Supplementary Information

Finite size and inner structure controlled by electrostatic screening in globular complexes of proteins and polyelectrolytes

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1: Measurement of the sulfonation rate of PSS chains by SANS

The sulfonation rate of PSS chains can be precisely measured by SANS experiments performed on pure solutions of concentrated chains. Figure A.1 presents the scattering spectra of PSS chains at 0.3 M in a 57%/43% H_2O/D_2O mixture for fully and partially deuterated chains. At large q, the scattering decays like q^{-1} for fully sulfonated chains because the strong repulsions between monomers give a local rigid 1-D structure to the chains. For the partially sulfonated chains, the scattering decay at large q is close to q^{-2}. As the partially sulfonated chains form hydrophobic pearls[1,2] due to hydrophobic interactions, the scattering is a combination of rods (q^{-1}) and spheres (q^{-4}). At low q, the scattering of the chains is very weak owing to the strong electrostatic repulsions between chains. At intermediate q, a correlation peak is clearly visible. The characteristic distance ξ ($\xi = 2\pi/q^*$) is the mesh of the transient network formed by the chains in semi-dilute regime. Chains are in semi-dilute regime at 0.3 M. q^* scales like $c^{1/2}$ [(3)] and $f^{2/7}$ [(4)]. We recover the literature value $q^* = 0.1$ Å^{-1} for fully

sulfonated chains at 0.3 M [3,5]. For the partially sulfonated chains, we also know by experience that the value of q* [6] is a very accurate measurement of f: we get $q^* = 0.05$ Å^{-1}, which gives f = 0.5.

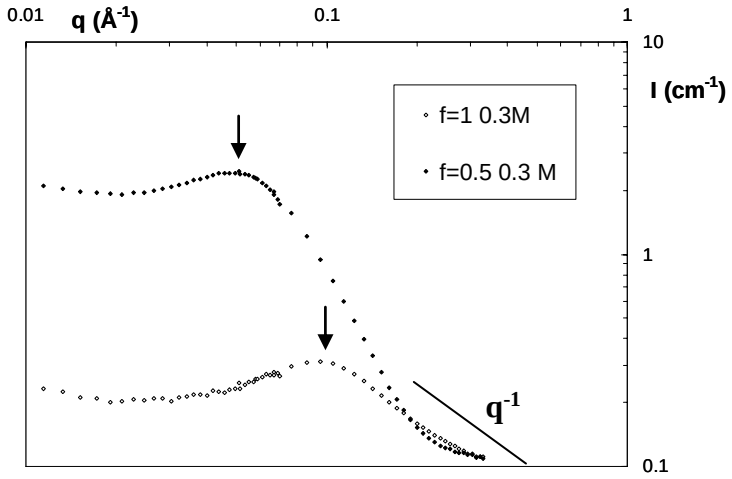

Figure S1: Scattering of pure solutions of PSS chains at 0.3M.

2: SANS measurements of dense globular complexes and data fitting

We recover for all samples described in this section the main features of the scattering spectra of the dense globular complexes, both for lysozyme (obtained in a fully D_2O buffer where d-PSS is matched, i.e. the scattering contribution is annihilated) and PSS chains (obtained in a 57%/43% H_2O/D_2O mixture). We summary here these features, as complexes have been extensively described in ref [7], as well as the fitting procedure of the scattering.

The **lysozyme scattering** shows: (i) a q^{-4} scattering above 0.2 Å^{-1} corresponding to the form factor of the lysozyme in its native compact conformation, (ii) a strong correlation peak at 0.2 Å^{-1} corresponding to contact distance between two proteins, (iii) a second q^{-4} behaviour at intermediate q, corresponding to the form factor of the primary compact complexes and (iv) a $q^{-2.1}$ behaviour for q < 0.02 Å corresponding to the larger scale fractal organisation of the primary complexes.

When $[-]/[+]_{intro} < 1$, there are free proteins in solutions. The scattering at large q is then a linear combination of the scattering of complexes and of the scattering free proteins, which

can be identified to their form factor as free proteins are diluted. This partially hides the peak at 0.2 $Å^{-1}$. The amount of free proteins is measured by UV spectroscopy after centrifugation of the samples. This allows subtracting the signal of the free proteins from the whole scattering to recover only the scattering of the complexes. In the following we present spectra with or without free proteins subtracting.

The fitting of the scattering at low q, based on a description of the globular complexes as spheres with a lognormal distribution of the radii, enables to get the most probable radius R_{lyso_comp} and a standard deviation σ. The volume fraction of proteins Φ_{lyso_inner} within the complexes is deduced from the absolute intensity.

As both PSS chains and lysozyme scattering have a similar spatial organisation within the primary complexes, **the PSS scattering** present the same features as the protein scattering at low q: a $q^{-2.1}$ behaviour at low q, a q^{-4} behaviour at intermediate q and a maximum ("peak") at 0.2 $Å^{-1}$, even if the latter is not easily visible on the spectra.

The fitting of the PSS scattering is also based on a description of the globular complexes as spheres with a lognormal distribution. Two situations are possible:

- When $[-]/[+]_{intro} \leq 1$, the primary complexes are "naked" (no dangling chains); the object formed by lysozyme is the same as the object formed by the chains, and $R_{PSS\_comp} = R_{lyso\_comp}$. $I_{PSS}(q)/I_{lyso}(q)$ has then constant a value which enables a direct reading of $\Phi_{PSS\_inner}/\Phi_{lyso\_inner}$ (see equation 2 of main text).

- When $[-]/[+]_{intro} > 1$, the primary complexes are 'hairy', i.e. surrounded by a shell of PSS chains. Then $R_{PSS\_comp} > R_{lyso\_comp}$ and $I_{PSS}(q)/I_{lyso}(q)$ increases monotonically when q tends towards 0. R_{PSS_comp}, σ and Φ_{PSS_inner} are then be determined by the fitting of PSS scattering in absolute scale.

R_{lyso_comp}, R_{PSS_comp}, σ, Φ_{lyso_inner} and Φ_{PSS_inner} finally enable to get the inner charge ratio $[-]/[+]_{inner}$ within the core of the primary complexes.

The error bars on the neutron spectra are lower than the symbols on the figures and are thus not represented. However, there are some uncertainties on the values of the sizes and composition of the complexes deduced from those spectra. Those values are mentioned in the tables and enable the plot of error bars represented on the figures of the main paper. They are estimated from the most different values (of R_{lyso_comp} and σ) that enable a correct fitting of the position of the peak arising from the globules radius and of the shape of the scattering in a I(q)q4 = f(q) representation (see figure 4 of ref [7] or insert of figure S5). Please note that in such a representation the fitting parameters that play on the radius of the globules (q-position of the peak and shape) and of the Φ_{inner} (intensity of the scattering curve in cm^{-5}) are decoupled. This allows in general a very accurate fitting of Φ_{inner}. Since the scattering of the lysozyme is generally much higher than the PSS one, the errors bars are higher on the lysozyme features. When $[-]/[+]_{intro} \leq 1$, we derive the errors from $I_{PSS}(q)/I_{lyso}(q)$, which lead to very small errors bars. When $[-]/[+]_{intro} > 1$, the errors bars are derived from the errors bars on R_{lyso_comp}, R_{PSS_comp}, σ, Φ_{lyso_inner} and Φ_{PSS_inner} and are much larger. In all tables we give the errors bars on all parameters (R_{0_lyso}, σ, R_{0_PSS}, R_{lyso_comp}, R_{PSS_comp}, Φ_{lyso_inner}, Φ_{PSS_inner}, $[-]/[+]_{inner}$, N_{lyso_comp}).

2.1 pH 3, f = 1, I = 5 10^{-2}, variation of $[-]/[+]_{intro}$

Table A.1 recalls the values obtained from the data fitting of the scattering spectra of samples made at pH 3 for fully sulfonated chains for 6 values of $[-]/[+]_{intro}$ lying from 0.5 to 2.5 (figure 1 from main text).

	R_{lyso} (Å); σ	R_{PSS} (Å); σ	R_{mean_lyso} (Å)	R_{mean_PSS} (Å)
$[-]/[+]_{intro}$ = 0. 5	70; 0.45	70; 0.45	95 ± 2	95 ± 5

$[-]/[+]_{intro}$ = 0.8	85; 0.45	85; 0.45	115± 2	115 ± 5
$[-]/[+]_{intro}$ = 1	95; 0.45	95; 0.45	129± 2	129 ± 5
$[-]/[+]_{intro}$ = 1.5	132; 0.31	158; 0.35	159± 2	189± 5
$[-]/[+]_{intro}$ = 2	145; 0.31	155; 0.31	167± 2	180 ± 5
$[-]/[+]_{intro}$ = 2.5	150; 0.32	155; 0.32	175± 2	180 ± 5

	Φ_{lyso_inner}	Φ_{PSS_inner}	$[-]/[+]_{inner}$	N_{lyso_comp}
$[-]/[+]_{intro}$ = 0. 5	0.29±0.01	0.085±0.005	0.87±0.05 [a]	61±6
$[-]/[+]_{intro}$ = 0.8	0.24±0.01	0.077±0.005	0.91±0.04 [a]	106±10
$[-]/[+]_{intro}$ = 1	0.27±0.01	0.08±0.0005	0.88±0.02 [a]	172±14
$[-]/[+]_{intro}$ = 1.5	0.25±0.01	0.083±0.005	0.97±0.13 [b]	296±23
$[-]/[+]_{intro}$ = 2	0.25±0.01	0.093±0.005	1.11±0.15 [b]	355±27
$[-]/[+]_{intro}$ = 2.5	0.23±0.01	0.091±0.005	1.2±0.17 [b]	357±28

Table S1: Primary complexes made at pH 3 and f = 1. Radius size of primary complexes from both lysozyme and PSS point of view, inner volume fraction of lysozyme and PSS within primary complexes and inner charge ratio in the primary complexes. [a]: errors bars estimated from $I_{PSS}(q)/I_{lyso}(q)$ in the low q region. [b]: errors bars estimated from R_{lyso_comp}, R_{PSS_comp}, σ, Φ_{lyso_inner} and Φ_{PSS_inner}.

2.2 pH 7, f = 1, I = 5 10^{-2}, variation of [-]/[+]$_{intro}$

Figure S2 presents the scattering spectra of samples made at pH 7 for fully sulfonated chains for 5 [-]/[+]$_{intro}$ lying from 0.5 to 3. For [-]/[+]$_{intro}$ = 3, the measurement has been performed on a reduced scattering vector range.

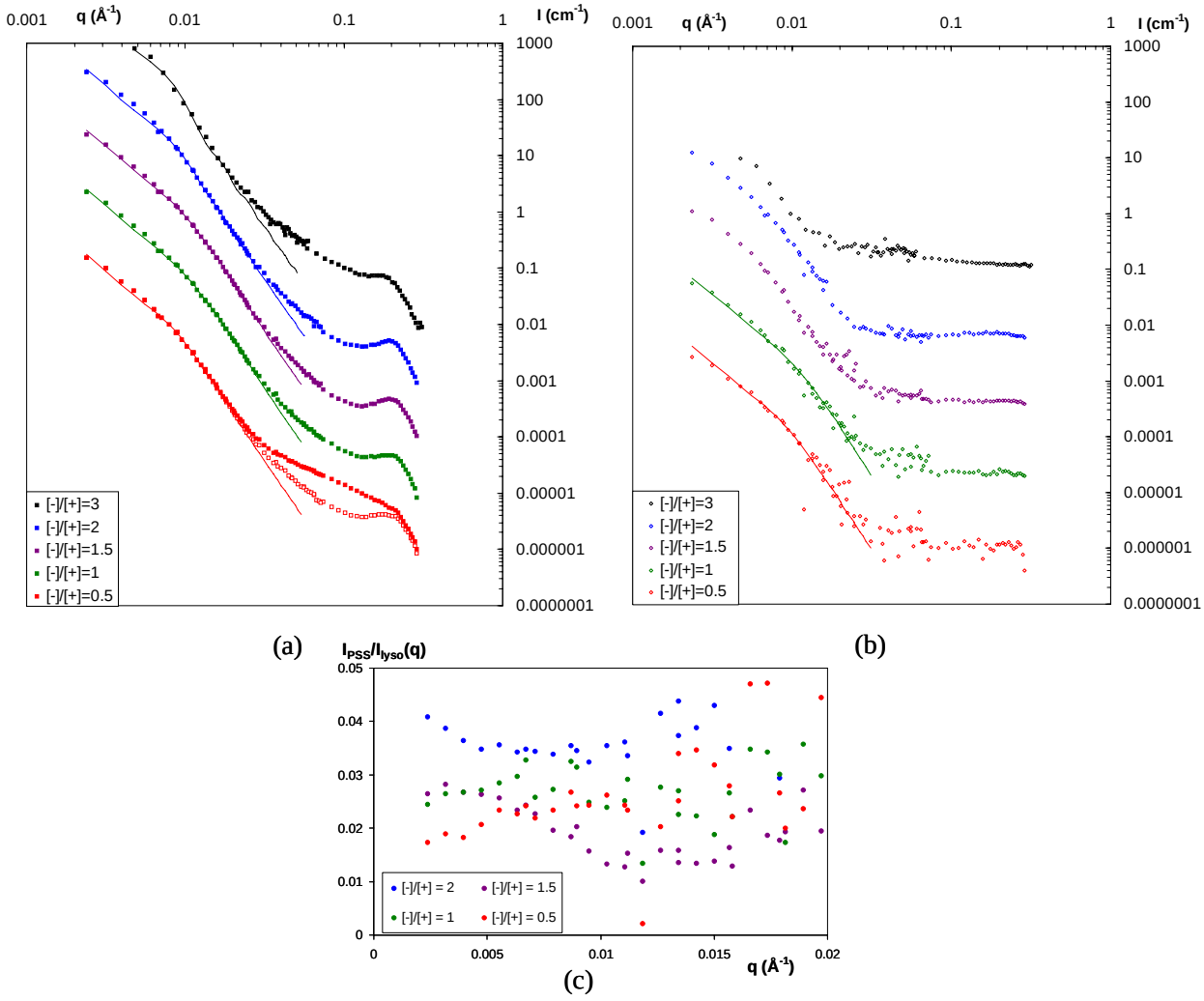

Figure S2: samples at pH 7, f = 1, I = 5 10^{-2} and [Lyso]$_{intro}$ = 40g/L : (a) lysozyme scattering. All curves are shifted from one to another by a decade for clarity. The scattering for the [-]/[+]$_{intro}$ = 0.5 sample is presented with or without the subtraction of free lysozyme. The intensity in absolute scale corresponds to the [-]/[+]$_{intro}$ = 3 sample. The full lines correspond to the fits. (b) PSS chains scattering. All curves are shifted from one to another by

a decade for clarity. The intensity in absolute scale corresponds to the $[-]/[+]_{intro} = 3$ sample. The full lines correspond to the fits. (c) $I_{PSS}(q)/I_{lyso}(q)$ in the low q regime.

It has not been here possible to fit the PSS scattering for the two following reasons. First, the primary complexes have at this pH a much larger size than at pH 3 or pH 4.7. The cut-off between the $q^{-2.1}$ and the q^{-4} regimes that enables the size determination is thus shifted towards low q, which limits the q-range for the fitting procedure. Second, the PSS concentration that provides charge stoichiometry is very weak at pH 7 since the global charge of lysozyme is low (+8). The coherent scattering becomes weak compared to the incoherent scattering (that stays important as it comes essentially from the solvent) and it would have taken a very long time to get good statistics.

We have nevertheless plotted $I_{PSS}(q)/I_{lyso}(q)$ for the charge ratios lying from 0.5 to 2 in figure S2.c. For $[-]/[+]_{intro} = 0.5$ and for $[-]/[+]_{intro} = 1$, $I_{PSS}(q)/I_{lyso}(q)$ is constant. This enables to get R_{PSS_comp}, σ and Φ_{PSS_inner}. For $[-]/[+]_{intro} = 1.5$, $I_{PSS}(q)/I_{lyso}(q)$ strongly increases when q tends towards 0 which proves that there a shell of PSS surrounding the complexes. For $[-]/[+]_{intro} = 2$, the increase of $I_{PSS}(q)/I_{lyso}(q)$ when q tends towards 0 is very weak, signature of a very thin layer of PSS around the complexes. Between 0.005 $Å^{-1}$ and 0.015 $Å^{-1}$, $I_{PSS}(q)/I_{lyso}(q)$ is close to a plateau. The value of this plateau enables an estimation of $\Phi_{PSS\_inner}/\Phi_{lyso\_inner}$. All the characteristics of samples are recalled in Table S2.

	R_{lyso} (Å); σ	R_{PSS} (Å); σ	R_{mean_lyso} (Å)	R_{mean_PSS} (Å)
$[-]/[+]_{intro}$ = 0. 5	120; 0.5	120; 0.5	175 ± 8	175 ± 8
$[-]/[+]_{intro}$ = 1	112; 0.45	112; 0.45	152 ± 8	152 ± 8
$[-]/[+]_{intro}$ = 1.5	120; 0.45		163 ± 10	
$[-]/[+]_{intro}$ = 2	150; 0.5		218 ± 10	
$[-]/[+]_{intro}$ = 3	185; 0.5		270 ± 10	

	Φ_{lyso_inner}	Φ_{PSS_inner}	$[-]/[+]_{inner}$	N_{lyso_comp}
$[-]/[+]_{intro}$ = 0. 5	0.17±0.01	0.085±0.005	0.95±0.05 [a]	450±88
$[-]/[+]_{intro}$ = 1	0.2±0.01		0.91±0.04 [a]	235±49
$[-]/[+]_{intro}$ = 1.5	0.22±0.01			419±91
$[-]/[+]_{intro}$ = 2	0.21±0.01	0.036±0.004 [a]	1.12±0.13 [a]	771±142
$[-]/[+]_{intro}$ = 3	0.25±0.01			1423±215

Table S2: Primary complexes made at pH 7 and f = 1. Radius size of primary complexes from both lysozyme and PSS point of view, inner volume fraction of lysozyme and PSS within primary complexes and inner charge ratio in the primary complexes. [*]: estimation from IPSS(q)/Ilyso(q). [a]: errors bars estimated from $I_{PSS}(q)/I_{lyso}(q)$ in the low q region. [b]: errors bars estimated from R_{lyso_comp}, R_{PSS_comp}, σ, Φ_{lyso_inner} and Φ_{PSS_inner}.

2.3 pH 4.7, f = 0.5, I = 5 10-2, variation of [-]/[+]intro

Figure S3 presents the scattering spectra of samples made at pH 4.7 for partially sulfonated chains (f = 0.5) for 6 values of $[-]/[+]_{intro}$ lying from 0.5 to 2.5. The lysozyme scattering displays all the typical features of the primary complexes and is easily modeled (Fig S3.a). But the PSS scattering spectra present some differences with the one from fully sulfonated chains. If the reminiscent peak of the protein contact at 0.2 $Å^{-1}$ is clearly visible, there is neither a q^{-4} decay at intermediate q nor a clear cut crossover between the $q^{-2.1}$ and the q^{-4} regimes at low q. This shows that the primary complexes have not a sharp interface from the polyelectrolyte point of view. This may come from the conformation of the hydrophobic PS repetitions units in the vicinity of the interface that can form hydrophobic pearls, as proposed theoretically [8] and checked experimentally [1,2] for pure solutions of partially sulfonated chains. At large q, we notice a shoulder in the log-log plot, at a scattering vector independent from the $[-]/[+]_{intro}$, and much larger that the one expected for the interaction peak in solution. It resembles very much the one observed in the scattering of pure partially sulfonated solutions, with no dependence over concentration in the range explored [2], and which was attributed to spherical pearls of diameter circa 20 Å. The chains seem therefore to keep, in average, a pearl necklace conformation very similar to pure solutions. These pearls may create a large roughness at the surface of the primary complexes from the PSS point of view and hinders the q^{-4} behavior at intermediate q. The PSS scattering can thus not be modeled. An estimation of $[-]/[+]_{inner}$ is nevertheless possible from $I_{PSS}(q)/I_{lyso}(q)$. The spatial scales probed at low q are much higher than the characteristic size of the primary complexes. The PSS scattering in this q-range is thus no longer sensitive to the complexes roughness. As $I_{PSS}(q)/I_{lyso}(q)$ tends towards an almost constant value on a large q range for all $[-]/[+]_{intro}$ (except for $[-]/[+]_{intro}$ =3 where it continuously increases, it is possible to determine $[-]/[+]_{inner}$. It stays close to 1 even for such partially hydrophobic chains (table S3).

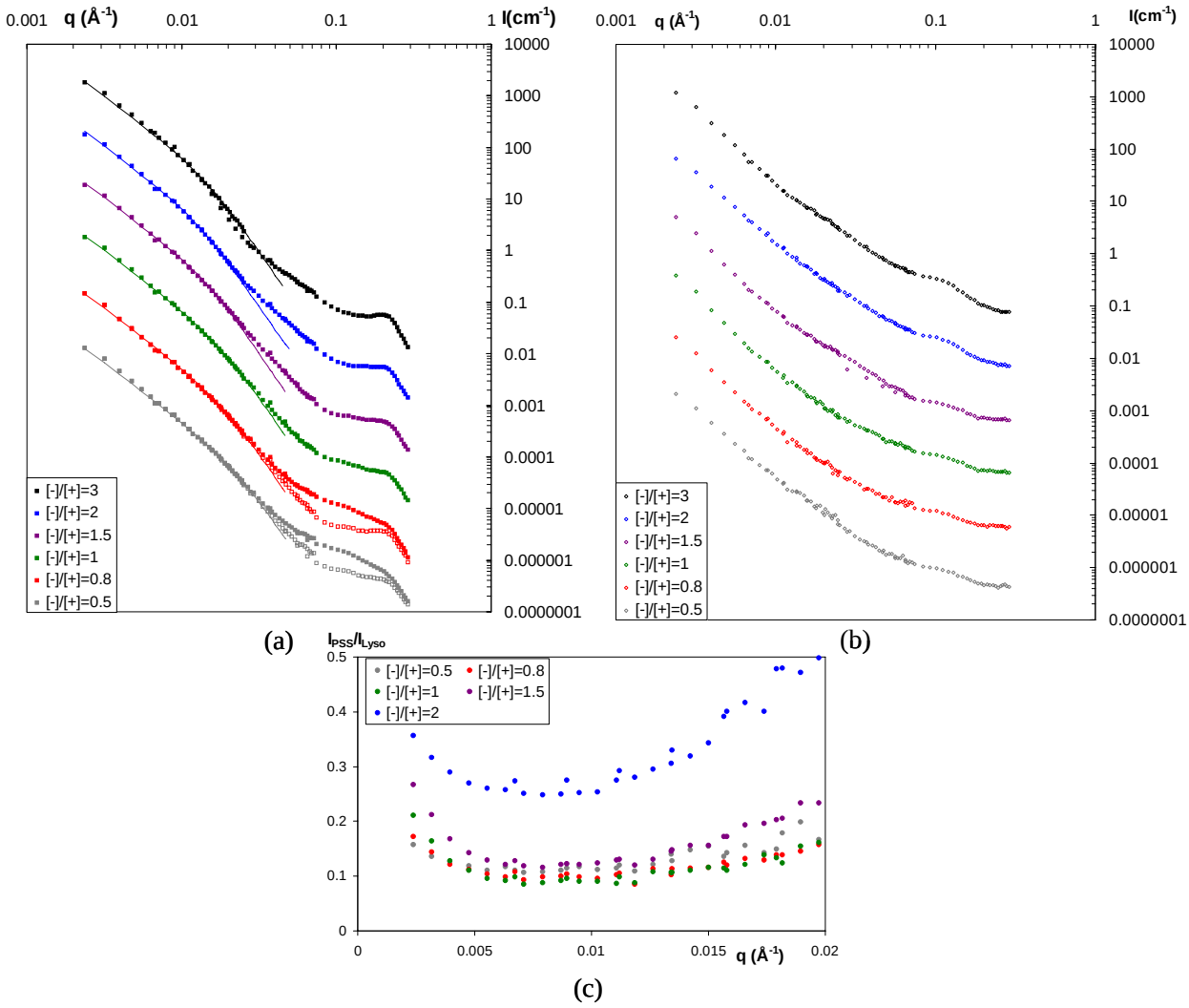

Figure S3: samples at pH 4.7, f = 0.5, I = 5 10^{-2} and $[Lyso]_{intro}$ = 40g/L : (a) lysozyme scattering. All curves are shifted from one to another by a decade for clarity. The scattering for both the $[-]/[+]_{intro}$ = 0.5 and the $[-]/[+]_{intro}$ = 0.8 samples are presented with or without the subtraction of free lysozyme. The intensity in absolute scale correspond to the $[-]/[+]_{intro}$ = 3 sample. The full lines correspond to the fits. (b) PSS chains scattering. All curves are shifted from one to another by a decade for clarity. The intensity in absolute scale correspond to the $[-]/[+]_{intro}$ = 3 sample. The full lines correspond to the fits. (c) $I_{PSS}(q)/I_{lyso}(q)$ in the low q regime.

	R_{lyso} (Å); σ	R_{mean_lyso} (Å)	Φ_{lyso_inner}	$[-]/[+]_{inner}$	N_{lyso_comp}
$[-]/[+]_{intro}$ = 0. 5	50; 0.5	75 ± 5	0.19±0.01	0.89±0.05 [b]	23±6
$[-]/[+]_{intro}$ = 0.8	60; 0.5	90± 5	0.18±0.01	0.89±0.11 [b]	38±8
$[-]/[+]_{intro}$ = 1	70; 0.4	95± 5	0.175±0.01	0.82±0.06 [b]	44±9
$[-]/[+]_{intro}$ = 1.5	85; 0.45	110± 5	0.175±0.01	0.91±0.08 [b]	68±13
$[-]/[+]_{intro}$ = 2	85; 0.45	120± 5	0.165±0.01	1.25±0.05 [b]	83±15
$[-]/[+]_{intro}$ = 3	110; 0.5	165± 5	0.16±0.01		208±32

Table S3: Primary complexes made at pH 4.7 and f = 0.5. Radius size of primary complexes from lysozyme point of view, inner volume fraction of lysozyme and inner charge ratio in the primary complexes. [a]: errors bars estimated from $I_{PSS}(q)/I_{lyso}(q)$ in the low q region. [b]: errors bars estimated from R_{lyso_comp}, R_{PSS_comp}, σ, Φ_{lyso_inner} and Φ_{PSS_inner}.

2.4 pH 4.7, f = 1, $[-]/[+]_{intro}$ = 3.33, initial variation of I

The influence of a modification of the ionic strength of the buffer on the complexation during synthesis has been investigated on a sample with $[-]/[+]_{intro}$ = 3.33 on fully sulfonated chains at pH 4.7. The spectra for I = 5 10^{-2} mol/L has been already presented in ref [7]. The intermediate peak on the PSS scattering is the signature of the 'polyelectrolyte peak' due to the free chains for such a high $[-]/[+]_{intro}$. An increase of the ionic strength increases the complex radius. We have tested two different buffers (NaCl and CH_3COONa) for the highest ionic strength (for I = 5 10^{-1} mol/L). Both results are similar. For such salinity, the complex

radius is too high to allow a satisfying fit. The order of R_{mean} is at least ~ 300 Å and the compactness should lie around 0.3. Results are presented in Figure S4.

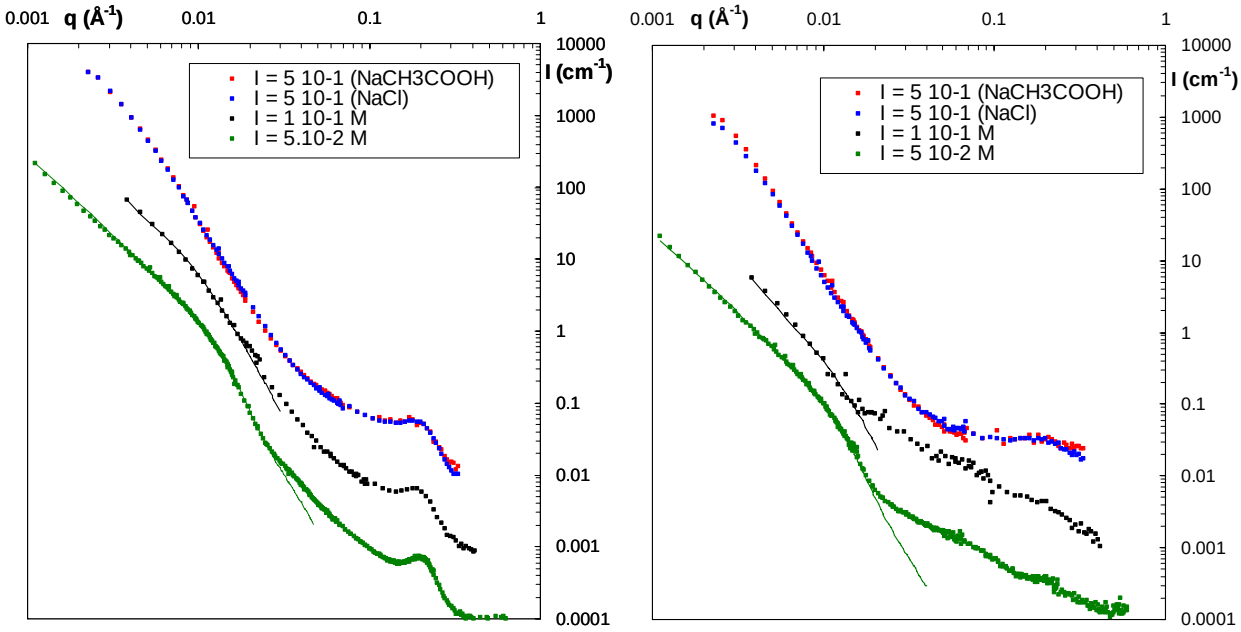

Figure S4: samples at pH 4.7, f = 1, and $[-]/[+]_{intro}$ = 3.33 and $[Lyso]_{intro}$ = 40g/L with different initial ionic strengths I of the buffer : (a) lysozyme scattering. All curves are shifted from one to another by a decade for clarity, except for the samples made with a ionic strength of 5 10^{-1} which are presented on the same scale but with different colors (red, $NaCH_3COOH$ buffer, blue, NaCl buffer). The intensity in absolute scale correspond to the I = 5 10^{-1} sample. The full lines correspond to the fits. (b) PSS chains scattering. All curves are shifted from one to another by a decade for clarity. The intensity in absolute scale correspond to the I = 5 10^{-1} sample. The full lines correspond to the fits.

	R_{lyso} (Å); σ	R_{PSS} (Å); σ	R_{mean_lyso} (Å)	R_{mean_PSS} (Å)
I = 5 10^{-2} mol/L	114; 0.37	154; 0.37	130± 2	190± 5
I = 1 10^{-1} mol/L	120; 0.4		150± 5	
I = 5 10^{-1} mol/L (NaCl)	> 300		> 300	
I = 5 10^{-1} mol/L ($NaCH_3COONa$)	> 300		> 300	

	Φ_{lyso_inner}	Φ_{PSS_inner}	$[-]/[+]_{inner}$	N_{lyso_comp}
I = 5 10^{-2} mol/L	0.19±0.01	0.054±0.005	1.19±0.24 [b]	84±9
I = 1 10^{-1} mol/L	0.18±0.01		1.02	160±20
I = 5 10^{-1} mol/L (NaCl)			1.08[*]	> 2000
I = 5 10^{-1} mol/L ($NaCH_3COONa$)			1[*]	> 2000

Table S4: Effect of increase of salinity on primary complexes made at pH 4.7 and f = 1 ($[-]/[+]_{intro}$ = 1.66). Radius size of primary complexes from both lysozyme and PSS point of view, inner volume fraction of lysozyme and PSS within primary complexes and inner charge ratio in the primary complexes. [*]: estimation from $I_{PSS}(q)/I_{lyso}(q)$. [a]: errors bars estimated from $I_{PSS}(q)/I_{lyso}(q)$ in the low q region. [b]: errors bars estimated from R_{lyso_comp}, R_{PSS_comp}, σ, Φ_{lyso_inner} and Φ_{PSS_inner}.

2.5 pH 4.7, f = 1, [-]/[+]$_{intro}$ = 1.66, I = 5 10^{-2}, variation of the concentration of species

In all samples described in this paper the initial lysozyme concentration is [Lyso] = 40g/L. We study here the effect of the species concentration on the characteristic of the samples, keeping all parameters influencing electrostatics constant (pH, sulfonation rate, [-]/[+]$_{intro}$ and ionic strength of the buffer). We chose to work with [-]/[+]$_{intro}$ = 1.66 with 6 different concentrations lying from 5g/l to 60g/L for lysozyme (respectively 0.00625M to 0.075M for PSS chains).

Only the lysozyme scattering has been measured since the PSS concentration is too low for the most diluted samples to provide a significant coherent scattering. Owing to a technical problem, the scattering of the samples at 60g/L is not exploitable at large q. The scattering spectra are presented in figure A.5.a. As the species concentration has a strong influence on the size complexes, we present the same results in a $I(q)q^4 = f(q)$ Porod representation which enhances the size features of the complexes (Insert of Fig S5). When the concentration is increased, the correlation peak, directly linked to the primary complexes radius in this representation, is shifted towards low q (large size) [7]. Conversely, the plateau after the peak as it is proportional to the specific area of complexes (~ $3/R_{comp}$).

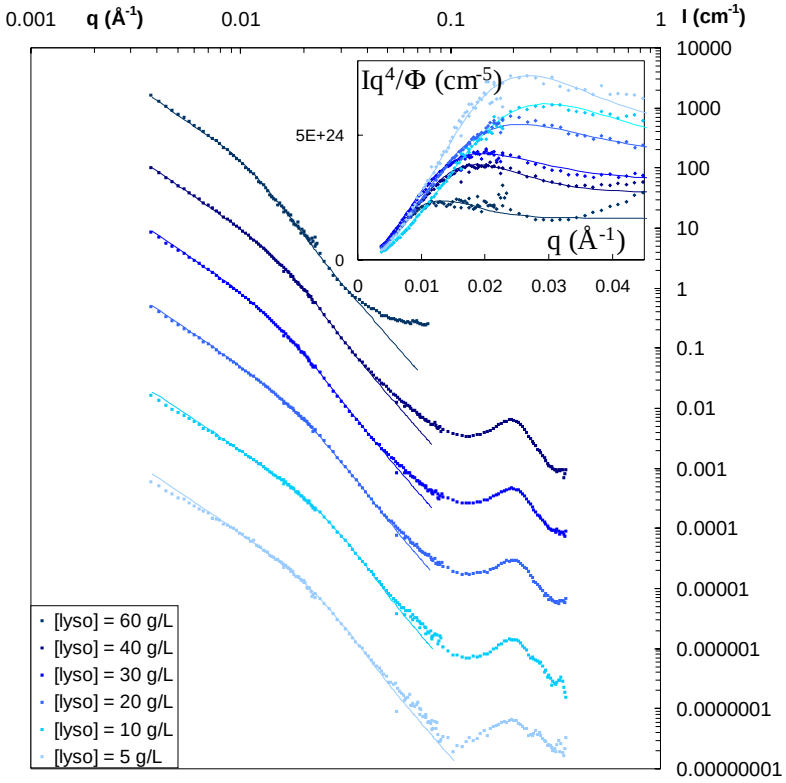

Figure S5: Lysozyme scattering of samples at pH 4.7, f = 1, I = 5 10^{-2}, and [-]/[+]$_{intro}$ = 1.66 in a log-log representation. All curves are shifted from one to another by a decade for clarity. The intensity in absolute scale correspond to the [Lyso]$_{intro}$ = 60g/L sample. The full lines correspond to the fits. Insert: Porod representation. The full lines correspond to the fits.

All the characteristics are of samples recalled in Table SI.5.

	R_{lyso} (Å); σ	R_{mean_lyso} (Å)	Φ_{lyso_inner}	N_{lyso_comp}
[Lyso]$_{intro}$ = 5g/L	55; 0.45	75 ± 1	0.20±0.01	24±2
[Lyso]$_{intro}$ = 10g/L	55; 0.45	75 ± 1	0.25±0.01	30±3
[Lyso]$_{intro}$ = 20g/L	75; 0.4	95 ± 1	0.27±0.01	70±5
[Lyso]$_{intro}$ = 30g/L	95; 0.3	125 ± 2	0.26±0.01	158±13

$[Lyso]_{intro}$ = 40g/L	145; 0.31	150 ± 2	0.24±0.01	235±19
$[Lyso]_{intro}$ = 60g/L	150; 0.32	182 ± 2	0.23±0.01	436±32

Table SI.5: Influence of the concentration of the species on the size of the primary complexes (pH 4.7, f = 1, $[-]/[+]_{intro}$ = 1.66, I = 5 10^{-2}). Radius size of primary complexes from lysozyme point of view and inner volume fraction of lysozyme.

2.6 pH 4.7, f = 1, I = 5 10^{-2}, variation of [-]/[+]intro

In this section we recall all the values already published in previous papers [7, 9] at pH 4.7, f = 1, [lyso] = 40g/L, I = 5 10^{-2}. They are presented here to enable a better reading of the main text.

	R_{lyso} (Å); σ	R_{PSS} (Å); σ	R_{mean_lyso} (Å)	R_{mean_PSS} (Å)
$[-]/[+]_{intro}$ = 0. 5	68; 0.48	68; 0.48	95 ± 5	95 ± 5
$[-]/[+]_{intro}$ = 0.65	73; 0.45	73; 0.45	100± 5	100± 5
$[-]/[+]_{intro}$ = 1	73; 0.45	73; 0.45	100± 5	100± 5
$[-]/[+]_{intro}$ = 1.33	90; 0.34	95; 0.4	115± 2	120± 5
$[-]/[+]_{intro}$ = 1.66	114; 0.37	154; 0.37	130± 2	190± 5
$[-]/[+]_{intro}$ = 2.5	130; 0.35	155; 0.35	150± 2	186± 5
$[-]/[+]_{intro}$ = 3.33	154; 0.31	164; 0.31	175± 2	190± 5

	Φ_{lyso_inner}	Φ_{PSS_inner}	$[-]/[+]_{inner}$	N_{lyso_comp}

$[-]/[+]_{intro}$ = 0. 5	0.3±0.01	0.06±0.005	0.77±0.07 [a]	74±14
$[-]/[+]_{intro}$ = 0.65	0.24±0.01	0.052±0.005	0.97±0.05 [a]	69±14
$[-]/[+]_{intro}$ = 1	0.19±0.01	0.0410.0005	0.91±0.04 [a]	55±11
$[-]/[+]_{intro}$ = 1.33	0.19±0.01	0.054±0.005	1.19±0.24 [b]	84±9
$[-]/[+]_{intro}$ = 1.66	0.27±0.01	0.069±0.005	1.06±0.16 [b]	171±14
$[-]/[+]_{intro}$ = 2.5	0.19±0.01	0.04±0.005	1.08±0.23 [b]	185±17
$[-]/[+]_{intro}$ = 3.33	0.3±0.01	0.075±0.005	1.04±0.14 [b]	465±32

Table SI.6: Primary complexes made at pH 4.7 and f = 1. Radius size of primary complexes from both lysozyme and PSS point of view, inner volume fraction of lysozyme and PSS within primary complexes and inner charge ratio in the primary complexes. [a]: errors bars estimated from $I_{PSS}(q)/I_{lyso}(q)$ in the low q region. [b]: errors bars estimated from R_{lyso_comp}, R_{PSS_comp}, σ, Φ_{lyso_inner} and Φ_{PSS_inner}.

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