

Electronic Supplementary Information

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Component	Assignment	Peak maxima wavenumber / cm ⁻¹	Peak range wavenumber / cm ⁻¹
Water	v(OH)	3330	3900-3120
Imidazole	v(C _{4,5} -H)	3100	3115-3080
Imidazole	v(C ₂ -H)	3058	3080-3025
Imidazole	v(N-C=N)	1575	1601-1553
Imidazole	v(Im)	1425	1447-1405

Table S1. Component, assignment, maxima and width of cation IR peaks.

Components	Assignment	Peak maxima wavenumber / cm^{-1}	Peak range wavenumber / cm^{-1}
Water	$\nu(\text{OH})$	3370	3900-3050
PSS, PDADMAC	$\nu(\text{CH})$	3028	3050-2980
PSS, PDADMAC	$\nu(\text{CH}_2)$	2953	2980-2920
Water	$\nu_b(\text{OH})$	1640	1818-1605
PDADMAC	$\nu_b(\text{CH})$	1475	1510-1428
PSS	$\nu_{\text{ar}}(\text{C}=\text{C})$	1405	1430-1380
PSS	$\nu_{\text{as}}(\text{SO}_3^-)$	1195	1260-1120
PSS	$\nu_{\text{s}}(\text{SO}_3^-)$	1005	1058-983

Table S2. Component, assignment, maxima and width of IR peaks of PSS/PDADMAC multilayers.

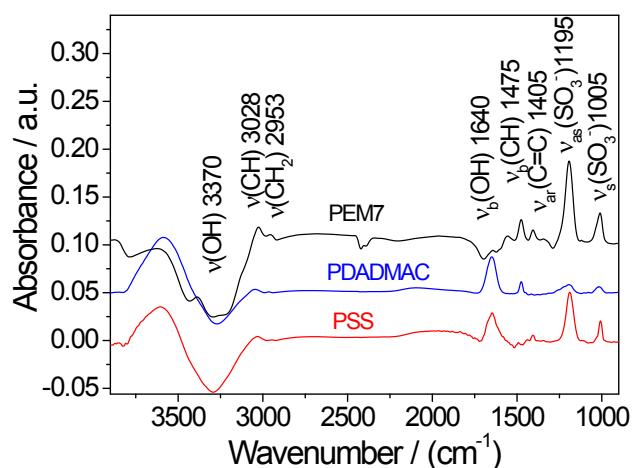


Figure S1. ATR-IR spectra of 0.25 M (monomer concentration) solutions of PSS and PDADMAC, respectively, and of a PEM7 film. The absorbance values on the y-axis are not the absolute values as the spectra are shown in stacked fashion.

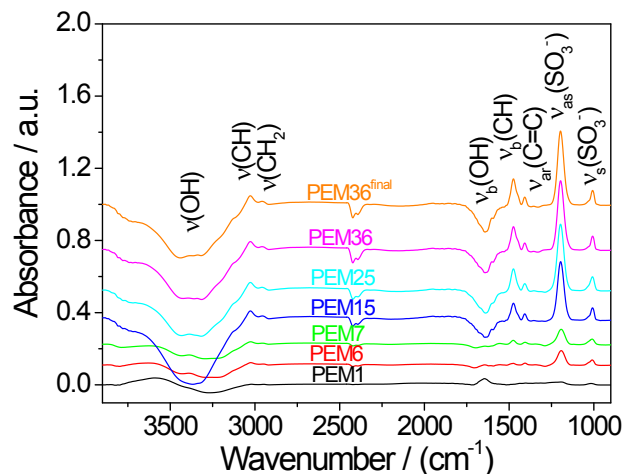


Figure S2. ATR-IR spectra for different layer numbers during build-up of PSS/PDADMAC film. The absorbance values on the y-axis are not the absolute values as the spectra are shown in stacked fashion.

Component	Assignment	Peak maxima wavenumber / cm^{-1}	Peak range wavenumber / cm^{-1}
Water	$\nu(\text{OH})$	3450	3880-3150
PSS, PAH	$\nu(\text{CH})$	3025	3080-2980
PAH	$\nu(\text{CH}_2)$	2950	2980-2915
Water	$\nu_b(\text{OH})$	1643	1760-1600
PAH	$\nu(\text{NH})$	1544	1595-1480
PSS	$\nu_{\text{ar}}(\text{C}=\text{C})$	1402	1430-1368
PSS	$\nu_{\text{as}}(\text{SO}_3^-)$	1192	1250-1130
PSS	$\nu_{\text{s}}(\text{SO}_3^-)$	1010	1035-983

Table S3. Component, assignment, maxima and width of IR peaks of PSS/PAH multilayer.

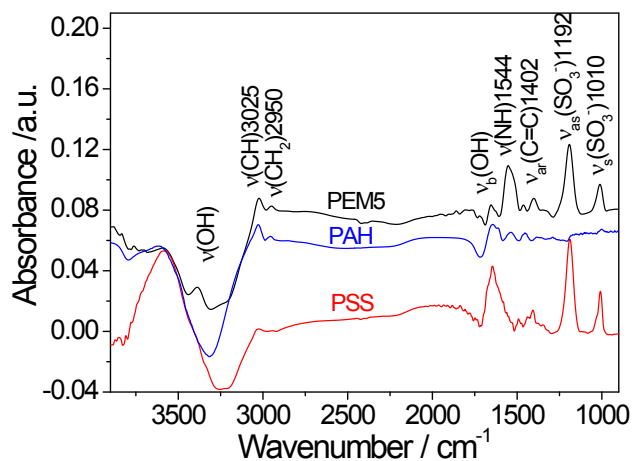


Figure S3. ATR-IR spectra of 0.25 M (monomer concentrations) solutions of PSS and PAH, respectively, at pH 9.5 and of a PEM5 film. The absorbance values on the y-axis are not absolute as the spectra are shown in a stacked fashion.

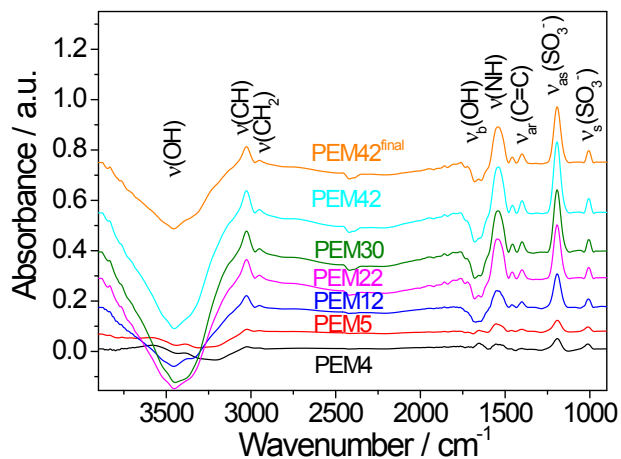


Figure S4. Different adsorbed polyelectrolyte layers during the build-up of PSS/PAH multilayers. The absorbance values on the y-axis are not absolute values, as the spectra are vertically shifted for clarity.

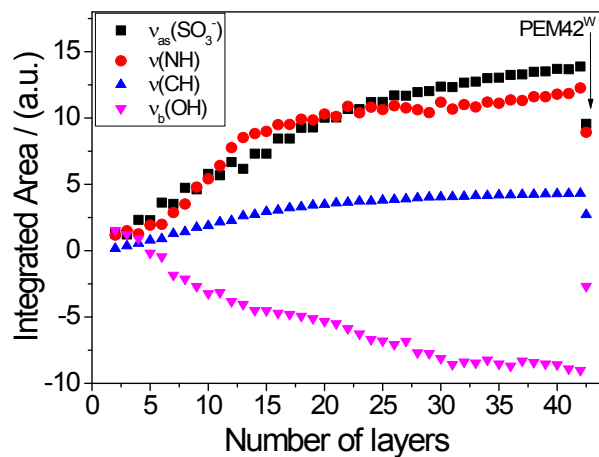


Figure S5. Area under the spectral lines of PSS/PAH multilayers in dependence of the number of adsorbed polyelectrolyte layers.

Components	Assignment	Peak maxima wavenumber / cm^{-1}	Peak range wavenumber / cm^{-1}
Water	$\nu(\text{OH})$	3472	3880-3080
PAA, PDADMAC	$\nu(\text{CH}_2)$	3034	3075-2985
PAA	$\nu(\text{C}=\text{O})$	1727	1785-1665
PAA	$\nu(\text{COO}^-)$	1556	1600-1494
PDADMAC	$\nu_b(\text{CH})$	1458	1494-1430
PAA	$\nu(\text{C}-\text{O})$	1220	1290-1150

Table S4. Component, assignment, maxima and width of IR peaks of PAA/PDADMAC multilayers.

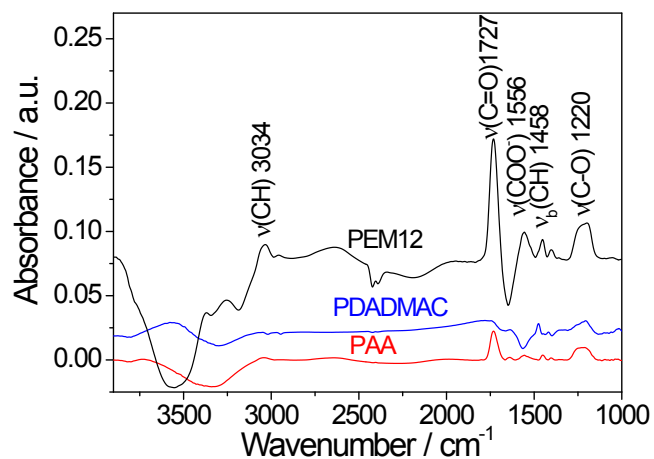


Figure S6. ATR-IR spectra of 0.25 M (monomer conc.) solutions of PAA and PDADMAC, respectively, at pH 3 and of a PEM12 film. The absorbance values on the y-axis are not absolute as the spectra are shown in a stacked fashion.

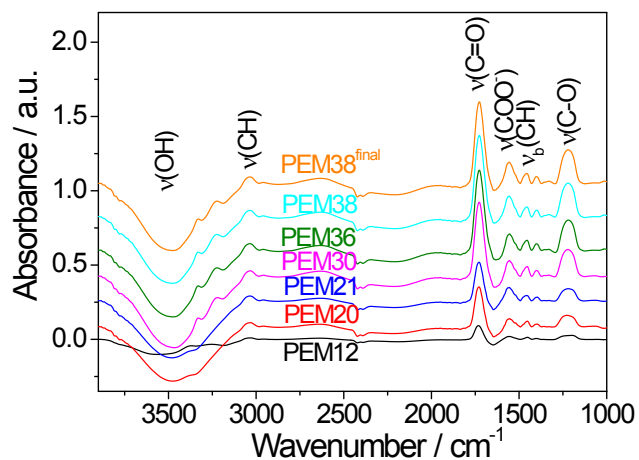


Figure S7. ATR spectra of adsorbed polyelectrolyte layers during build-up of PAA/PDADMAC multilayers. The absorbance values on the y-axis are not absolute as the spectra are shown in a stacked fashion.

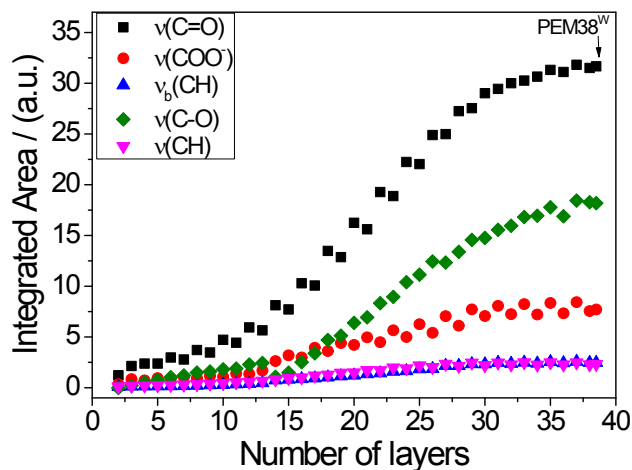


Figure S8. Integrated area under the spectral lines of PAA/PDADMAC multilayers in dependence of the number of the adsorbed polyelectrolyte layers.

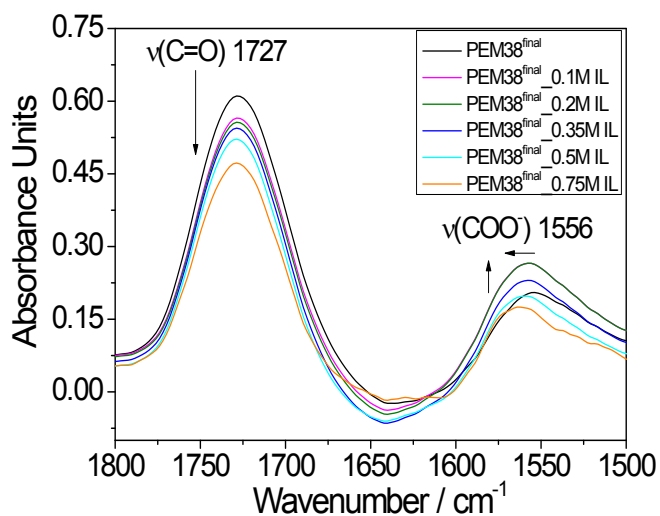


Figure S9. The $\nu(\text{COO}^-)$ and $\nu(\text{C}=\text{O})$ peaks of PEM38^{final} in reversible contact with IL solution and water.

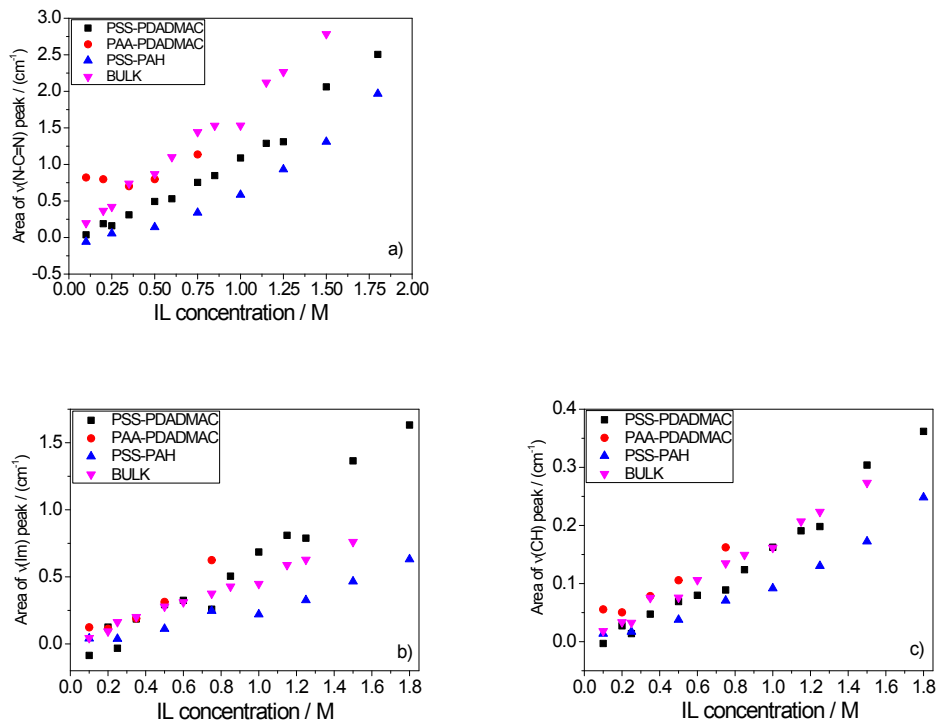


Figure S10. Integrated area under a) $\nu(\text{N-C=N})$ b) $\nu(\text{Im})$ and c) $\nu(\text{CH})$ peaks of MMIM^+ incorporated in PSS/PDADMAC, PAA/PDADMAC and PSS/PAH multilayers and from the bulk MMIM^+Cl^- solutions. Film data are identical to those of Figures 3c, 4c and 5d in the main text, but presented here separately for the three resonances. Due to the larger scatter of the data from the weak resonances (see b) and c)) the cation concentration is based on the $\nu(\text{N-C=N})$ resonance alone.

Paragraph 1

IL quantification from IR peak area of IL. The peak area under the specific IR signals of bulk IL solutions is calculated, see magenta reverse triangles in Figure S10. Here bulk IL solution is the IL solution at the respective concentration directly in contact with the Si surface of ATR-IR. Thus the IR peak areas correspond to a known IL concentration and can serve as a reference. Upon MMIM^+ uptake in PEM, the peak areas under the IR peaks are also determined (see other data sets in Fig. S10) and divided by the bulk IL solution peak areas at the respective concentration. This

N. Parveen, M. Schönhoff, **Quantifying and Controlling Hydrated Cation Uptake upon Ionic Liquid –Induced Swelling of Polyelectrolyte Multilayers**. *Soft Matter*, 2016.

ratio multiplied with the respective bulk IL concentration yields the absolute concentration of MMIM⁺ ions incorporated in PEM.