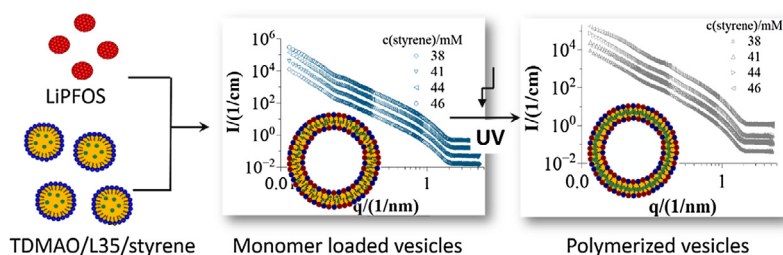


## Regular Article

## Controlled formation of vesicles with added styrene and their fixation by polymerization

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## GRAPHICAL ABSTRACT



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## ABSTRACT

**Hypothesis:** An effective way for fixing vesicle structures is the insertion of monomers and cross-linking agents into their bilayer, and their subsequent polymerization can lead to the formation of polymeric nanocapsules. Particularly attractive here are vesicle systems that form spontaneously well-defined small vesicles, as obtaining such small nanocapsules with sizes below 100 nm is still challenging.

**Experiments:** A spontaneously forming well-defined vesicle system composed of the surfactants TDMAO (tetradecyldimethylamine oxide), Pluronic L35, and LiPFOS (lithium perfluorooctylsulfonate) mixture was used as template for fixation by polymerization. Therefore, styrene monomer was incorporated into the vesicle bilayer and ultimately these structures were fixed by UV induced radical polymerization. Structural alteration of the vesicles upon loading with monomer and the cross-linker as well as the effect of subsequent polymerization in the membrane were investigated in detail by turbidity measurements, dynamic and static light scattering, (DLS, SLS), and small angle neutron scattering (SANS).

**Findings:** The analysis showed the changes on vesicle structures due to the monomer loading, and that these structures can become permanently fixed by the polymerization process. The potential of this approach to produce well-defined nanocapsules starting from a self-assembled system and following polymerization is critically evaluated.

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**Abbreviations:** TDMAO, tetradecyldimethylamine oxid; L35, pluronic L35; LiPFOS, lithium perfluorooctylsulfonate; SLS, static light scattering; DLS, dynamic light scattering; SANS, small angle neutron scattering.

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## 1. Introduction

Controlling the formation and morphological properties as well as the stability of nanoscaled structures has become of great interest in recent years based upon their functionality in biomedical, catalytic or electronical applications [1–5]. Self-assembled structures of surfactants, due to the ease of their formation, have been widely used as templates in nanoscience, often with the aim of

producing nanocarriers [6,7]. Particularly, vesicles are a very interesting self-assembled structures due to their structural capacity for encapsulation [8–11]. These closed bilayer systems are analogous to biological membranes and can either transport hydrophobic compounds within their lipid shell or hydrophilic moieties in their core. In addition, vesicles are often well-defined systems that can be formed spontaneously by appropriate choice of the surfactant (s) [12–14].

A common way for keeping the stability of these submicron structures and to modify the permeability, is to strengthen the bilayer with the help of polymers i.e., by introducing a (cross-linked) polymer layer. In that context for instance polymerizable surfactants or amphiphilic block copolymers have been used for stabilization [15–17]. Vesicles formed from styrene containing surfactant systems were investigated in terms of polymerization kinetics by Fendler [18]. Later on, German reported approaches for polymerization reactions in vesicle membranes with polymerizing the vesicles formed from functional amphiphiles carrying styryl groups, strengthening the network with copolymerization and constituting two-dimensional interpenetrating network in the vesicle bilayer [19]. A different study focused on synthesis of cationic, anionic, and zwitterionic surfactants with polymerizable chains, and obtained polymerized vesicles with reduced permeability [20].

Another efficient approach is based on introducing hydrophobic monomers into the shell interior of the vesicles and fixing them by subsequent polymerization. As a common monomer that can polymerize accurately, styrene has played an important role in the structural stabilization of vesicles. Murtagh and Thomas obtained cross-linked polystyrene by polymerization of a vesicle system retaining the physical properties while examining the membrane permeability and could control the mobility of guest molecules [21]. Similarly dioctadecyldimethylammonium bromide vesicles could be transformed to polymer-containing vesicles by radical polymerization of styrene [22]. Jung et al. pointed out that polymerization in dodecyltrimethylammonium bromide (DTAB) vesicles caused a phase separation in the bilayer, and particularly styrene polymerization in dioctadecyldimethylammonium bromide (DODAB) vesicles formed so called parachute-like shape [23,24]. In another work, Kaler presented the polymerization of styrene within the bilayer of a vesicle system formed from the mixture of cationic and anionic surfactants [25]. Moreover, the study from McKelvey *et al.* templated hollow polymer spheres of styrene from catanionic vesicles with cross-linking successfully [26]. Recent experiments on polymerized vesicles have shown that here nanocapsules with a polymer shell of about one nm thickness can be formed [27].

In our work we employed a surfactant mixture composed of zwitterionic tetradecyldimethylamine oxid (TDMAO) and anionic lithium perfluorooctylsulfonate (LiPFOS) that had been shown previously to form very monodisperse (PDI ~ 0.05) vesicles as a result of the kinetics of the formation path [28,29]. Due to the synergistic interaction between the surfactant pairs, vesicle structures are formed, as the head groups interact strongly attractively and thereby reduce the joint head group area substantially. Stability and size of these vesicles can be controlled in a range of radii of 15–60 nm by addition of Pluronic triblock copolymers (EO<sub>n</sub>-PO<sub>m</sub>-EO<sub>n</sub>) [30,31]. Consequently, small, monodisperse and kinetically long-time stabilized vesicles are formed in their mixtures.

In the present study, we investigated the effect of styrene monomer on these systems and the effect of polymerization for permanently fixing these well-defined TDMAO/LiPFOS vesicles, as obtaining such small and well-defined capsule like colloids is still an open challenge. In our investigation a mixture with molar ratio of 55:45 in the presence of 1 mol% Pluronic L35 was employed, as this ratio had been shown before to yield the most well-defined

vesicles [30,31], and the L35 delivering additional steric stabilization to the vesicle system. It might be noted that the addition of styrene to TDMAO solution has been shown before to promote a transition from micellar to vesicular structures in the TDMAO/L35 system [32]. However, in that system these vesicles could not be permanently fixated as the polymerization lead to transition from the rather polar styrene to the purely hydrophobic polystyrene and therefore a transition from vesicles to rod-like aggregates takes place. In contrast this paper focuses on the effect of styrene monomer and its subsequent polymerization in the formation of polymerically fixated TDMAO/LiPFOS/L35 vesicles.

## 2. Experimental section

### 2.1. Materials

Nonionic surfactant, N,N-dimethyltetradecylamine N-oxide (TDMAO, C<sub>14</sub>H<sub>29</sub>N(CH<sub>3</sub>)<sub>2</sub>O, Mw = 257.46 g/mol, cmc = 0.12 mM [33]) was kindly provided by Stepan company (Illinois, USA) as a 25% TDMAO solution in water named Ammonyx M. The solution was freeze-dried and used without any further purification. Anionic surfactant, lithium heptadecafluoro-1-octanesulfonate (LiPFOS, C<sub>8</sub>F<sub>17</sub>SO<sub>3</sub>Li, Mw = 506.06 g/mol, cmc = 6.3 mM [34]) was purchased from TCI Europe (purity >96%). Pluronic L35 (L35, EO<sub>11</sub>PO<sub>16</sub>EO<sub>11</sub>) was kindly given by BASF SE (Ludwigshafen, Germany). Benzoyl peroxide (DBPO, C<sub>14</sub>H<sub>10</sub>O<sub>4</sub>) was obtained from Sigma-Aldrich and used as photo-initiator. These compounds were used without further purification. Styrene (C<sub>8</sub>H<sub>8</sub>, >99% GC, solubility in water = 300 mg/L (at 25 °C) [35]) and divinylbenzene (DVB, C<sub>10</sub>H<sub>10</sub>, technical grade 80%) as cross-linking agent were purchased from Sigma-Aldrich and washed through an inhibitor remover column before usage. All stock solutions were prepared by dissolving the compounds in Millipore water and homogenized by vigorous shaking with a vortex mixer before being equilibrated at 25 °C. Samples for small angle neutron scattering (SANS) experiments were prepared in D<sub>2</sub>O (D content >99.9%) from Eurisotop company (Saint-Aubin, France).

### 2.2. Sample preparation

Stock solutions of 50 mM TDMAO containing 1 mol% (relative to the TDMAO) L35 were mixed with increasing amounts of monomer and cross-linker in a 0.1 M ratio, and were equilibrated by stirring for 3 days at room temperature in the dark. Monomer loaded vesicles were prepared by mixing monomer loaded TDMAO stock solutions (containing elongated micelles [31]) with 50 mM LiPFOS stock solutions at a molar ratio of 55:45 (yielding the most monodisperse vesicles [29,30]). Polymerized samples were prepared by dissolving 3 mol% initiator in monomer/cross-linker mixtures, varying due to the total monomer concentration, and prior to mixing them with TDMAO/L35 stocks. For polymerization, TDMAO/L35/LiPFOS/styrene mixtures were placed in a three-neck round bottom flask and dissolved oxygen was removed from the system by repeatedly flushing with nitrogen. The reaction mixture was stirred vigorously with a PTFE stir bar and irradiated by using a Spectroline Quartz Pencil shape UV lamp with a wavelength of 365 nm inserted into the reaction flask from the middle neck up until it was fully submerged in the reaction mixture but did not touch the stirrer and ran for 15 h under nitrogen atmosphere with moderately stirring at 18 °C. All stock solutions used in this work were prepared by dissolving the proper masses of the compounds in Millipore water or for small angle neutron scattering measurements in D<sub>2</sub>O to enhance the contrast and lower the incoherent background (samples in D<sub>2</sub>O were prepared at the same concentrations as the ones in H<sub>2</sub>O, i.e., accounting for their density difference).

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