

Supplementary Information

Solubility behaviour of the polymeric macrosurfactant

The behaviour of the macrosurfactant in a solvent provides an indication of how it would behave in the emulsion. Therefore we dissolved both macrosurfactants (which distinguish in the type of the hydrophilic block and block length) in water, cyclohexane and chloroform, the same solvents as we used in the emulsions. In an organic solvent, the block copolymers form in general inverse micelles with the hydrophobic block (BuMA) forming the shell (stretched chains) and the hydrophilic block (PEGMA or DMAEMA) coiled in the core. The theoretical value of the inverse PEGMA₁₆-*b*-BuMA₄₂ micelles is 25.4 nm, for BuMA₅₉-*b*-DMAEMA₈₃ 46 nm. In chloroform and cyclohexane, we found an average feature size close to the theoretical values of inverse micelles for both macrosurfactants (see Fig. S1), i.e. they form inverse micelles in these solvents. In addition, there appears a peak at a few nm when dissolved in chloroform. These are coiled single molecules (theoretically PEGMA₁₆-*b*-BuMA₄₂: 2.84 nm, BuMA₅₉-*b*-DMAEMA₈₃: 4.44 nm) because all homopolymers of the block copolymers are well soluble in chloroform. The exception is PEGMA₁₆-*b*-BuMA₄₂ in chloroform where average size of the features is 100 nm.

In water, micelles are formed in theory but the features we found are much larger than expected (see Fig. S1). For BuMA₅₉-*b*-DMAEMA₈₃, the features are about the double of the theoretical value (57 nm). Most probably, micelles with not as collapsed chains in the core or small aggregates are formed. For PEGMA₁₆-*b*-BuMA₄₂, even bigger aggregates are formed.

The theoretical value of the inverse PEGMA₁₆-*b*-BuMA₄₂ micelles is 25.4 nm, for BuMA₅₉-*b*-DMAEMA₈₃ 46 nm. The theoretical value assumes that the polymer chains are fully extended and that the hydrophilic block is in the core of the micelle, while the hydrophobic block in the corona of the micelle (similar to Raduan et al²⁵).

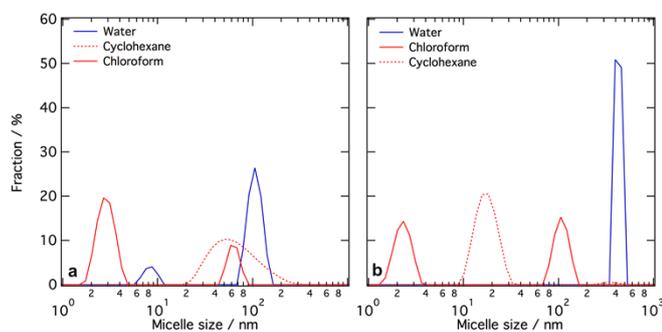


Fig. S1: Size distribution of a) BuMA₅₉-*b*-DMAEMA₈₃ and b) PEGMA₁₆-*b*-BuMA₄₂ micelles, respectively, in water, chloroform or cyclohexane.