Supporting information for paper:

Transient Network Topology of Interconnected Polyelectrolyte Complex Micelles

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Multiple form factor fits

We employed several models for the form factor to model the complex coacervate core micelles. Some examples are shown in figure 1. The simplest model is a Gaussian distribution of homogeneous spheres. This fit yields homogeneous spheres with an average radius of 8.2 nm. However, the fit does not describe the data very well for $q > 0.5$ nm^{-1}, see fit 1 in figure 1. The mismatch is probably caused by the inhomogeneity of the core of a polyelectrolyte complex core micelle, as explained in the main text. To correct for the inhomogeneous core, we apply a model containing two contributions: i) a monodisperse sphere of radius R_{sphere} with fixed relative contrast; ii) a polydisperse (Gaussian) 'interface' of radius R_{int} surrounding the monodisperse sphere, with an adjustable thickness and relative contrast. The fitting quality increases considerably using this model, see fits 2–5 in figure 1. As shown in table 1, the total radius $R_c = R_{\text{sphere}} + R_{\text{int}}$ is approximately the same for all fits.

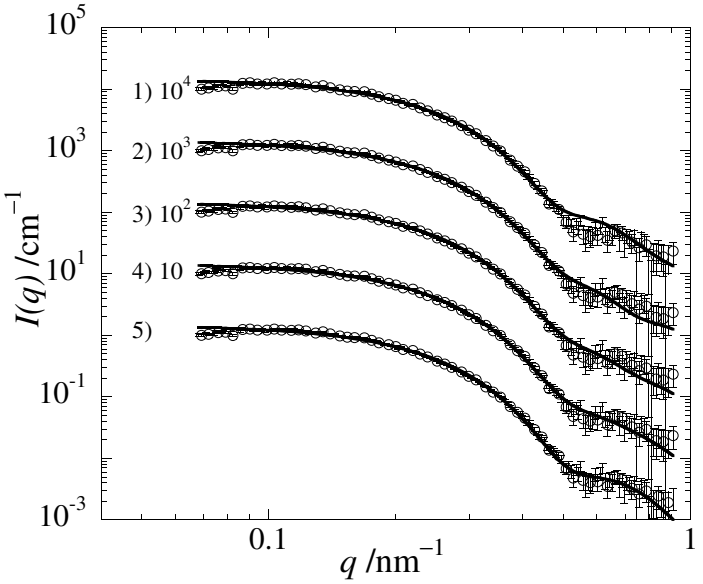

Figure 1: SAXS intensity as a function of q for polymer concentration of 1%(w/w) and salt concentration of 0.4 M KCl. Shown are different form factor fits to the data: 1) Homogeneous sphere of radius 8.2 nm; 2) Sphere-interface model with $R_{\text{sphere}} = 4$ nm; 3) Sphere-interface model with $R_{\text{sphere}} = 5$ nm; 4) Sphere-interface model with $R_{\text{sphere}} = 6$ nm; 5) Sphere-interface model with $R_{\text{sphere}} = 6.7$ nm as is shown in the main text. Shift factors are indicated in the graph.

Table of fitting parameters

Table 1 describes the parameters used to fit the SAXS data of the 1% 0.4 M KCl sample, as displayed in figure 1. The standard deviation of the Gaussian distribution of the interface thickness is taken as error value for the total core radius. The relative scattering length density difference between the sphere and the solvent is equal in all fits: $\eta_{\text{sphere}} = 10^{-6}$ cm^{-2}. The relative scattering length density difference between the interface and the solvent is indicated by η_{int}.

Table 1: Table with fitting parameters for the different fits of the 1%(w/w) 0.4 M KCl SAXS data.

Fit number	R_{sphere} nm	R_{int} nm	η_{int} 10^{-6} cm^{-2}	R_c nm
1	8.2 ±1.7	0	-	8.2 ±1.7
2	4.0	4.5 ±1.6	0.74 ±0.03	8.5 ±1.6
3	5.0	3.5 ±1.6	0.80 ±0.025	8.5 ±1.6
4	6.0	2.3 ±1.7	0.84 ±0.025	8.3 ±1.7
5	6.7	1.4 ±1.8	0.85 ±0.03	8.1 ±1.8

SAXS curves 16%(w/w) [KCl] series

Figure 2 displays the SAXS data of a series of samples with constant polymer concentration 16%(w/w) and varying KCl concentration. Note that the features of the curve become less and less pronounced as the [KCl] increases. This is mainly caused by an increase in polydispersity of the scatterers. For the 1.5 M KCl sample in particular, the form factor is not well defined. However, the structure factor contribution is still well defined. To compute the aggregation number of the scatterers we use only the structure factor information, see main text. In the high salt concentration samples, the fits cannot describe the scattering at high q. This implies that the form factor that we use is not fully compatible with the real flowerlike micelles at these salt concentrations. Differences can also be caused by errors in background subtraction, additional to the errors on the data itself.

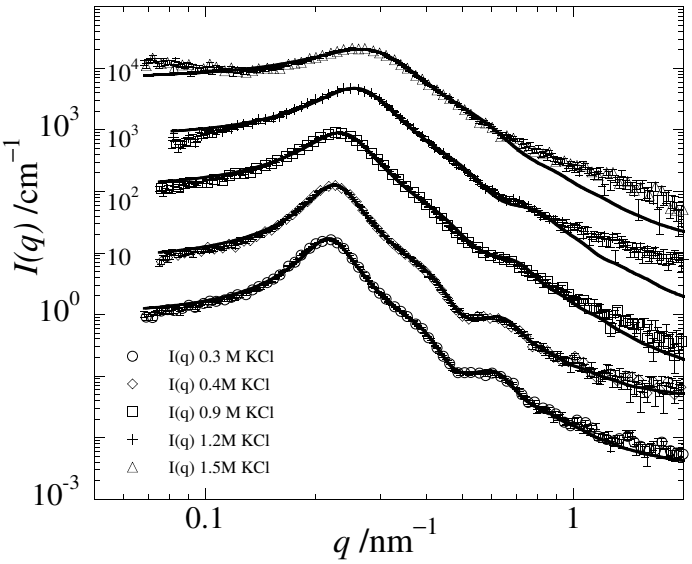

Figure 2: SAXS intensity as a function of q for different KCl concentrations and fixed polymer concentration of 16%(w/w). Lines are fits to the data. Symbols and corresponding KCl concentration are indicated in the graph. Curves are shifted with respect to each other for graphical reasons. Shift factors are indicated in the graph.

Table 2: Table with fitting parameters for the 16%(w/w) KCl concentration series.

[**KCl**] M	R_{sphere} nm	R_{shell} nm	η_{shell} 10^{-6} cm^{-2}	R_c nm	R_{HS} nm	ϕ -	background cm^{-1}
0.3	6.7	2.4 ±1.4	1.0	9.1 ±1.4	15.0	0.40	0.0035
0.4	6.7	1.7 ±1.5	1.0	8.4 ±1.5	14.3	0.39	0.0045
0.9	4.8	2.3 ±1.9	1.2	7.1 ±1.9	13.2	0.33	0.001
1.2	4.0	1.1 ±2.0	1.4	5.1 ±2.0	11.8	0.30	0.001
1.5	2.0	1.0 ±2.4	1.6	3.0 ±2.4	10.3	0.23	0.0015

Table of fitting parameters

Table 2 describes the parameters used to fit the SAXS data of the 16%(w/w) KCl concentration series. The standard deviation of the Gaussian distribution of the interface thickness is taken as error value for the total core radius. Errors in the R_{HS} and ϕ are estimated to be within 5%. The relative scattering length density difference between the sphere and the solvent is equal in all fits: $\eta_{\text{sphere}} = 10^{-6}$ cm^{-2}. The relative scattering length density difference between the interface and the solvent is indicated by η_{int}. An additional background contribution was sometimes used to indicate the limit of $I(q)$ for high q-values.

Fitting parameters scattering curves in main text

The following tables describe the parameters used to fit the SAXS data of the two concentration series, as shown in the main text. The standard deviation of the Gaussian distribution of the interface thickness is taken as error value for the total core radius. Errors in the R_{HS} and ϕ are estimated to be within 5%. The relative scattering length density difference between the sphere and the solvent is equal in all fits: $\eta_{\text{sphere}} = 10^{-6}$ cm^{-2}. The relative scattering length density difference between the interface and the solvent is indicated by η_{int}. An additional background contribution was sometimes used to indicate the limit of $I(q)$ for high q-values.

0.4 M KCl polymer concentration series

Table 3: Table with fitting parameters for the polymer concentration series at 0.4 M KCl.

Concentration %(w/w)	R_{sphere} nm	R_{int} nm	η_{int} 10^{-6} cm^{-2}	R_c nm	R_{HS} nm	ϕ -	background cm^{-1}
1	6.7	1.4 ±1.8	0.85	8.1 ±1.8	-	0	-
4	6.7	0.5 ±1.8	0.81	7.2 ±1.8	15.6	0.11	-
6	6.7	0.9 ±1.7	0.93	7.6 ±1.7	15.3	0.17	-
8	6.7	0.4 ±1.7	1.0	7.1 ±1.7	14.5	0.23	-
9	6.7	1.5 ±1.5	0.91	8.2 ±1.5	15.2	0.24	-
12	6.7	1.7 ±1.7	1.0	8.4 ±1.7	15.8	0.32	0.004
14	6.7	1.8 ±1.5	1.0	8.5 ±1.5	14.9	0.36	0.001
16	6.7	1.7 ±1.5	1.0	8.4 ±1.5	14.3	0.39	0.005
18	6.7	3.3 ±1.7	1.0	10.0 ±1.7	16.3	0.37	0.007
20	6.7	2.6 ±1.5	1.0	9.3 ±1.5	15.3	0.39	0.005

1.0 M KCl polymer concentration series

Table 4: Table with fitting parameters for the polymer concentration series at 1.0 M KCl.

Concentration %(w/w)	R_{sphere} nm	R_{int} nm	η_{int} 10^{-6} cm^{-2}	R_c nm	R_{HS} nm	ϕ -	background cm^{-1}
1	4.8	3.7 ±1.5	0.66	8.5 ±1.5	-	0	-
5	4.8	2.6 ±1.5	1.07	7.4 ±1.5	15.3	0.14	-
10	4.8	1.4 ±1.8	1.23	6.2 ±1.8	12.6	0.26	0.006
15	4.8	0.5 ±1.9	1.33	5.3 ±1.9	11.9	0.31	0.007
20	4.8	0.4 ±1.9	1.33	5.2 ±1.9	11.6	0.37	0.0095