Kinetics of the formation of polymer modified vesicles studied with the SAXS-stopped-flow technique

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Vesicles have been studied extensively in the past[1]. 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 than close to form vesicles.[1,2] The stability of the discs is controlled by the line tension of the disc-rim. The balance between the line tension of the discs and the bending elasticity of the vesicle bilayers determines the size and polydispersity of the initially formed vesicles.

In our study we modified the previously studied TDMAO (tetradecyldimethylamine oxide) /LiPFOS (lithium perfluorooctylsulfonate) system by addition of amphiphilic copolymers, e.g. of the PEOₘ-PPOₙ-PEOₘ-type. The hydrophobic part of these copolymers is incorporated into the surfactant bilayers and is assumed to accumulate in the disc-rim and therefore lower the line tension. That leads to an increase in the maximum size of the disc-like micelles and to a slower vesicle formation. The kinetics of the vesicle formation process has been studied by means of the stopped-flow technique with SAXS detection. This rapid-mixing technique allows the observation of kinetic processes in the ms time range and gives excess to detailed structural information about size, shape, and polydispersity of the aggregates. In addition the long-time stability of the vesicles has been followed by DLS-measurements. It could be seen, that addition of hydrophobically modified polymers increases the vesicle stability. In summary, a clear correlation between formation process, structure of the formed vesicles and their long-time stability are established.

The metastable vesicles can be used for templating processes to fix the structure. First experiments have been performed to incorporate monomers of the styrene type into the vesicle bilayer and to encapsulate the vesicles by UV-initiated radical polymerisation.

Influence of polymer incorporation into the disc-rim on the vesicle formation behaviour