Electronic Supplementary Information for paper:

The influence of charge ratio on transient networks of polyelectrolyte complex micelles

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1 Polymer characterization

1.1 NMR spectrum of the triblock copolymer

^{1}H-NMR of the triblock copolymer was performed in D_2O on a Bruker Advance III 400MHz NMR spectrometer. 64 Scans were performed, with a relaxation time between two subsequent pulses of 60 s to allow full relaxation of the protons in the PEO middle-block. The average number of charged groups on the triblock copolymers was determined by comparing the integral values of the peak corresponding to the protons in the PEO middle-block ($\delta \approx 3.6$ ppm) and the peak of the protons of the trimethylamino group ($\delta \approx 3.2$ ppm), taking into account the relative amount of protons per group. We obtain an average value of 68 monomers per PEO middle-block, corresponding to an average of 34 charged monomers per A block. The ^{1}H-NMR spectrum of the triblock copolymer is shown in figure ESI-1. The origin of each peak is indicated in the graph.

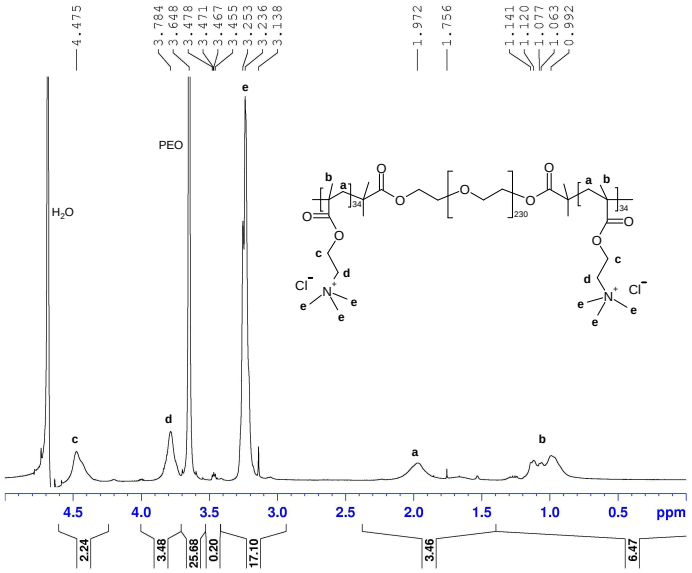

Figure ESI-1: ^{1}H-NMR spectrum of the ABA triblock copolymer as synthesized according to the procedure indicated in the experimental section.

1.2 NMR spectrum of the PSPMA homopolymer

Figure ESI-2 shows the ^{1}H-NMR spectrum of the PSPMA homopolymer. The spectrum was recorded in D_2O on a Bruker Advance III 400MHz NMR spectrometer. 166 Scans were performed, with a relaxation time between two subsequent pulses of 60 s. The origin of each peak is indicated in the graph.

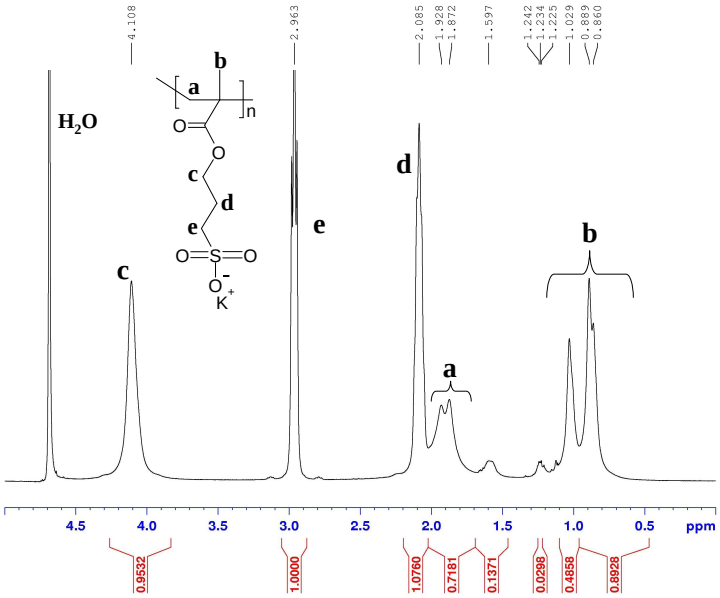

Figure ESI-2: ^{1}H-NMR spectrum of the PSPMA homopolymer as synthesized according to the procedure indicated in the experimental section.

2 Sample preparation

2.1 Relative concentration of neutralized units

Figure ESI-3 displays the relative amount of neutralized units present in solution, and is the graphical presentation of the numbers in table 1 in the main text. Basically the numbers mean that for a 20wt% sample at 1:1 charge ratio, we have 20wt% of neutralized units. However, for a 20wt% sample at $f^+ = 0.1$ it means that we have $0.24 \times 20 = 4.8$wt% of neutralized units in solution. All concentrations of neutralized units have been calculated and are shown in table ESI-1.

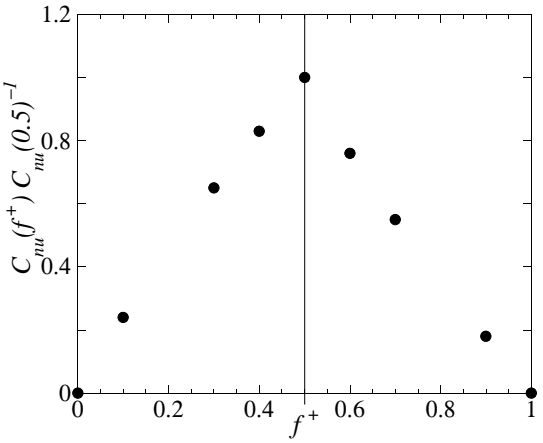

Figure ESI-3: Relative ratio of neutralized units in solution, as defined in the main text.

Table ESI-1: Table with the values for the weight concentration of neutralized units, per charge ratio.

f^+	$\frac{C_{nu}(f^+)}{C_{nu}(0.5)}$	20 wt%	15 wt%	10 wt%	5 wt%
0.1	0.24	4.8	3.6	2.4	1.2
0.3	0.65	13.0	9.8	6.5	3.3
0.5	1.00	20.0	15.0	10.0	5.0
0.7	0.55	11.0	8.3	5.5	2.8
0.9	0.18	3.6	2.7	1.8	0.9

3 Dynamic Light Scattering

3.1 Additional graphs

Figure ESI-4a shows the dependence of the diffusion coefficient on the scattering vector. Diffusion coefficients are obtained from CONTIN[1,2] fits of the correlation functions, see also figure ESI-5. There is no dependence of the diffusion coefficient on the scattering vector, except for small q-values. The lowering of the diffusion coefficient might be caused be a small fraction of larger aggregates present in the sample. Figure ESI-4b shows the hydrodynamic radius, based on the same CONTIN[1,2] fits as in figure ESI-4a, as a function of scattering angle θ. For $\theta > 50°$, there is no dependence of the hydrodynamic radius of the aggregates. At lower scattering angles an upturn can be caused by the presence of a small fraction of larger aggregates.

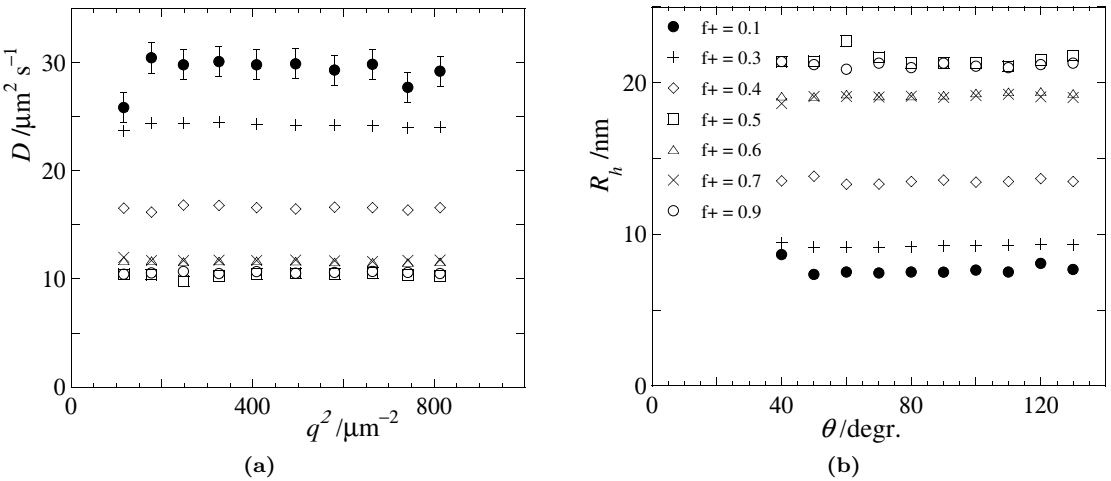

Figure ESI-4: (a) Values for the diffusion coefficients as a function of q^2. The symbols for the different charge compositions are similar as displayed in (b). Standard deviations are in the order of the size of the symbols, except for $f^+ = 0.1$, where they are displayed in the graph. (b) Values for the measured hydrodynamic radius as a function of scattering angle θ. The symbols for the different charge compositions are indicated in the graph. Standard deviations are in the order of the size of the symbols.

Typical intensity correlation functions and fits for 0.5wt% samples for three charge compositions are

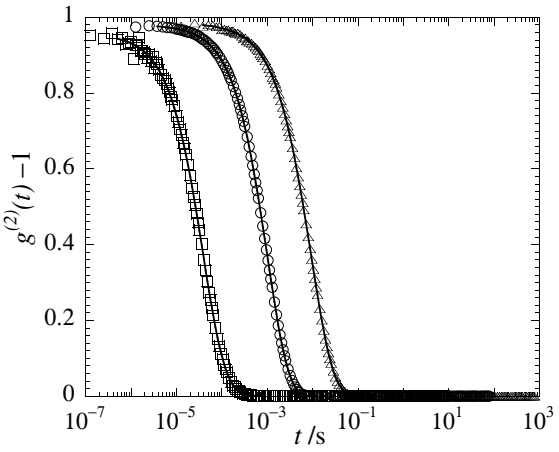

Figure ESI-5: Intensity correlation as a function of correlation time for samples of 0.5wt% at three charge compositions; $f^+ = 0.1$ (□), $f^+ = 0.5$ (◯) and $f^+ = 0.9$ (△). The correlation functions are shifted by a factor of 10 in correlation time for reasons of clarity. Lines are fits to the data.

shown in figure ESI-5. The curves are shifted in correlation time by a factor of ten from each other, to prevent overlap. Fits to the data are displayed as lines through the data points.

3.2 Refractive index increment

Here we derive an estimate for the value of the refractive index increment of the neutralized units. A neutralized unit is defined as a triblock copolymer exactly neutralized with oppositely charged homopolymer. The mass of such a neutralized unit is 41.1 kg mol^{-1}, of which 25.0wt% is PEO, 34.2wt% is TMAEMA and 40.8wt% is PSPMA. The refractive index increment of each individual component is known.[3–5] If we assume that the refractive index increment is weakly dependent on the wavelength of the light, and if we assume that each component contributes proportional to its mass fraction in a neutralized unit, we estimate the refractive index increment of a neutralized unit to be $1.39 \cdot 10^{-4}$ m^3 kg^{-1}. This value is close to the value obtained for polymers with zwitter-ionic side chains that contain both the TMAEMA and the SPMA moiety in one chain.[6,7] The actual values and references are given in table ESI-2.

Table ESI-2: Values used to estimate the refractive index increment of a neutralized unit

Component	Mass kg mol^{-1}	Mass fraction	$\left(\frac{dn}{dC}\right)$ ml g^{-1}	Contribution to $\left(\frac{dn}{dC}\right)$ ml g^{-1}
PEO	10.3	0.250	0.135[3]	0.034
PTMAEMA	14.1	0.342	0.158[5]	0.054
PSPMA	16.7	0.407	0.125[4]	0.051
Neutralized unit	41.1	1	-	0.139

3.3 Estimation of I_{bg}

We estimate the background scattering over the whole charge ratio domain by interpolating between the two points at the extremities. Hence we subtract the contribution of single polymer scattering, as if no aggregates would form. Since the weight concentration of all samples is equal, we overestimate the contribution of the background scattering at charge compositions where polymers end-up in aggregates. The values for the two extremities are: $< I > (0.0) = 18.5$ and $< I > (1.0) = 11.4$. Linear interpolation yields the relation between the hypothetical background and charge ratio: $I_{bg} = 18.5 - 7.1 \cdot f^{+}$. This relation was used to obtain a value for I_{bg} at all charge compositions.

4 Small Angle X-ray Scattering

4.1 Additional graphs

The $f^{+} = 0.5$ low salt concentration sample (10 mM KCl) shows somewhat more features in the SAXS curve than the 0.35 M KCl samples, however still no clear form factor minimum can be seen, see figure ESI-6. The curve could be fitted by a model employing a polydisperse homogeneous core and homogeneous shell. Fitting parameters can be found in table ESI-3.

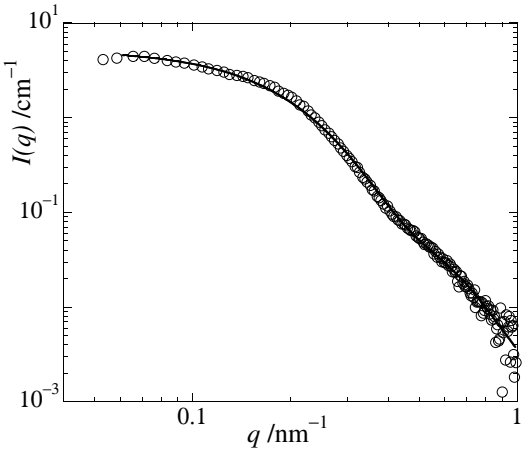

Figure ESI-6: Data and fit of the 0.5wt% $f^{+} = 0.5$ sample at a KCl concentration of 10 mM.

SAXS curves and model fitting results of 0.5wt% samples for different charge stoichiometries are given in figure ESI-7. The curves are similar as in figure 3 of the main text, but now shifted for reasons of clarity. Lines indicate the results of model fitting. The data was fitted with a model comprising a polydisperse homogeneous core and homogeneous shell. The fitting parameters are given in table ESI-4.

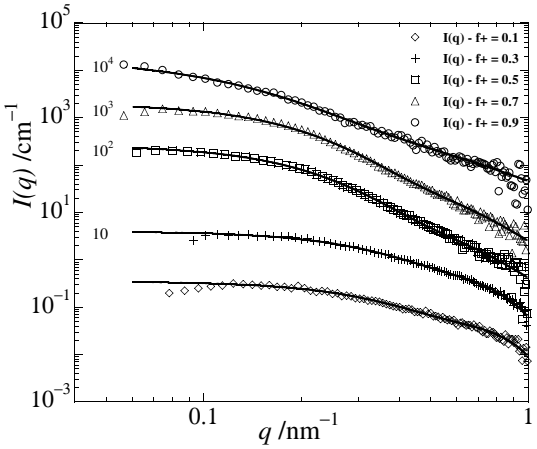

Figure ESI-7: Data (symbols) and fits (lines) of the 0.5wt% samples for different charge ratios, as shown in the legend, and fixed KCl concentration of 0.35 M. Curves are shifted with respect to each other by shift factors as indicated in the graph. Only 20% of the data points are shown for reasons of clarity.

SAXS curves and model fitting results of 20wt% samples for different charge stoichiometries are given in figure ESI-8. The curves are similar as in figure 5 of the main text, but now shifted for reasons of clarity. Lines indicate the results of model fitting. The data were fitted with a model consisting of a polydisperse homogeneous core and homogeneous shell, combined with a Percus-Yevick closure for the modelled hard-sphere interactions. The fitting parameters are given in table ESI-5.

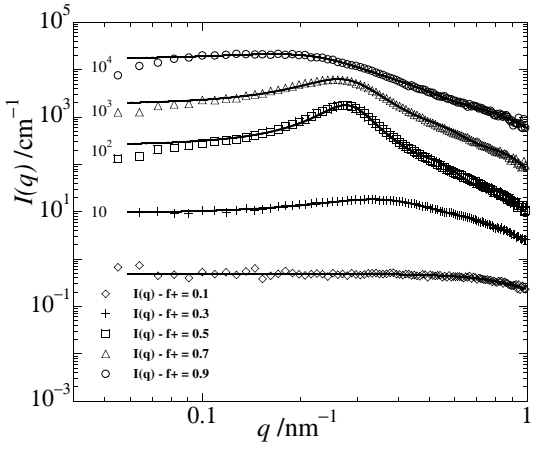

Figure ESI-8: Data (symbols) and fits (lines) of the 20wt% samples for different charge ratios, as shown in the legend, and fixed KCl concentration of 0.35 M. Curves are shifted with respect to each other by shift factors as indicated in the graph. Only 20% of the data points are shown for reasons of clarity.

Figure ESI-9 shows the fitted $I(0)$ values for both 0.5wt% and 20wt% fits. The figure is in agreement with the light scattering results.

Figures ESI-10, ESI-11 and ESI-12 show the SAXS curves for the 5wt%, 10wt% and 15wt% samples,

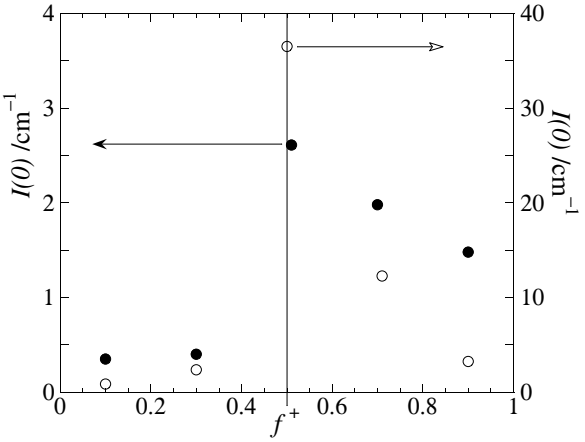

Figure ESI-9: Fitted $I(0)$ values as a function of charge ratio for 0.5wt% (•, left axis) and 20wt% (○, right axis) SAXS data fits.

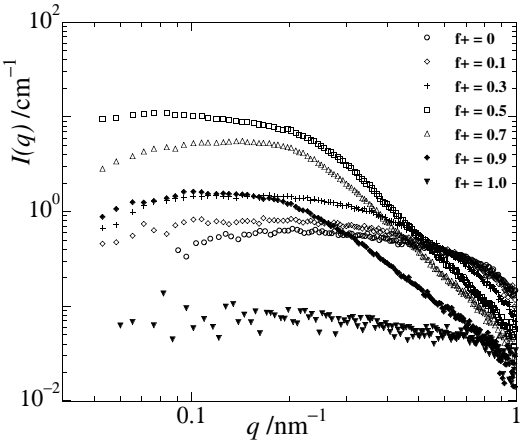

Figure ESI-10: SAXS curves for 5wt% total polymer concentration. 30% of the data points are shown. Symbols correspond to charge compositions as indicated in the graph.

respectively.

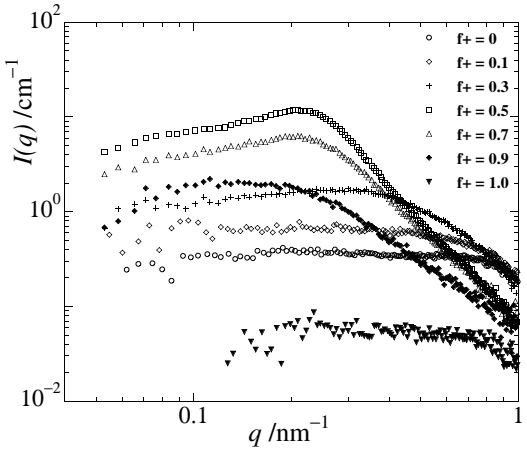

Figure ESI-11: SAXS curves for 10wt% total polymer concentration. 30% of the data points are shown. Symbols correspond to charge compositions as indicated in the graph.

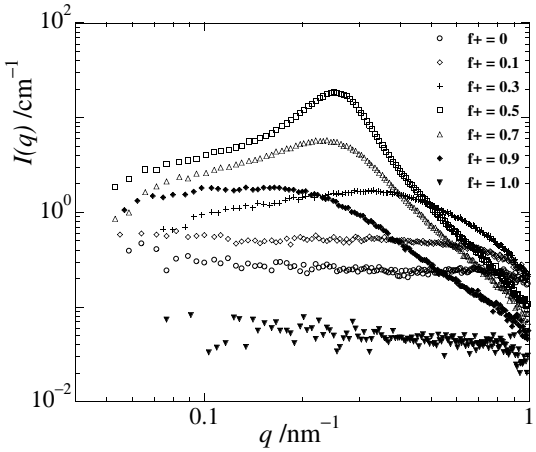

Figure ESI-12: SAXS curves for 15wt% total polymer concentration. 30% of the data points are shown. Symbols correspond to charge compositions as indicated in the graph.

4.2 Fitting parameters

Table ESI-3: Table with model fitting parameters for the 0.5wt% SAXS curves at 10 mM KCl.

f^+	$I(0)$ cm^{-1}	R_{core} nm	R_{shell} nm	R_{agg} nm	density shell/core
0.51	5.36	5.9 ±1.3	8.9	14.8 ±1.3	0.14

Table ESI-4: Table with model fitting parameters for the 0.5wt% SAXS curves at 0.35 M KCl.

f^+	$I(0)$ cm^{-1}	R_{core} nm	R_{shell} nm	R_{agg} nm	density shell/core
0.10	0.35	3.4 ±0.3	7.0	10.4 ±0.3	0.02
0.30	0.40	3.8 ±0.5	6.9	10.7 ±0.5	0.03
0.51	2.61	5.4 ±1.6	9.2	14.6 ±1.6	0.12
0.70	1.98	5.6 ±1.7	10.0	15.5 ±1.7	0.12
0.90	1.48	4.1 ±1.8	18.1	22.1 ±1.8	0.04

Table ESI-5: Table with model fitting parameters for the 20wt% SAXS curves at 0.35 M KCl.

f^+	$I(0)$ cm^{-1}	R_{core} nm	R_{shell} nm	R_{agg} nm	density shell/core	R_{HS} nm	ϕ
0.10	0.86	2.8 ±1.1	0.3	3.1 ±1.1	0.06	3.2	0.07
0.30	2.38	3.2 ±0.9	1.5	4.7 ±0.9	0.11	7.7	0.12
0.50	36.5	4.3 ±0.7	6.1	10.4 ±0.7	0.12	11.1	0.34
0.71	12.3	3.9 ±0.6	6.0	9.9 ±0.6	0.08	10.7	0.24
0.90	3.25	3.4 ±0.7	6.8	10.2 ±0.7	0.05	12.6	0.08

References

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(2) S. W. Provencher, *Computer Physics Communications*, 1982, **27**, 229–242.

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