Electronic Supplementary Material (ESI) for Soft Matter.

Supporting Information For

Comparing Water-Mediated Hydrogen-Bonding in Different Polyelectrolyte Complexes

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Table S1. The number of water molecules in the molecular dynamics simulations at different water wt%. The number of water molecules per repeat unit is provided in brackets.

	26 wt%	**30 wt%**	**34 wt%**	**38 wt%**
PAH-PSS	1884 (2.355)	2298 (2.8725)	2762 (3.4525)	3286 (4.1075)
PDADMA-PAA	1554 (1.9425)	1895 (2.36875)	2278 (2.8475)	2710 (3.3875)

Table S2. Details of MD simulation protocol. For each step, the simulation duration, time step, temperature, and simulation ensemble with box size or barostat setup are specified. Step 1 - initial PE hydration with position restraints applied on PE chains, step 2 - initial compression, step 3 - initial equilibration in elevated temperature, step 4 - continuation of equilibration with a more flexible simulation box, step 5 - cooling and relaxation, and step 6 - production run.

STEP	**DURATION [NS]**	**TIME STEP [FS]**	**TEMPERATURE [K]**	**ENSEMBLE**
1	1	0.5	290	NVT (20×20×20 nm^3 box)
2	0.5	0.5	290	NPT (isotropic pressure
3	50	2	370	coupling)
4	50	2	370	NPT (anisotropic pressure
5	10	2	370 → 290 (6 ns), 290 (4 ns)	coupling)
6	225	2	290 → 360 (steps every 5 K)	

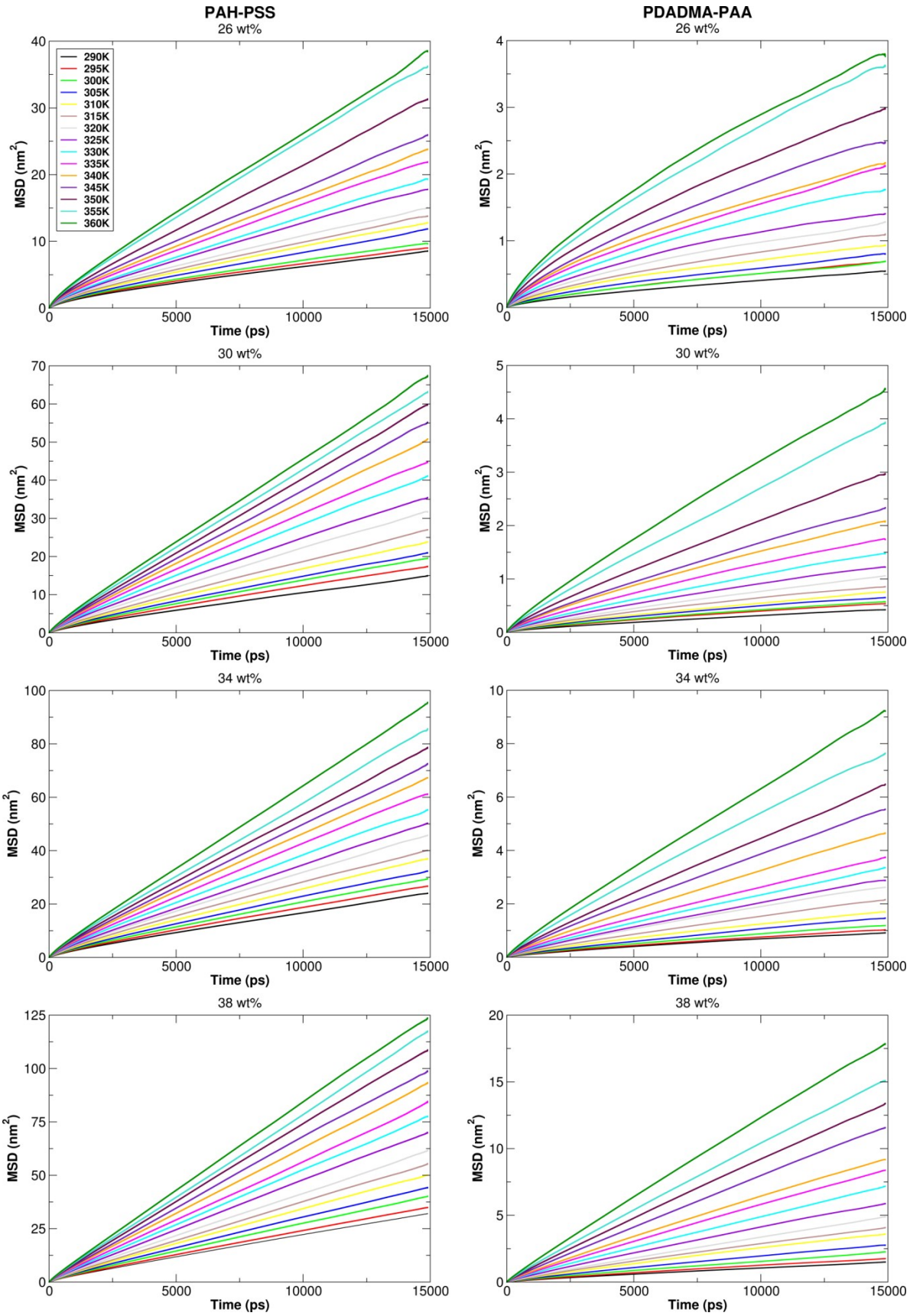
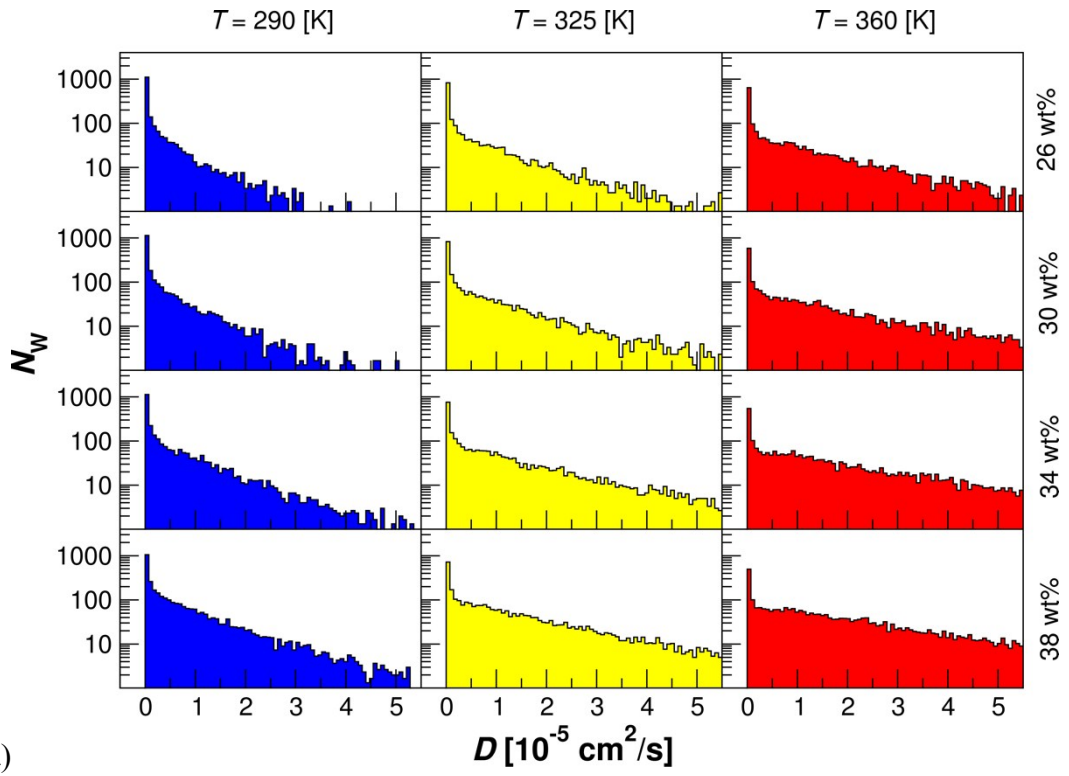
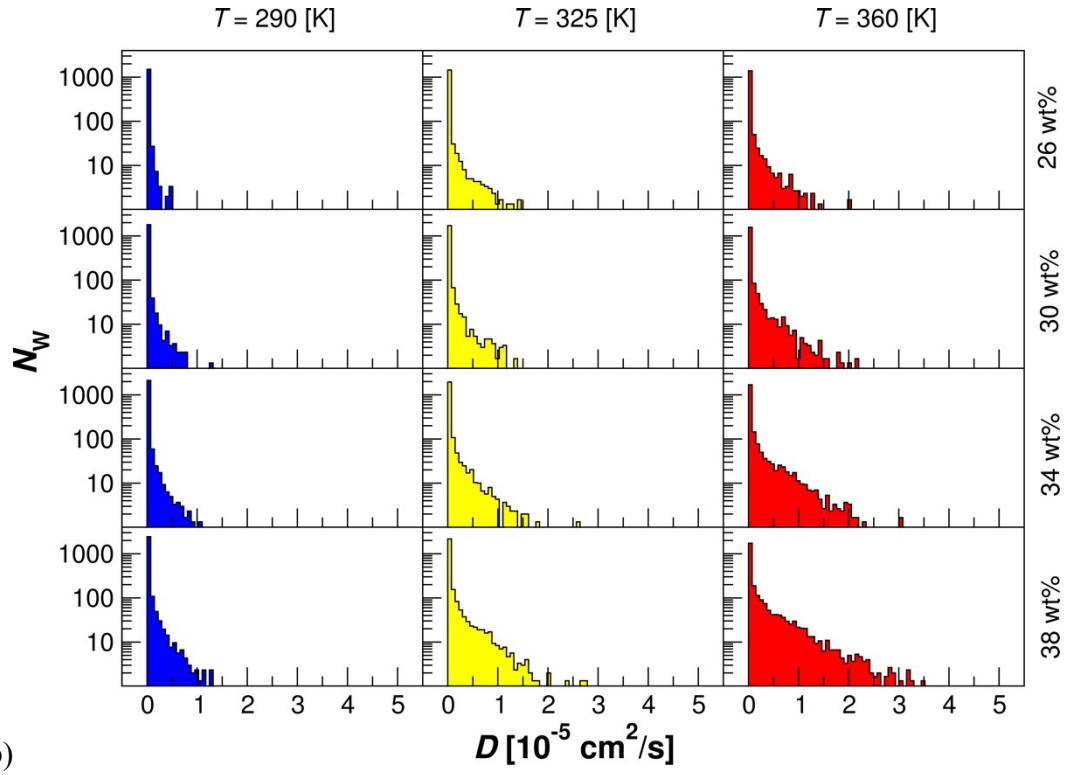


Figure S1. Mean square displacement as a function of the simulation time for the PAH-PSS and PDADMA-PAA PECs at different water contents and temperatures. The temperature legend applies to all graphs.



(a)



(b)

Figure S2. Individual water molecule diffusion coefficients as population frequency histograms for the **(a)** PAH-PSS and **(b)** PDADMA-PAA PECs at different water contents and temperatures. The data corresponds to the average from three different initial configurations and is calculated over a period of 20 ps.

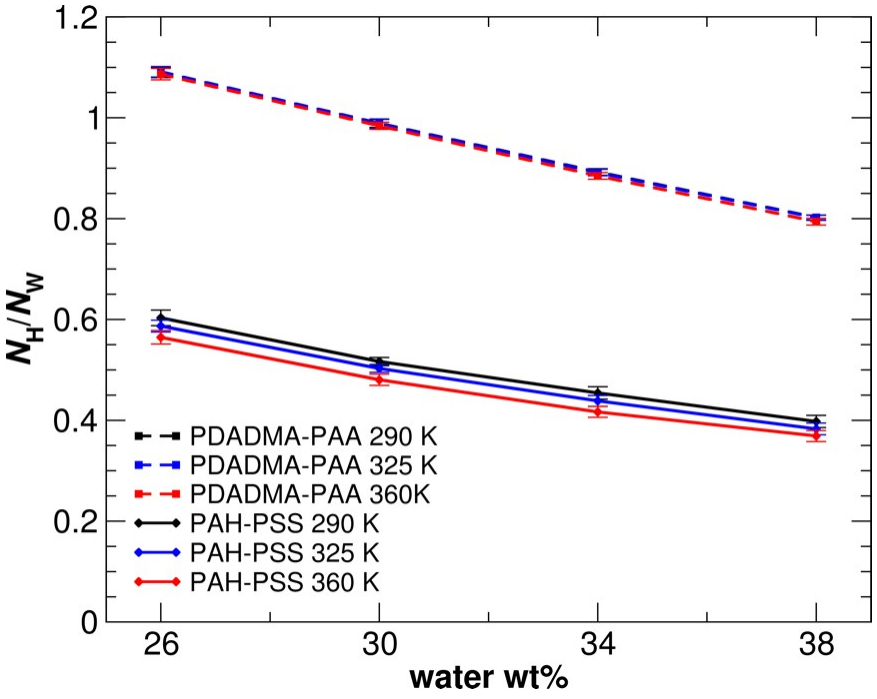
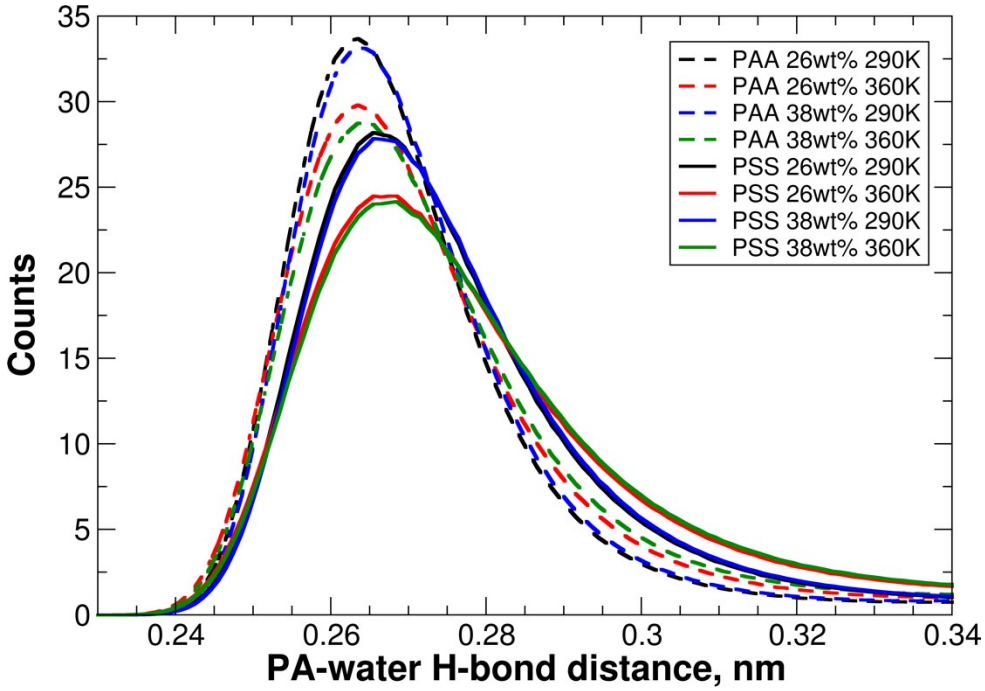
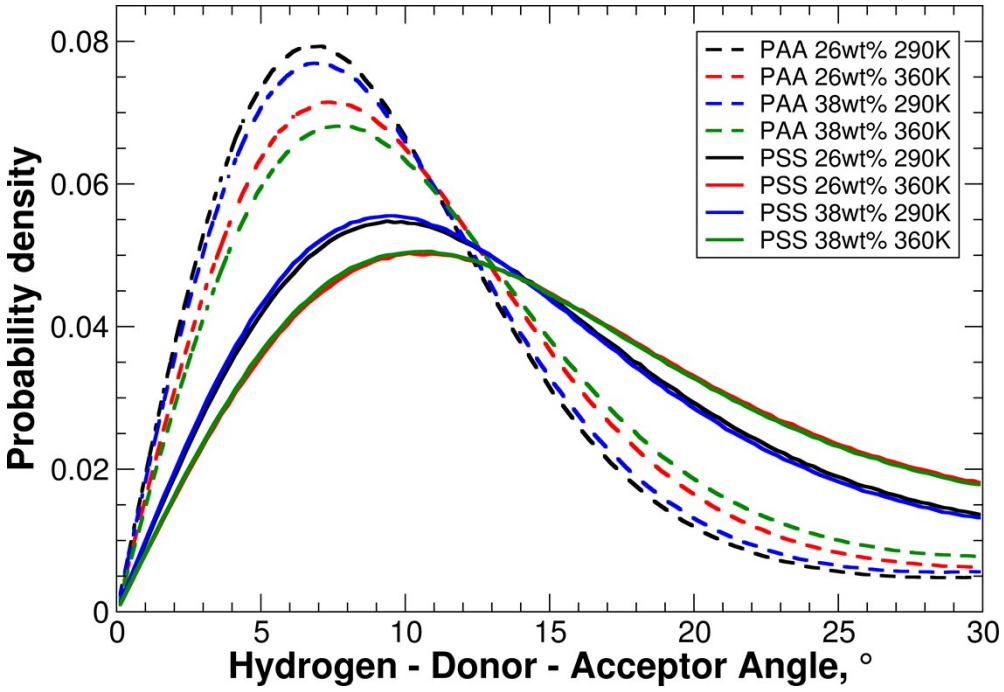


Figure S3. The number of H-bonds (N_H), between the polyanion and water, per number of water molecules (N_W) as a function of the PEC type, temperature, and water wt%.



(a)



(b)

Figure S4. (a) The distance and (b) angle distribution of H-bonds between the polyanion and water as a function of the temperature, and water wt% in PDADMA-PAA and PAH-PSS PECs.

(a) (b)

Figure S5. Photographs of (a) PAH-PSS and (b) PDADMA-PAA precipitates.