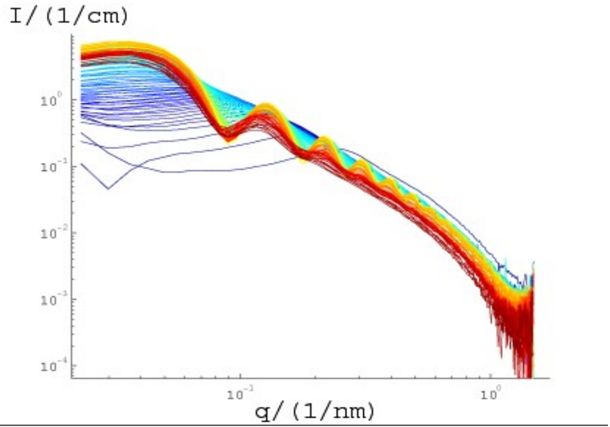

Fig. 2: *Radial averaged SAXS diffraction pattern for TDMAO:LiPFOS (5.5:4.5), ctot=50mM, c(Plu.L35)=0.275mM*

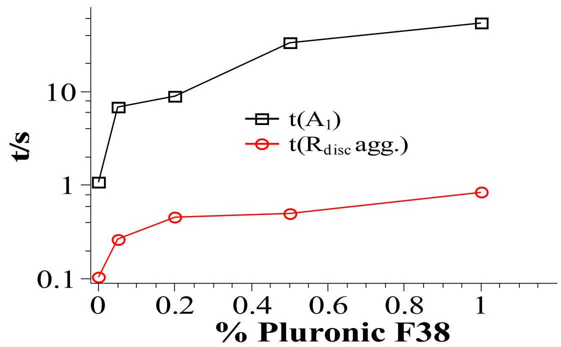

Fig. 3: *charcteristic times for the disc growth and for the vesicle formation in the dependency of the polymer concentration*

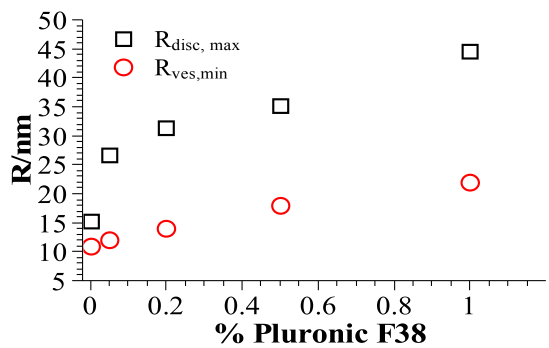

Fig. 4: *correlation between maximum disc radius $R_{disc,\ max}$ of the micelles and minimum vesicle radius $R_{ves,\ min}$*

An interesting question that arises from the analysis of these experiments is if the growth mechanism of the discs is caused by fusion of micelles or by Ostwald ripening. The time dependent evolution of the disc radius and the kinetics of the growth process indicate that the fusion process takes place. An experiment that could answer this question would be to change the chain length of one of the surfactants and to determine the kinetics in dependency on the cmc of the surfactants.

References

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