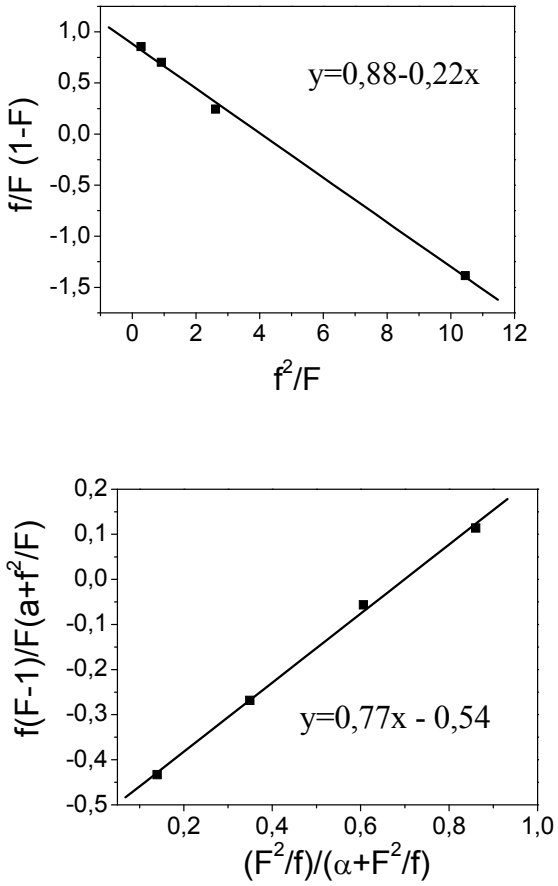
Supporting information.

1. Synthesis of block-gradient copolymers and kinetic of copolymerization.

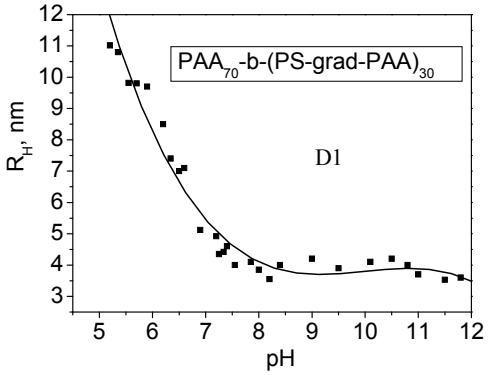
The reactivity ratios for styrene and acrylic acid were determined from the kinetic experiment using two methods: Finemann-Ross (r(St)=0.22±0.01, r(AA)=0.88±0.04) and Kelen-Tüdos (r(St)=0.23±0.03, r(AA)=0.91±0.01).

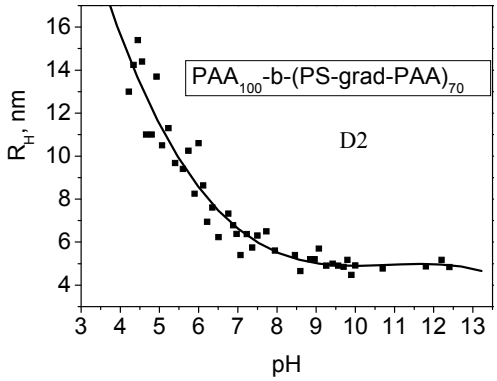


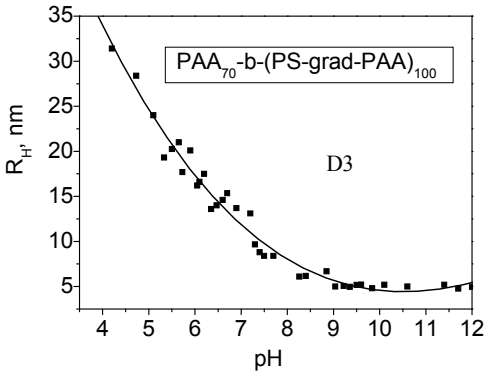
(a) (b)

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.







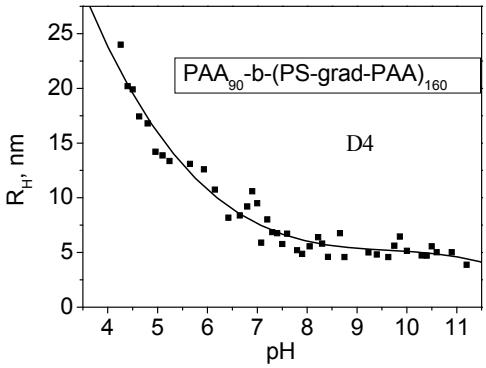
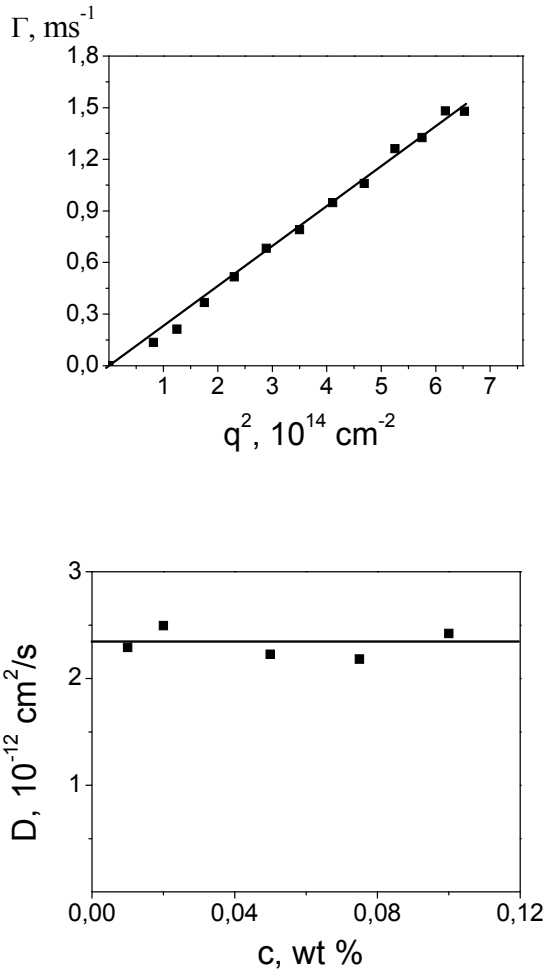
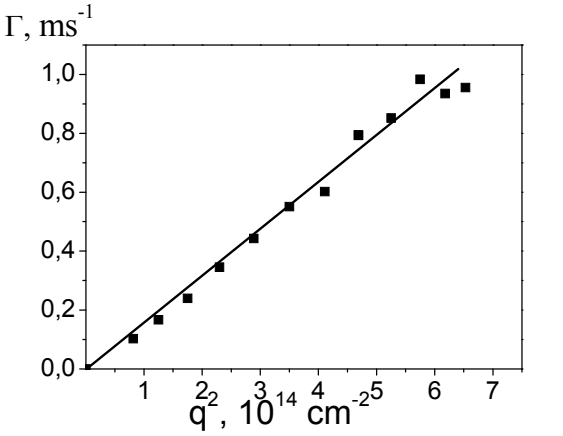
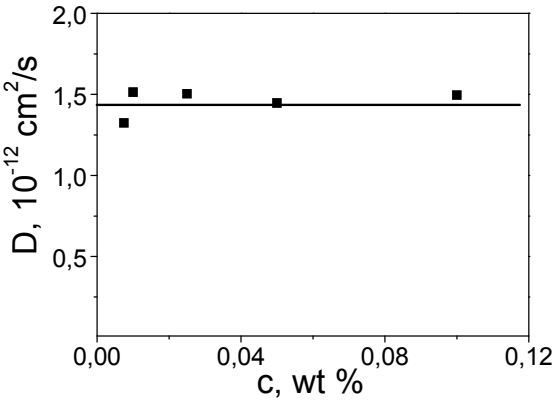


Figure SI-2. DLS-titration curves for solutions of block-gradient copolymers D1, D2, D3, D4 at concentration C=1 g/L.



(a) (b)

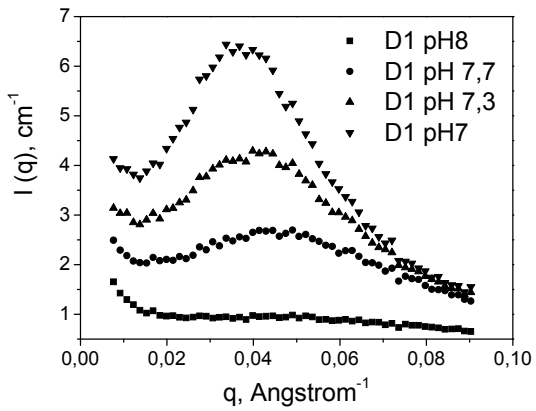




(c) (d)

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.



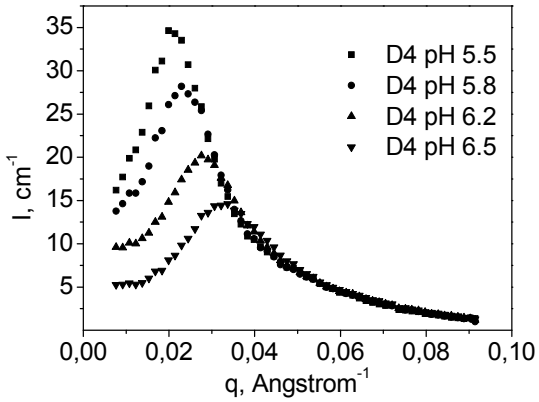


Figure SI-4. Scattered intensity as a function of the scattering vector value for block-gradient copolymers D1 and D4 in heavy water at concentration C=100 g/L at different pH.

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

The form factor of polydisperse spheres is given by

$$F(q) = (a(q) - b(q)\cos(2qR_g) + c(q)\sin(2qR_g))\exp(-2(q\sigma)^2))/2/q^6$$

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 σ is the radius standard deviation.

The hard sphere structure factor in the Percus-Yevick approximation [54] is given by

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

where

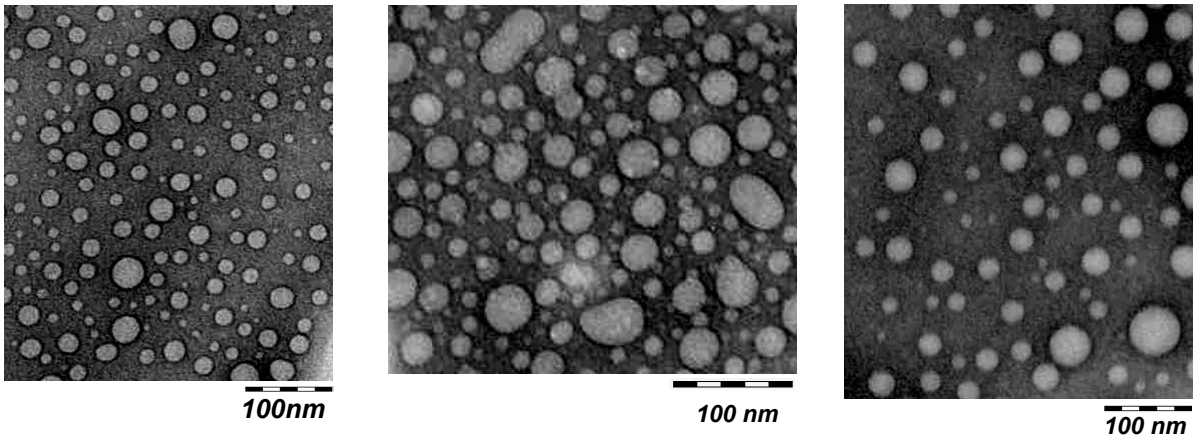
$$G(u) = \alpha(\sin(u) + u\cos(u))/u^2 + \beta(2u\sin(u) + (2-u^2)\cos(u) - 2)/u^3 + \gamma(-u^4\cos(u) + 4((3u^2-6)\cos(u) + (u^3+6u)\sin(u) + 6))/u^5$$

and

$$\alpha = \frac{(1+2\phi)^2}{(1-\phi)^4} \qquad \beta = \frac{-6\phi(1+\phi/2)^2}{(1-\phi)^4} \qquad \gamma = \phi\alpha/2 \qquad u = 2qR_{HS}$$

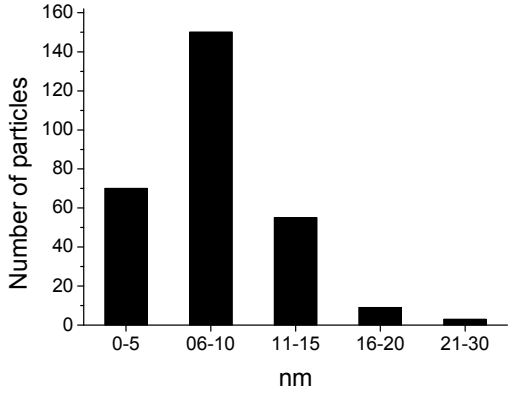
with ϕ the volume fraction of the equivalent hard spheres and R_{HS} the hard sphere radius ($\phi = \frac{4\pi}{3} R_{HS}^3 \cdot n$, where n is the number of scattering particles per unit volume).

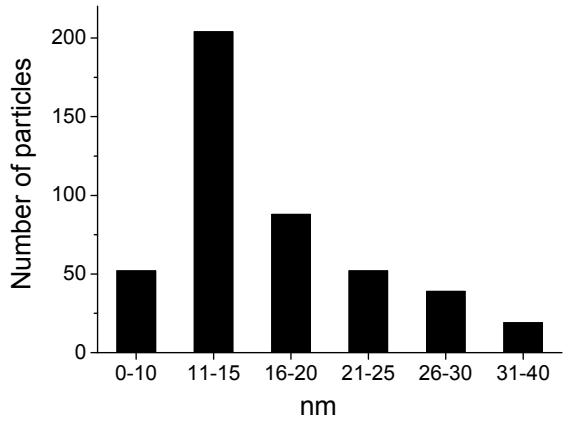
5. TEM



(a) (b) (c)

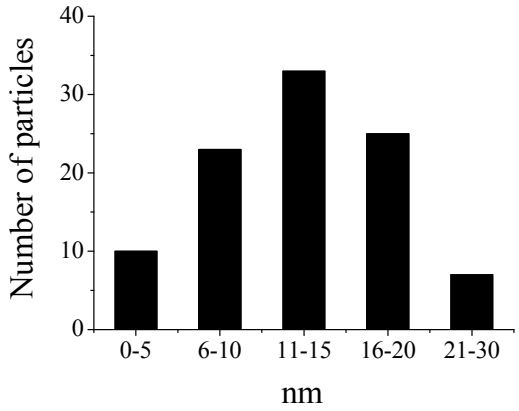
Figure SI-5. TEM images of the aggregates formed by (a) D2, (b) D3, (c) D4.





(a)

(b)



(c)

Figure SI-6. Size distribution of the micelles of block-gradient copolymers: D2 (a), D3 (b), D4 (c).