The aggregation behaviour of amphiphilic block or gradient copolymers depends on the molecular structure as well on the external parameters. We have synthesized polystyrene-b-poly(styrene-grad-(acrylic acid)) copolymers (PS-b-P(S-g-AA)) with a very short starting polystyrene block via Nitroxide Mediated Free-Radical Polymerization (NMP). In a gradient copolymer the relative amount of acrylic acid increases with the distance to the hydrophobic polystyrene block. The aim is to determine how the architecture of the gradient copolymers affects the structure of the formed micellar aggregates. A very important aspect in this investigation is the charging of the PS-grad-PAA block that was controlled by the amount of added sodium hydroxide (thereby changing the pH), so that the acrylic acid may be fully deprotonated or significantly less deprotonated. This is described by the ionization alpha of the acrylic acid. Measurements of the surface tension showed no pronounced surface activity of these compounds, while light scattering confirms the formation of aggregates, where the size of these aggregates depend on the gradient as well as on the pH. These aggregates are relatively complex with respect to their structural behaviour. Similar effects were seen for other copolymers with a similar gradient block structure. The detailed structure of the copolymer micelles was studied by SANS measurements where mostly the core of the micelles is observed:

The aggregation and phase behaviour of these molecules is of interest to understand higher-level assemblies as well to use them in applications. There exist a lot of applications e.g. in cosmetics, pharmaceutical, petroleum industry and different manufacturing processes. In that way they can be used for example to encapsulate or releases active ingredients for drug delivery under specific external conditions, as additives to control rheological behaviour, as a model membrane in the case of vesicles or as stabilizer in emulsion polymerization.