Supporting Information

Contraction and Coagulation of Spherical Polyelectrolyte Brushes in the Presence of Ag^{+}, Mg^{2+} and Ca^{2+} Cations

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S1. Effect of $NaNO_3$ on Ag^+-Induced Shrinking of SBB(HMEM)

Figure S1 compares the shrinking of SPB(HMEM) induced with Ag^+ cations in the absence of additional $NaNO_3$ and in the presence of added $NaNO_3$ whereby $NaNO_3$ is added at constant overall ionic strength of 0.01 M. Figure S1 also illustrates the determination of the threshold $[M^{n+}]_{shr}$ at which the shrinking of the NaPA shell is completed. The threshold, here established as $[Ag^+]_{shr}$ is identified as follows. The first data point which is part of the final plateau in L, denoted as $[Ag^+]_{pl}$ has been connected with the data point $[Ag^+]^*$ neighboring it to the left, i. e. toward decreasing $[Ag^+]$. The first data point which is considered to be part of the plateau in L, $[Ag^+]_{pl}$, has been included beforehand in the data set used to calculate this very plateau value L_{pl} as an average and its standard deviation. Successively, the mean value of $[Ag^+]^*$ and $[Ag^+]_{pl}$ is taken as $[Ag^+]_{shr}$ value. The width of the connecting line projected onto the $[Ag^+]$–axis is used as an estimation for the uncertainty of the respective $[Ag^+]_{shr}$ value.

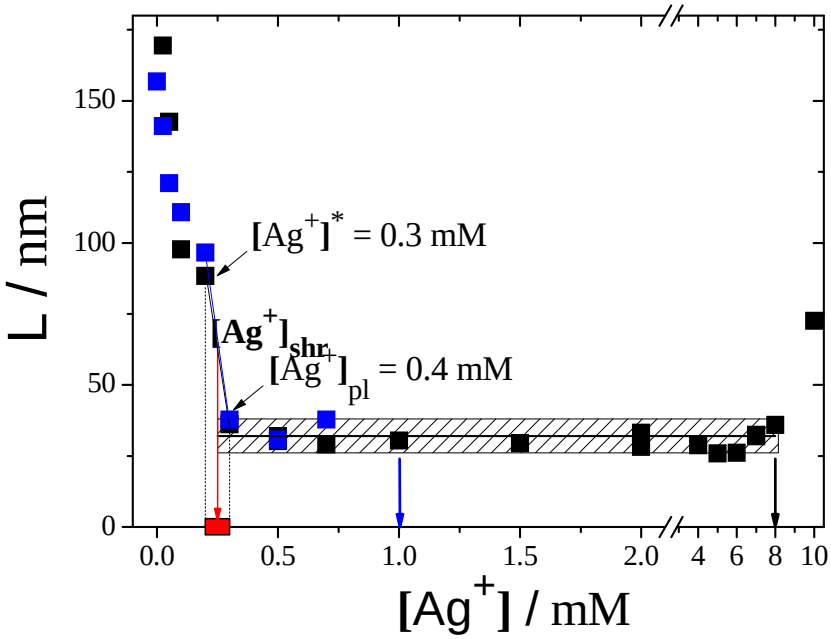

Figure S1. Thickness L of the PA-layer of SPB(HMEM) in Ag^+-SPB solutions at a pH of 6.5 as a function of $AgNO_3$ concentration in salt free solution (■) and in 0.01 M $NaNO_3$ (■). The concentration of $[COO^-]$ is 0.1 mM. The black horizontal line corresponds to the plateau value L_{pl} = 32 nm of the maximally shrunken PA-layer. The shaded area indicates the standard deviation of L_{pl} which is ±6 nm. The red arrow shows the $[Ag^+]_{shr}$ where the shrinking of the PA-layer is completed, the red area on the x-axis indicates the experimental uncertainty of $[Ag^+]_{shr}$. Blue and black arrows pointing down denote the coagulation threshold $[Ag^+]_c$ in salt free and in 0.01 M $NaNO_3$, respectively.

S2. Effect of Sample History on Ag^+-Induced Shrinking of SBB(HMEM)

Figure S2a shows trends of L extracted from angular dependent DLS experiments with SPB(HMEM) at pH=4.4 and 6.5 and at [$NaNO_3$] = 0.01 M respectively. The data demonstrate reproducibility of the experiments and the stability of the samples for at least three days.

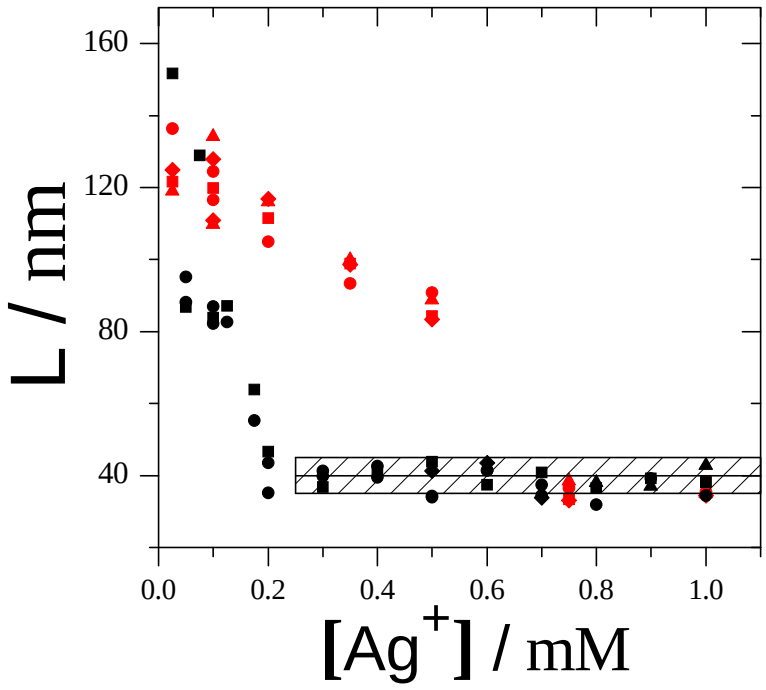

Figure S2a. Thickness L of the PA-layer of SPB(HMEM) in solutions at a pH of 4.4 (red symbols) and of 6.5 (black symbols) as a function of $AgNO_3$ concentration in 0.01 M $NaNO_3$. The concentration of [COO^-] is 0.05 mM. The black horizontal line corresponds to the plateau value L_{pl} = 40 nm of the maximally shrunken PA-layers. The shaded area indicates the standard deviation of L_{pl} which is ±5 nm. Symbols indicate that DLS analysis was performed on the 1st (■,■), 2nd (●,●), 3rd (▲,▲) and 4th (◆,◆) day after the solution had been prepared.

In addition, joint SLS and DLS curves are presented in **Figure S2b**, which have been selected from the experiments at pH = 6.5 and [$NaNO_3$] = 0.01 M in **Figure S2a**. All curves recorded in the presence of Ag^+ cations are measured at the day where the SPB solutions had been mixed with the Ag^+ solutions respectively. **Figure S2b** helps to rule out aggregation caused by non-equilibrium effects during mixing of the two solutions. The SLS curves recorded in the low angle region of $30° \leq \theta \leq 74°$ are straight lines close to each other showing no sign of a downward bending at lowest q and yielding apparent values of the radius of gyration R_g at all four conditions which agree within a range of 20%. Addition of

Ag^+ leads to small increases of the scattering signals visible as shifts in the curves, with the largest shift of the apparent molar mass M_w of 40% being observed at $[Ag^+]$=0.05 mM. The linear nature of all curves and the fact that the shift gets weaker with increasing Ag^+ content suggest that these shifts stem from slight but systematic variations in the scattering contrast of the shells, due to Na^+ cations being increasingly exchanged by Ag^+ cations, due to hydration shells of the ionic residues in the shell being heavily affected by ion bonding and finally due to a Donnan effect. Any quantitative discussion of the apparent parameters going beyond the qualitative interpretation just outlined is prohibited for the following reasons: Determination of the refractive index increment dn/dc of colloids/SPBs, required to calculate the contrast factor K and along with it molar mass values, is difficult if not impossible because SPB solutions get turbid already at fairly low concentrations. Aside from this, our SPBs have a polystyrene core and a NaPA-shell, both differing in their scattering contrast (dn/dc). The non-homogeneous dn/dc inhibits direct interpretation of the initial slopes of the curves in terms of mean square radii of gyration R_g^2.

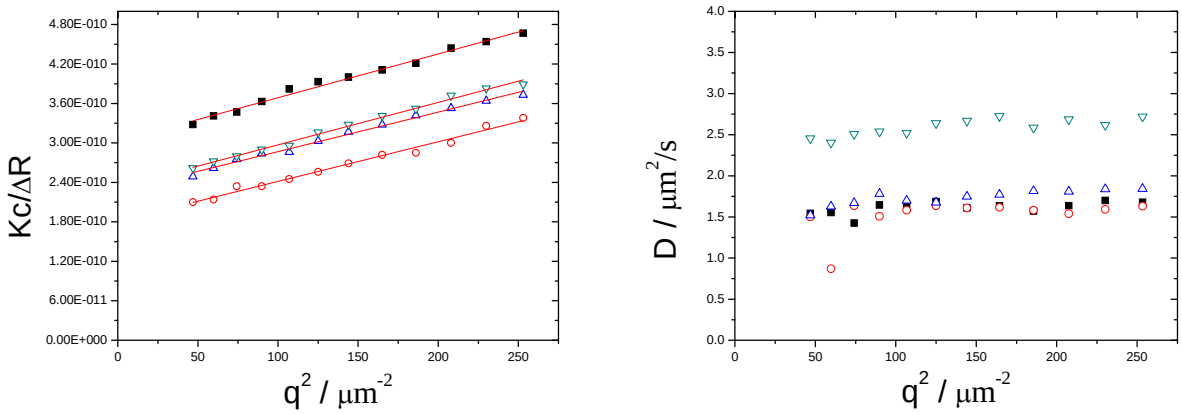

Figure S2b. Joint SLS/DLS-experiments at a SPB(HMEM) concentration of $[COO^-]$ = 0.05 mM, at pH = 6.5 and $[NaNO_3]$ = 0.01 M at four different contents of Ag^+ indicated as follows: ($[Ag^+]$=0 (■); $[Ag^+]$=0.05 mM (○); $[Ag^+]$=0.1 mM (△); $[Ag^+]$=0.2 mM (▽)). The data are part of the experiments shown in **Figure S2a**. **Left**: SLS-curves expressed as inverse Rayleigh ratios ΔR (in arbitrary units). The straight lines are based on a linear Zimm-plot (Zimm, B. *J.Chem.Phys.* **1948**, *16*, 1093) leading to the following apparent radii of gyration R_g from slopes and apparent molecular weights $M_w \sim [\Delta R/Kc]_{q=0}$ from intercepts: R_g = 81 nm and M_w = $3.31 \cdot 10^9$ ($[Ag^+]$=0 mM); R_g = 100 nm and M_w = $5.21 \cdot 10^9$ ($[Ag^+]$=0.05 mM); R_g = 89 nm and M_w = $4.41 \cdot 10^9$ ($[Ag^+]$=0.1 mM); R_g = 91 nm and M_w = $4.30 \cdot 10^9$ ($[Ag^+]$=0.2 mM). **Right**: DLS-curves expressed as diffusion coefficients D for the same experiments as the SLS curves on the left hand side.

Absence of any aggregation is corroborated by the respective DLS curves also included in **Figure S2b**. None of the curves shows a significant q-dependence, which proves occurrence of just one narrowly distributed translational diffusion mode.

S3. Ag^+-Induced Shrinking of SBPs at Variable SBP Content for Three Different Types of SPBs

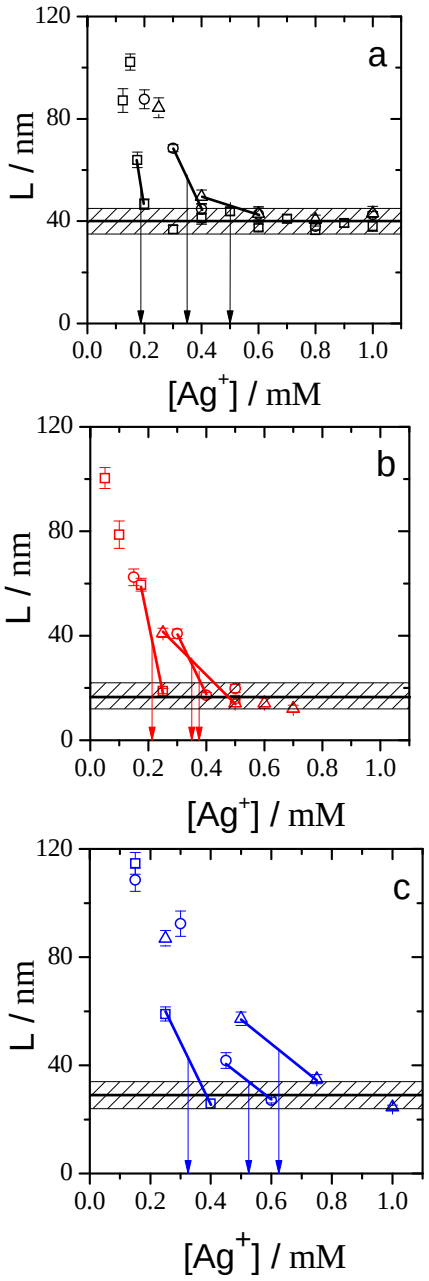

Figure S3 Thickness L of the PA-layer in Ag^+-SPB solutions at a pH of 6.5 as a function of $AgNO_3$ concentration in 0.01 M $NaNO_3$. Three types of SPB in the presence of Ag^+ ions are analysed: SPB(HMEM) – graph **a**, SPB(ABP) – graph **b**, SPB(BA) – graph **c**. The concentration of [COO^-] is 0.05 mM (squares), 0.15 mM (circles) and 0.25 mM (triangles). The black horizontal lines correspond to the plateau values L_{pl} of the maximally shrunken PA-layers: 40 nm (**a**), 17 nm (**b**) and 29 nm (**c**). The shaded area indicates the standard deviation of L_{pl} which is ±5 nm in all three cases. The arrows indicate the shrinking thresholds $[Ag^+]_{shr}$ which are established according to a procedure outlined in Chapter S1.

Table S1. Parameters defining the thresholds of shell shrinking in Ag^+-SPB solutions in 0.01 M $NaNO_3$ at a pH of 6.5. The silver cation concentrations have the following meaning: $[Ag^+]^*$ is the highest silver cation concentration establishing the decay of L, $[Ag^+]_{pl}$ is first value considered to belong to the plateau value of L, $[Ag^+]_{shr} = ([Ag^+]^*+[Ag^+]_{pl})/2$ is the value where shrinking is considered to be completed.

SPB type	$[COO^-]$ / mM	$[Ag^+]^*$ / mM	$[Ag^+]_{pl}$ / mM	$[Ag^+]_{shr}$ / mM	Estimated uncertainty of $[Ag^+]_{shr}$
SPB(HMEM)	0.05	0.175	0.2	0.1875	0.025
	0.15	0.3	0.4	0.35	0.1
	0.25	0.4	0.6	0.5	0.2
SPB(ABP)	0.05	0.175	0.25	0.2125	0.075
	0.15	0.3	0.4	0.35	0.1
	0.25	0.25	0.5	0.375	0.25
SPB(BA)	0.05	0.25	0.4	0.325	0.15
	0.15	0.45	0.6	0.525	0.15
	0.25	0.5	0.75	0.625	0.25

S4. Ag^+-Induced Coagulation of SBP(HMEM) at Variable SBP Content

Turbidity of Ag^+-SPB solutions at SPB contents of $[COO^-] > 0.25$ mM prevents a meaningful DLS analysis of those solutions. Hence, stability of solutions at $[COO^-] > 0.25$ mM was scrutinized by visual inspection. 36 vials were furnished with 2 ml of Ag^+-SPB in aqueous $NaNO_3$ at [+] = 0.01 each, covering a concentration regime of $7 \leq [Ag^+] \leq 15$ mM and $1 \leq [COO^-] \leq 4$ mM. All vials were visually inspected for one month.

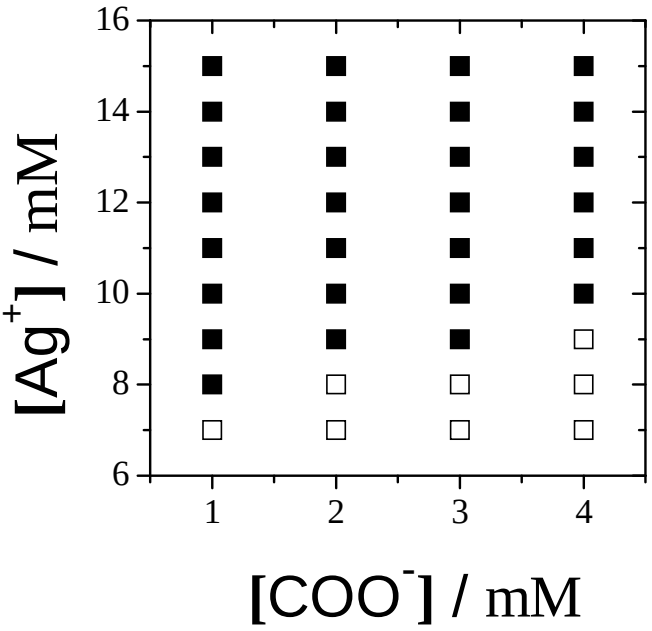

Figure S4. Results from visual monitoring of Ag^+-SPB solutions in aqueous $NaNO_3$ at [+] = 0.01 M (for $[Ag^+] \leq 10$ mM) and at a pH of 6.5. Full squares denote Ag^+-SPB in solution coagulating within a month, whereas empty squares correspond to Ag^+-SPB solutions stable for at least a month. The SPB sample used is SPB(HMEM).

Table S2. Parameters characterizing coagulation of Ag^+-SPB(HMEM) solutions . The threshold value $[Ag^+]_c$ is established as mean value of highest silver cation concentration $[Ag^+]_1$ where SPBs are still stable (hollow squares in Figure S4) and first silver cation concentration $[Ag^+]_2$ where coagulation has been observed (filled squares in Figure S4).

$[COO^-]$ / mM	$[Ag^+]_1$ / mM	$[Ag^+]_2$ / mM	$[Ag^+]_c$ / mM	Estimated uncertainty of $[Ag^+]_c$
1	7	8	7.5	1
2	8	9	8.5	1
3	8	9	8.5	1
4	9	10	9.5	1

S5. Mg^{2+}- and Ca^{2+}-Induced Shrinking of SBP(HMEM) at Variable SBP Content

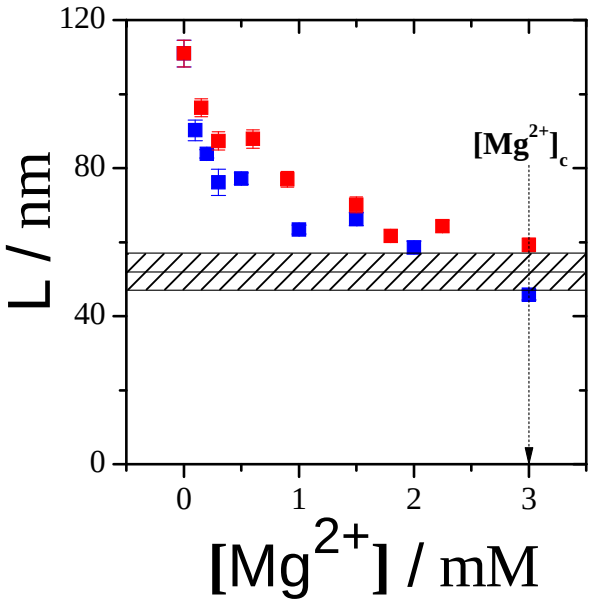

Figure S5a. Thickness L of the PA-layer in Mg^{2+}-SPB(HMEM) solutions at a pH of 6.5 as a function of $MgCl_2$ in 0.01 M NaCl. The concentration of $[COO^-]$ is 0.1 (■) and 0.15 (■) mM. The black horizontal line corresponds to the plateau value of the maximally shrunken PA-layers L_{pl} = 52 nm. The shaded area indicates the standard deviation of L_{pl} , which is ±5 nm. The black arrow shows the coagulation threshold $[Mg^{2+}]_c$ = 3 mM, which within experimental uncertainty coincides with the value $[Mg^{2+}]_{shr}$ where the shrinking plateau is reached.

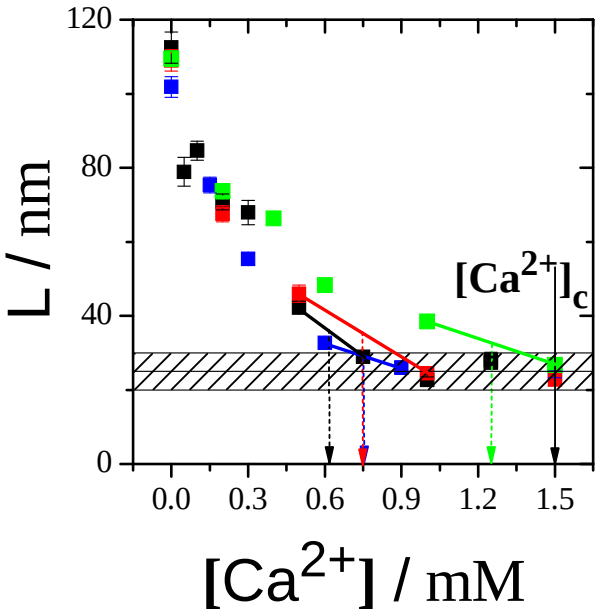

Figure S5b. Thickness L of the PA-layer in Ca^{2+}-SPB(HMEM) solutions at a pH of 6.5 as a function of $CaCl_2$ in 0.01 M NaCl. The concentration of [COO^-] is 0.05 (■), 0.1 (■), 0.15 (■) and 0.2 (■) mM. The data recorded with [COO^-] = 0.1 mM reproduce the respective experiments shown in Figure 5 of the manuscript. The black horizontal line corresponds to the plateau value of the maximally shrunken PA-layers L_{pl} = 25 nm. The shaded area indicates the standard deviation of L_{pl} , which is ±5 nm. Arrows emanating from the coloured lines, which connect $[Ca^{2+}]^*$ with $[Ca^{2+}]_{pl}$ denote the concentration limits $[Ca^{2+}]_{shr}$ where the shrinking is completed (i. e. L_{pl} is approached) respectively. The right most (black) arrow shows the coagulation threshold $[Ca^{2+}]_c$. The results are also summarized in Table S3.

Table S3. Parameters defining the thresholds of shell shrinking in Ca^{2+}-SPB(HMEM) solutions at a pH of 6.5 in 0.01 M NaCl.

[COO^-] / mM	$[Ca^{2+}]^*$ / mM	$[Ca^{2+}]_{pl}$ / mM	$[Ca^{2+}]_{shr}$ / mM	Estimated uncertainty of $[Ca^{2+}]_{shr}$
0.05	0.5	0.75	0.625	0.25
0.1	0.5	1	0.75	0.5
0.15	0.6	0.9	0.75	0.3
0.2	1	1.5	1.25	0.5

S6. Ca^{2+}-Induced Coagulation of SBP(HMEM) at Variable SBP Content

Turbidity of Ca^{2+}-SPB solutions at SPB contents of $[COO^-] > 0.25$ mM prevents a meaningful DLS analysis of those solutions. Hence, stability of solutions at $[COO^-] > 0.25$ mM was scrutinized by visual inspection. 19 vials were furnished with 2 ml of Ca^{2+}-SPB in aqueous NaCl at [+] = 0.01 each, covering a concentration regime of $0.6 \leq [Ca^{2+}] \leq 2.4$ mM and $0.5 \leq [COO^-] \leq 1.5$ mM. All vials were visually inspected for one month.

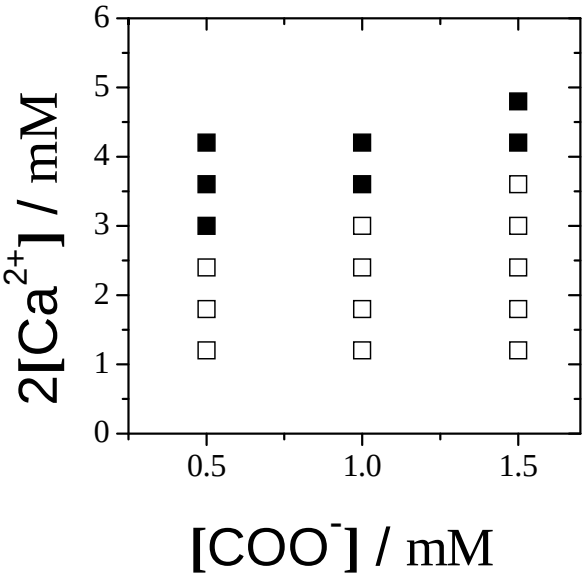

Figure S6. Results from visual monitoring of Ca^{2+}-SPB solutions in aqueous NaCl at [+] = 0.01 M and at a pH of 6.5. Full squares denote Ca^{2+}-SPB in solution coagulating within a month, whereas empty squares correspond to Ca^{2+}-SPB solutions stable for at least a month. The SPB sample used is SPB(HMEM).

Table S4 Parameters describing the coagulation of Ca^{2+}-SPB(HMEM) solutions . The threshold value $[Ca^{2+}]_c$ is established as mean value of highest calcium cation concentration $[Ca^{2+}]_1$ where SPBs are still stable (hollow squares in Figure S6) and first calcium cation concentration $[Ca^{2+}]_2$ where coagulation has been observed (filled squares in Figure S6).

$[COO^-]$ / mM	$2[Ca^{2+}]_1$ / mM	$2[Ca^{2+}]_2$ / mM	$2[Ca^{2+}]_c$ / mM	Estimated uncertainty of $2[Ca^{2+}]_c$
0.5	3.6	4.2	3.9	0.6
1.0	3	3.6	3.3	0.6
1.5	2.4	3	3	0.6