Supporting information.


The reactivity ratios for styrene and acrylic acid were determined from the kinetic experiment using two methods: Finemann-Ross \( r(\text{St})=0.22 \pm 0.01, \ r(\text{AA})=0.88 \pm 0.04 \) and Kelen-Tüdos \( r(\text{St})=0.23 \pm 0.03, \ r(\text{AA})=0.91 \pm 0.01 \).

![Graph](a)

![Graph](b)

**Figure SI-1.** Kinetic data plotted in coordinates of Fineman-Ross (a) and Kelen-Tüdos (b) equations for determination of reactivity ratios of styrene and acrylic acid.

2. DLS-measurements.
Figure SI-2. DLS-titration curves for solutions of block-gradient copolymers D1, D2, D3, D4 at concentration C=1 g/L.
Figure SI-3. Auto-correlation function decay rate vs. $q^2$ and concentration dependence of diffusion coefficient for copolymer D2 without salt (a, b) and with 0.1M NaCl (c, d).

3. SANS-measurements.
Figure SI-4. Scattered intensity as a function of the scattering vector value for block-gradient copolymers D1 and D4 in heavy water at concentration C=100 g/L at different pH.

4. The model for fitting the results obtained in SANS-experiments.

The form factor of polydisperse spheres is given by

\[ F(q) = \frac{(a(q) - b(q) \cos(2qR_g) + c(q) \sin(2qR_g)) \exp(-2(q\sigma)^2))}{2 / q^6} \]

with

\[ a(q) = 1 + q^2(R_g^2 + \sigma^2) \]
\[ b(q) = 1 - q^2(R_g^2 + \sigma^2) + 4(q\sigma)^2(1 + (q\sigma)^2) \]
\[ c(q) = 2(1 + 2(q\sigma)^2)qR_g \]

where \( R_g \) is the average (form factor) radius of the sphere and \( \sigma \) is the radius standard deviation.

The hard sphere structure factor in the Percus-Yevick approximation \(^{54}\) is given by

\[ S(q) = \frac{1}{1 + 24\phi \frac{G(2R_{HS}q)}{2R_{HS}q}} \]

where
\[ G(u) = \alpha(\sin(u) + u \cos(u))/u^2 + \beta(2u \sin(u) + (2 - u^2) \cos(u) - 2)/u^3 + \gamma(-u^3 \cos(u) + 4((3u^2 - 6) \cos(u) + (u^3 + 6u) \sin(u) + 6))/u^5 \]

and

\[ \alpha = \frac{(1 + 2\phi)^2}{(1 - \phi)^3}, \quad \beta = \frac{-6\phi(1 + \phi / 2)^2}{(1 - \phi)^4}, \quad \gamma = \phi \alpha / 2, \quad u = 2qR_{HS} \]

with \( \phi \) the volume fraction of the equivalent hard spheres and \( R_{HS} \) the hard sphere radius

\( \phi = \frac{4\pi}{3} R_{HS}^3 \cdot n \), where \( n \) is the number of scattering particles per unit volume.

5. TEM

Figure SI-5. TEM images of the aggregates formed by (a) D2, (b) D3, (c) D4.
Figure SI-6. Size distribution of the micelles of block-gradient copolymers: D2 (a), D3 (b), D4 (c).