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| | Experiment title: Investigation of the formation process of polymersomes | Experiment number: SC 2285 |
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Report:

Amphiphilic block copolymers aggregate in aqueous solution in a fashion similar to that of surfactants. Accordingly one may find spherical and rodlike micelles but also closed bilayers, i.e. vesicles which are called “polymersomes”. The aggregation behaviour of block copolymers in solution has received increasing interest during recent years because of their excellent stability, the slow dynamics involved, and the potential to control physical, chemical, and biological properties via tailoring of block lengths, block chemistry, and functionalization [1-3]. In addition, a large variety of such block copolymers has become accessible during recent years due to substantial advances in the synthetic techniques.

However, despite the fact that they have been intensively investigated with respect to their static behaviour so far only relatively little is known with respect to their dynamics and especially with respect to the morphological transitions involved in the formation process of aggregates. In order to address this interesting question of formation of block copolymer aggregates we performed stopped-flow experiments in which aggregation was induced by diluting solutions of well-defined block copolymers (obtained by a tailor-made synthesis by ionic polymerisation) in a good solvent in which the polymers are dissolved molecularly by water. The sudden change of solvent quality induces aggregate formation where, depending on the polymer, the formed aggregates may be micelles, micellar rods, or vesicles.

In fig. 1 scattering curves as a function of time are given for the case of diluting a 4 wt% solution of polyisoprene-*b*-polyethyleneoxide (PI-PEO) with the 4-fold amount of water, where this process was followed with exposure times of 10 ms. One can clearly observe that after about 10 s a peak around 0.5 nm^{-1} is formed. Apparently the originally formed large dispersion is transformed after this time into well defined micellar aggregates of a size of about 13 nm with a distinct core-shell structure with PI being in the core, PEO constituting the shell. Prior to the micelle formation the copolymer is apparently present of rather large dispersion droplets that only in a rather slow process are transformed into well-defined micellar aggregates. It is also evident from the data in fig. 1 that there is no growth process of the micellar aggregates taking place but instead the relative amount of micellar aggregates is increasing with time until finally (after about 10 mins) all of the copolymeric material is transformed into these micelles.

In summary it can be stated that this experiment has been very successful as this has been one of the first experiments to follow such aggregation processes in block copolymers in comprehensive structural detail. Taking advantage of the power of such time-resolved SAXS stopped-flow experiments we were able both to study the formation of micelles and vesicles formed by block copolymers in aqueous solution, which is of key importance for understanding these interesting systems in more comprehensive detail.

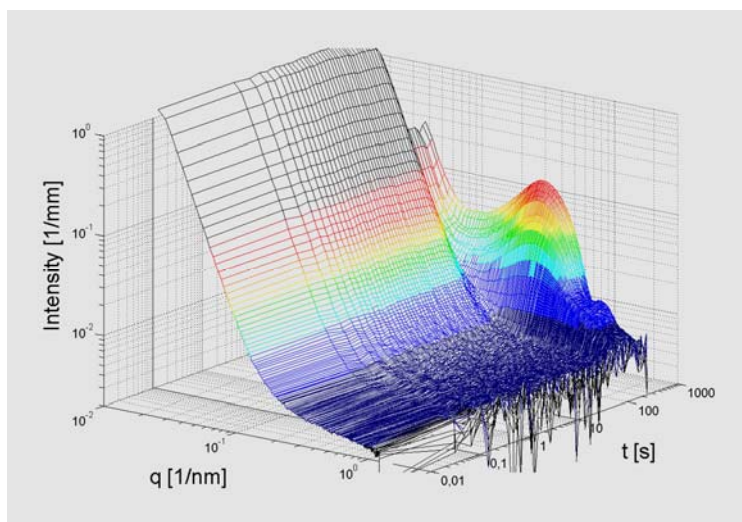


Fig. 1: SAXS intensity curves for various times after mixing a 4 wt% solution of PI-PEO with the 4-fold amount of water (25°C)

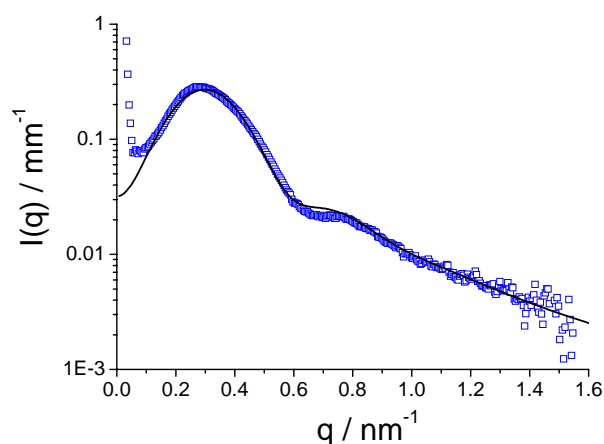


Fig. 2: Scattering intensity of fig. 1 after about 10 mins fitted with a core-shell micelle model with core radius of 8.5 nm, shell thickness of 4.5 nm (ratio of scattering length densities shell/core = -0.37)

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