Experimental Report

Proposal: **9-10-1393** **Council:** 4/2014

Title: Monomer insertion into vesicle membranes and fixation of monodispersekinetically stabilised vesicles

This proposal is a new proposal

Researh Area: Chemistry

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Samples: C14H29(CH3)2NO +H2O/D2O
LiPFOS/C8F17SO3Li + H2O/D2O
PluL35/EO11PO16EO11 + H2O/D2O
Styrene/C8H8

Instrument	Req. Days	All. Days	From	To
D11	2	2	01/10/2014	03/10/2014

Abstract:

The formation of monodisperse vesicles in the system TDMAO (tetradecyldimethylamine oxide) - LiPFOS (lithium perfluorooctylsulfonate) can be finely controlled by the presence of a polymer of the pluronic type (EOn-POm-EOn). Thereby vesicles with a low polydispersity of 5% and controlled size depending on the polymer concentration can be produced, that are sterically stabilised by polymers attached to the vesicle bilayer. In our investigation we aim to use these vesicles as templates to produce well-defined hollow polymer capsules. SANS will be used to determine the location of monomers and resulting polymer (using deuterated compounds) and the effect on the vesicles' structures. From this study valuable information regarding a systematic and optimized formation of such nano-sized polymer capsules shall be gained as they would be interesting for instance as containers for active agents.

Monomer insertion into vesicle membranes and fixation of monodisperse kinetically stabilised vesicles

doi:10.5291/ILL-DATA.9-10-1393

The formation of monodisperse vesicles in the system TDMAO (tetradecyldimethylamine oxide) - LiPFOS (lithium perfluorooctylsulfonate) can be finely controlled by the presence of a polymer of the pluronic type (EOn-POm-EOn). Thereby vesicles with a low polydispersity of 5% and controlled size depending on the polymer concentration can be produced, that are sterically stabilised by polymers attached to the vesicle bilayer.[1] In our investigation we used these vesicles as templates to produce well-defined hollow polymer capsules.

Here we use a vesicle system that consists of 27.5mM TDMAO and 22.5mM LiPFOS with two different Pluronic L35 (EO_{11}-PO_{16}-EO_{11}) concentrations of 0.1375mM and 0.275mM since these mixtures have proven to deliver vesicles with a low polydispersity of less than 10%. SANS measurements were performed on D11 at the ILL at three different configurations of SD=1.2, 8, and 40m and Coll=5.5, 8, and 40.5m at l=6Å.

We investigated the ability of the vesicle system to incorporate styrene as a polymerisable monomer. Therefore we loaded the TDMAO solution with different amounts of styrene and mixed these TDMAO/styrene solutions with micellar LiPFOS solution.

Since the vesicle structure is determined by its mechanism of formation we first characterised the TDMAO/styrene solutions. Up to a styrene concentration of 20mM the rod-like micellar structure of the aggregates remains uneffected. At 40mM a certain amount of the material is in vesicle state and at 60mM and 80mM we find mostly vesicles. The Pluronic L35 concentration does not have any effect on the structure of the aggregates.

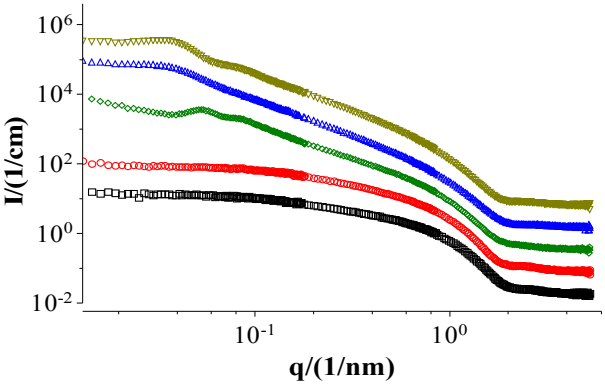

Figure 1: c(TDMAO)=50mM; c(Pluronic L35)=0.25mM in D2O; black squares: c(styrene)=0; red circles: 20mM; green diamonds: 40mM; blue triangles up: 60mM; yellow triangles down: 80mM

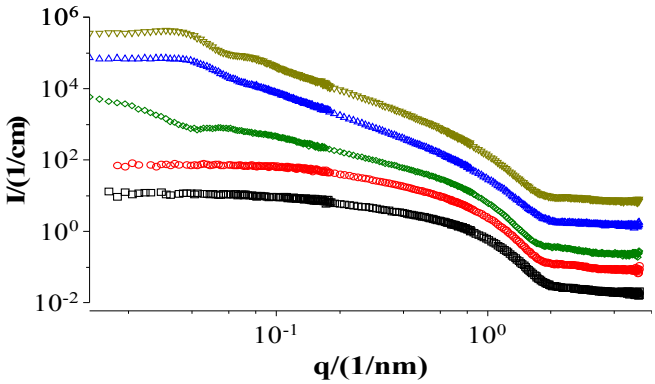

Figure 2: c(TDMAO)=50mM; c(Pluronic L35)=0.5mM in D2O; black squares: c(styrene)=0; red circles: 20mM; green diamonds: 40mM; blue triangles up: 60mM; yellow triangles down: 80mM

After adding the LiPFOS solution to the TDMAO/styrene solution vesicles are observed in the solution. At zero styrene concentration these vesicles have a low polydispersity of ~5% which increases upon addition of styrene and the vesicle size increases by 70%. Up to a styrene concentration of 33mM a plateau area can still be observed, but above 39mM the scattering intensity still increases at low *q* values which indicates the presence of larger particles. In the area below 33mM styrene the vesicles are formed from a micellar

TDMAO/styrene solution so that the vesicle structure is still better defined than above 33mM.

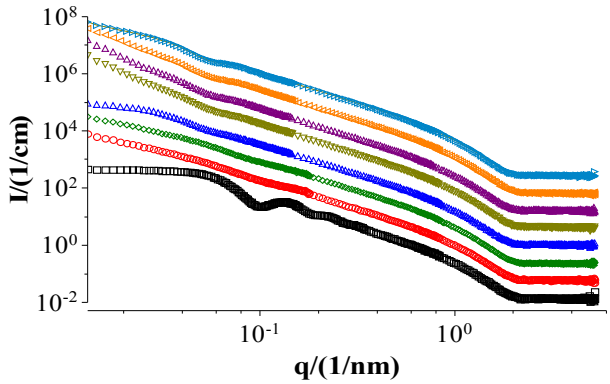

Figure 3: c(TDMAO)=27.5mM; c(LiPFOS)=22.5mM; c(Pluronic L35)=0.1375mM in D2O; black squares: c(styrene)=0; red circles: 11mM; green diamonds: 22mM; blue triangles up: 33mM; yellow triangles down: 39mM; purple triangles down: 42mM; orange triangles down: 44mM; light triangles down: 46mM

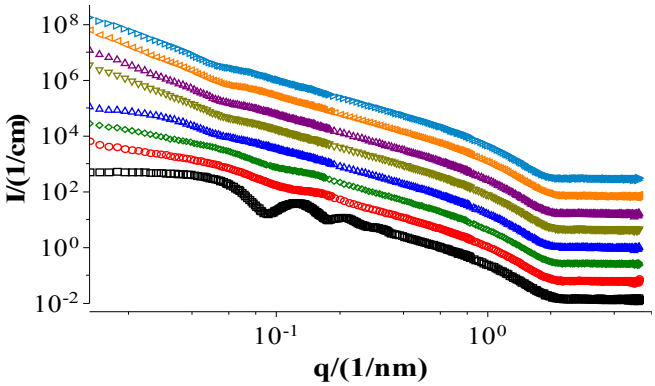

Figure 4: c(TDMAO)=27.5mM; c(LiPFOS)=22.5mM; c(Pluronic L35)=0.275mM in D2O; black squares: c(styrene)=0; red circles: 11mM; green diamonds: 22mM; blue triangles up: 33mM; yellow triangles down: 39mM; purple triangles down: 42mM; orange triangles down: 44mM; light triangles down: 46mM

In vesicle solutions with c(TDMAO)=27.5mM, c(LiPFOS)=22.5mM and c(Pluronic L35)=0.275mM and styrene concentrations between 33mM and 47mM UV-induced polymerisations were performed. Figure 5 shows that polymerisation does not effect the structure of the aggregates and that vesicle structure can be retained and that no larger objects are formed. This means that SANS allowed us to prove the successful template reaction of our vesicles to form small, well-defined polymeric capsules.

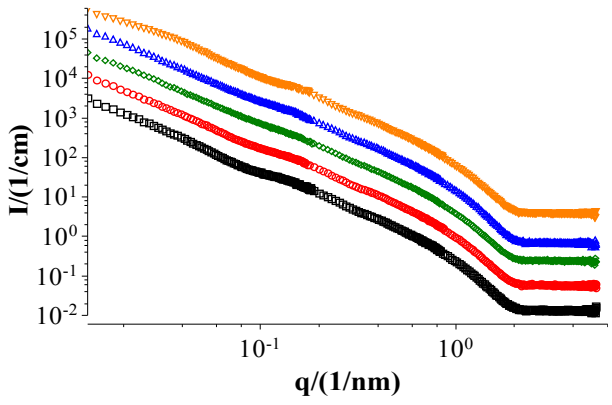

Figure 5: c(TDMAO)=27.5mM; c(LiPFOS)=22.5mM; c(Pluronic L35)=0.275mM in D2O, after UV-initiated polymerisation; black squares: c(styrene)=33mM; red circles: 11mM; green diamonds: 22mM; blue triangles up: 33mM; orange triangles down: 39mM

[1] K. Bressel, M. Muthig, S. Prevost, J. Gummel, T. Narayanan, M. Gradzielski, *ACS Nano*, 2012, **6**, 5858-5865