Experimental report

20/09/2016

Proposal: **9-10-1444** **Council:** 4/2015

Title: Vesicle Based Polymer Nanocapsules- Controlling their Structure by the Preparation Process

Research area: Chemistry

This proposal is a continuation of 9-10-1393

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Local contacts: Peter LINDNER

Samples: $C_{14}H_{29}N(CH_3)_2O$ in D_2O
$C_8F_{17}SO_3Li$ in D_2O
styrene in D_2O
$C_9H_{15}O_2$ in D_2O

Instrument	Requested days	Allocated days	From	To
D11	2	2	02/12/2015	04/12/2015
D33	2	0		
D22	2	0		

Abstract:

The formation of monodisperse vesicles in the system TDMAO (tetradecyldimethylamine oxide) - LiPFOS (lithium perfluorooctylsulfonate) can be finely controlled by admixing copolymers of the Pluronic type (EOn-POm-EOn). Their size is controlled by the copolymer concentration (radii of 20-80 nm) and they possess low polydispersities of 5%. These vesicles are used as templates to produce hollow, spherical polymer capsules by UV-induced radical polymerization of appropriate monomers. SANS will be used to determine the effect of the monomer and cross-linker concentration on the structure of the finally formed polymer capsules. The polymerised vesicle based capsules will be compared to the initially present vesicles and to the extracted polymer casules redispersed in d-DMSO in order to gain information about the structure of the pure polymer capsules. This study will yield valuable information regarding the quality of this template reaction and help substantially to develop such nano-sized polymer capsules further and optimise them for corresponding applications, for instance as containers for active agents.

Vesicle Based Polymer Nanocapsules - Controlling their Structure by the Preparation Process

Experiment number: 9-10-1393

Beamline: D11

Date of experiment: 02/12/15-04/12/115

Date of report: 20/09/2016

Local contact: Peter Lindner

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Vesicle system containing zwitterionic TDMAO (tetradecyldimethylamine oxide) - anionic LiPFOS (lithium perfluorooctylsulfonate) surfactants can be controlled finely by addition of plurionic type of copolymers (Eon-POm-EOn).[1] Pluronic copolymer accumulates on the disc rim and lowers the line tension.[2] By controlling the size and stability; small, monodisperse, kinetically stable vesicles with a low polydispersity of 5% are formed. In this work these vesicles are used as templates to produce hollow polymer nanocapsules by stabilizing their structure with UV induced radical polymerization.

For this experiment we used a vesicle system that consists of 27.5mM TDMAO and 22.5mM LiPFOS with 1 mol % Pluronic L35 (EO_{11}-PO_{16}-EO_{11}) and bilayer structure in corporation with increasing amount of hexyl acrylate monomer and cross-linker as 1,6-hexandiol diacrylate. The addition and insertion of monomeric precursors which were solubilized and homogenized into the micellar TDMAO/L35 solutions and then mixing with LiPFOS stocks formed bilayer structures. Finally, these monomer loaded vesicles were cross-linked polymerized and after removing of vesicle template pure polymer nanocapsules were dispersed in d-THF for SANS analyses. With this work the effect of monomer/cross-linker amount and ratio on vesicle structures and final polymer nanocapsule products were investigated. SANS measurements were performed on D11 instrument at three different configurations of SD=1.2, 8, and 40m and Coll=8 and 40 at λ=6Å.

In order to follow the effect of polymerization during the vesicle formation and later on, we analyzed the polymerized vesicles and pure nanocapsule dispersed in deuterated solvent. From the SANS analyses we investigate the vesicles formed radii of 26 nm with low polydispersity and remained unaffected after polymerization (Fig.1). However pure nanocapsules dispersed in d-THF scattered very poor at low q meaning there is no bigger aggregates into the system while at high and mid q areas we observe these structures has small and spherical shape as expected (Fig. 2).

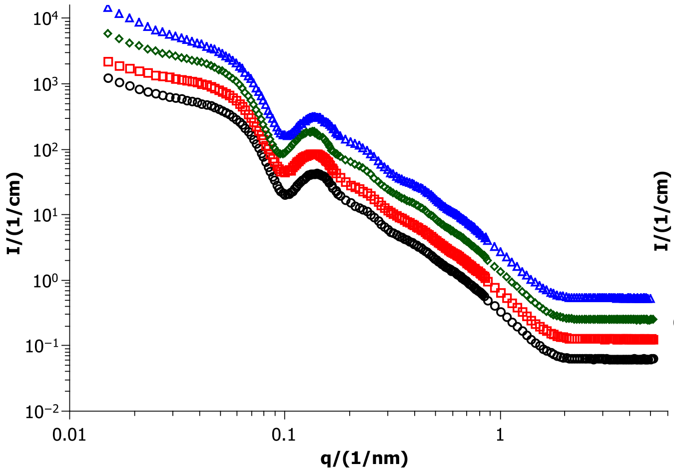

Figure 1. c(TDMAO)=27.5mM; c(LiPFOS) =22.5mM; c(Pluronic L35)=0.275mM in D2O; black: c(monomer/cross-linker ratio)=15mM/0.1; red: c(monomer/cross-linker ratio)=15mM/0.2; green: c(monomer/cross-linker ratio)=20mM/0.1; blue: c(monomer/cross-linker ratio)=20mM/0.2 polymerized vesicles.

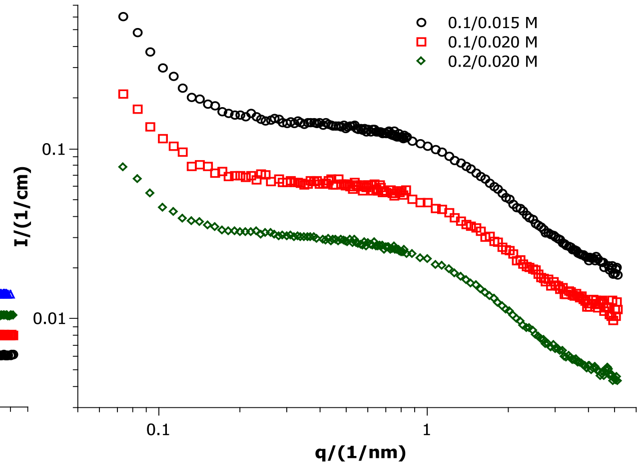

Figure 2. Cross-linked polymerized pure nanocapsules in d-THF; black: c (monomer/cross-linker ratio) =15mM/0.1; red: c (monomer/cross-linker ratio) =20mM/0.1; green: c (monomer/cross-linker ratio) =20mM/0.2

In addition to this system, from previous SANS analyses at D11 (Fig. 3) we obtained the co-surfactant effect of styrene monomer when more than 50 mM styrene introduces into the TDMAO micellar solutions, it forms vesicle aggregates. We analyze samples of polymerized 50mM TDMAO with 50mM Styrene and 70mM Styrene monomer and also investigate these polymerized TDMAO/Styrene aggregates (Fig. 4). As already known TDMAO surfactant has rod-like micelles and SANS plots showed spherical domains with hard sphere interactions in this system with mixture of bilayer structure in polymer network.

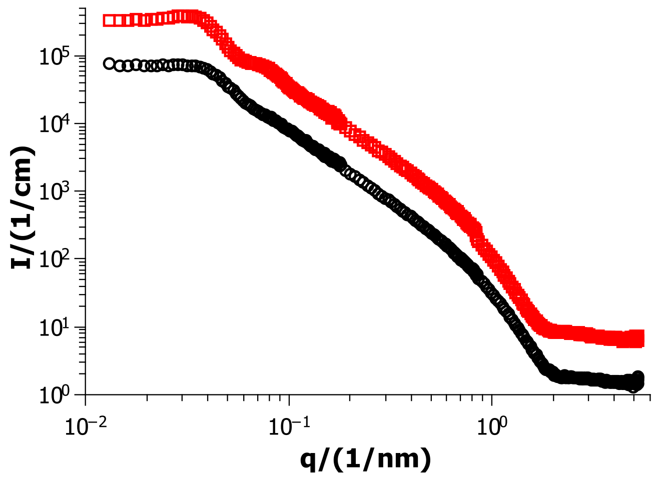

Figure 3. c(TDMAO)=50mM; c(Pluronic L35)=0.5mM in D2O; black: c(styrene)=60mM; red c(styrene)=80mM mixtures.

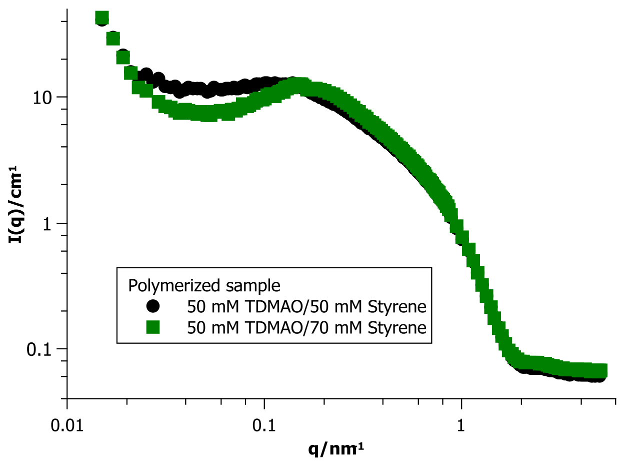

Figure 4. c(TDMAO)=50mM; c(Pluronic L35)=0.5mM in D2O; black: c(styrene)=50mM; greenc(styrene)=70mM polymerized structures.

[1] Bressel K., Gradzielski M.; Soft Matter, **2015**, 11, 2445-2453.

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