Supporting Information

Ion Distribution In Dry Polyelectrolyte Multilayers: A Neutron Reflectometry Study

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Table S1. Comparison between fit parameters employed by Lösche et al., reference 30, and this study. The multilayer employed by Lösche et al. was more complex, with deuterated PSS layers interspersed with protiated PSS layers. The main purpose of the Lösche study was to analyze the layering architecture within a multilayer.

Parameter	Lösche study	This study	Comments
H_2O volume	known	n/a	dry film
D_2O volume	known	n/a	dry film
Na^+ volume	known	n/a	no Na^+ present (measured)
Cl^- volume	known	known	PDADMA/acetate density measured
total film thickness	fit	fit	
PSS layer thickness	fit	n/a	PDADMA and PSS intermixed
PAH layer thickness	fit	n/a	PDADMA and PSS intermixed
PSS monomer volume	fit	known	density of PSS/PDADMA measured
PAH monomer volume	fit	known (here, PDADMA)	density of PSS/PDADMA measured
H_2O per PSS monomer	fit	n/a	dry film
H_2O per PAH monomer	fit	n/a	dry film
water void volume	fit	n/a	dry film
Na^+/Cl^- per monomer	fit	known	measured with radiochemistry
substrate roughness	fit (constant)	fit (constant)	
interface roughness	fit	fit	
SiO_2 thickness	fit	fit	

Calculating overcompensation

Samples F3, F4 and F5: To obtain the overcompensation values for samples F3, F4 and F5 in this experiment (shown in Table 2), equation 1 was used. Since all three samples are obtained from samples F1 and F2 (see Scheme 4) by adding PDADMA for 5 min (sample F3) or 2 h (samples F4 and F5), the amounts of intrinsic sites were calculated from the thickness obtained in the neutron reflectometry analysis (Table 3). Specifically, 320.5 Å for $(PDADMA/PSS)_6$ and 745.8 Å for $(PDADMA/PSS)_{10}$* were converted to 131 and 306 μmol m^{-2} respectively. The excess PDADMA* amounts obtained by sulfate radiolabeling are divided by the intrinsic amounts to yield 25, 44 and 40% respectively (Table 2).

Sample F6: Obtaining the overcompensation value is performed indirectly through a multi-step procedure. Since the accumulation of sites in this film happens progressively at the addition of its PDADMA layers, there is no clear intrinsic thickness (and therefore quantity) to compare the excess to. Instead, the ionic content value obtained from the radiolabeling experiment (107 μmoles m^{-2}, Table 2) is converted to a thickness of extrinsic sites ($t_{extrinsic}$) using the measured PDADMA:acetate density. From the analysis of samples F3 – F5, the extrinsic sites are not expected to be located exclusively within a slab, but this serves as an approximation to calculate the overcompensation value. The thickness of the PEMU occupied by intrinsic sites (PDADMA:PSS) is represented by $t_{intrinsic}$ and can be obtained using:

$$t_{intrinsic} = t_{total} - t_{extrinsic} \quad \text{(S1)}$$

where t_{total} is the total thickness of the films obtained using ellipsometry under dry conditions (see Table S2 below). Using the molecular weight (309.4 g mol^{-1}) and density (1.27 g mol^{-1}) of PDADMA:PSS unit, $t_{intrinsic}$ was converted to the amount of PDADMA:PSS per surface area expressed in μmol m^{-2}. Knowing the amount of intrinsic and extrinsic sites, the percent of overcompensation was calculated using equation S1 above to be 39% (Table 2).

Samples F7 and F8: A similar procedure to Sample F6 was employed.

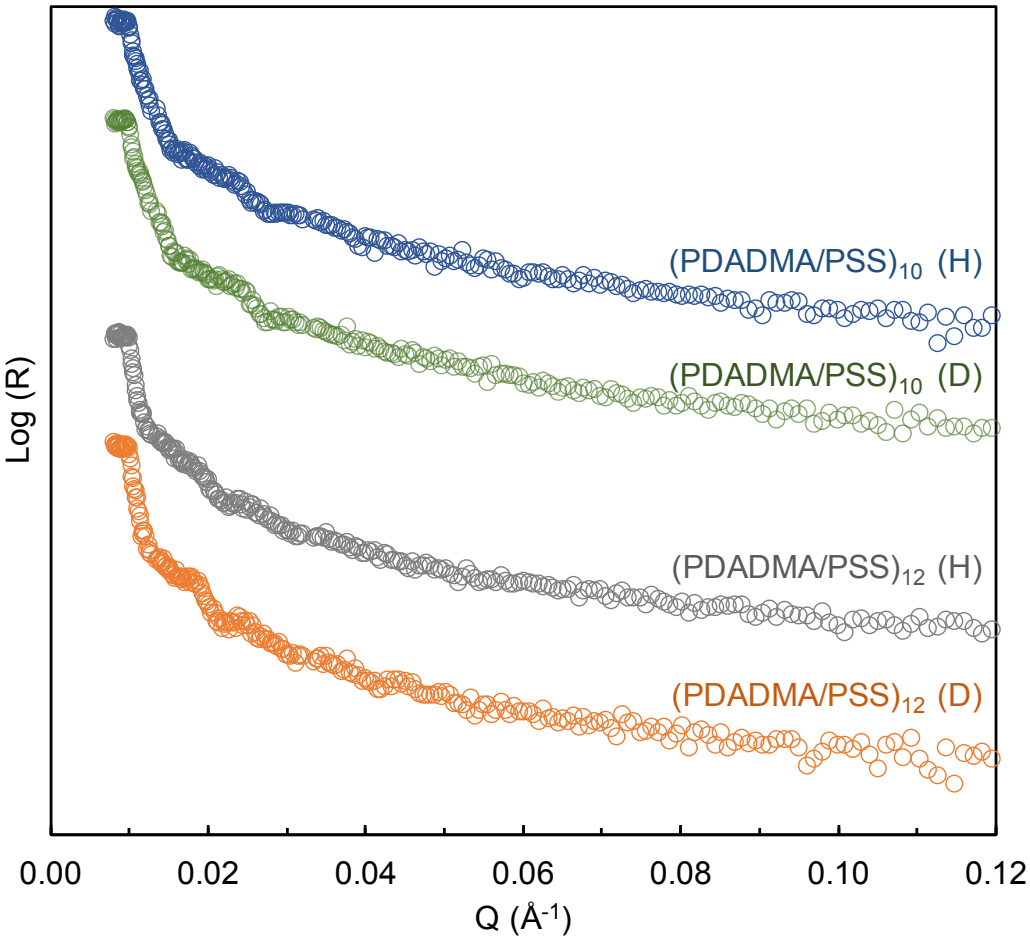

Figure S1. Neutron reflectivity profiles of PSS-capped $(PDADMA/PSS)_{10}$ (Sample F7) and $(PDADMA/PSS)_{12}$ (Sample F8) PEMUs with CH_3COO^- (H, hydrogen) and CD_3COO^- (D, deuterium).

Table S2. Ambient (in air) and dry (under nitrogen) thicknesses of films measured by ellipsometry.

Film	Sample	t_{air} (Å)	t_{dry} (Å)
F1	$(PDADMA/PSS)_6$	380	340
F2	$(PDADMA/PSS)_{10}$*	800	680
F3	$(PDADMA/PSS)_{10}$*$PDADMA_{5min}$	950	780
F4	$(PDADMA/PSS)_{10}$*$PDADMA_{2h}$	870	710
F5	$(PDADMA/PSS)_6PDADMA_{2h}$	380	340
F6	$(PDADMA/PSS)_{10}PDADMA_{5min}$	1000	860

Table S3. Atomic composition of polyelectrolyte multilayers. The composition was determined using sulfate radiolabeling and thicknesses obtained by ellipsometry directly (samples F1, F2) or indirectly (samples F3, F4, F5, and F6).

	Sample	C	H	O	N	S	D
F1	$(PDADMA/PSS)_6$ (H)	16.00	23.00	3.00	1.00	1.00	-
F1	$(PDADMA/PSS)_6$ (D)	16.00	23.00	3.00	1.00	1.00	-
F2	$(PDADMA/PSS)_{10}$* (H)	16.00	23.00	3.00	1.00	1.00	-
F2	$(PDADMA/PSS)_{10}$* (D)	16.00	23.00	3.00	1.00	1.00	-
F3	$(PDADMA/PSS)_{10}$*$PDADMA_{5min}$ (H)	18.50	27.75	3.50	1.25	1.00	-
F3	$(PDADMA/PSS)_{10}$*$PDADMA_{5min}$ (D)	18.50	27.00	3.50	1.25	1.00	0.75
F4	$(PDADMA/PSS)_{10}$*$PDADMA_{2h}$ (H)	20.40	31.36	3.88	1.44	1.00	-
F4	$(PDADMA/PSS)_{10}$*$PDADMA_{2h}$ (D)	20.40	30.04	3.88	1.44	1.00	1.32
F5	$(PDADMA/PSS)_6PDADMA_{2h}$ (H)	20.00	30.60	3.80	1.40	1.00	-
F5	$(PDADMA/PSS)_6PDADMA_{2h}$ (D)	20.00	29.40	3.80	1.40	1.00	1.20
F6	$(PDADMA/PSS)_{10}PDADMA_{5min}$ (H)	19.90	30.41	3.78	1.39	1.00	-
F6	$(PDADMA/PSS)_{10}PDADMA_{5min}$ (D)	19.90	29.24	3.78	1.39	1.00	1.17

*represents cycling in 2.0 M NaCl and 10 mM PSS in 0.5 M NaCl.

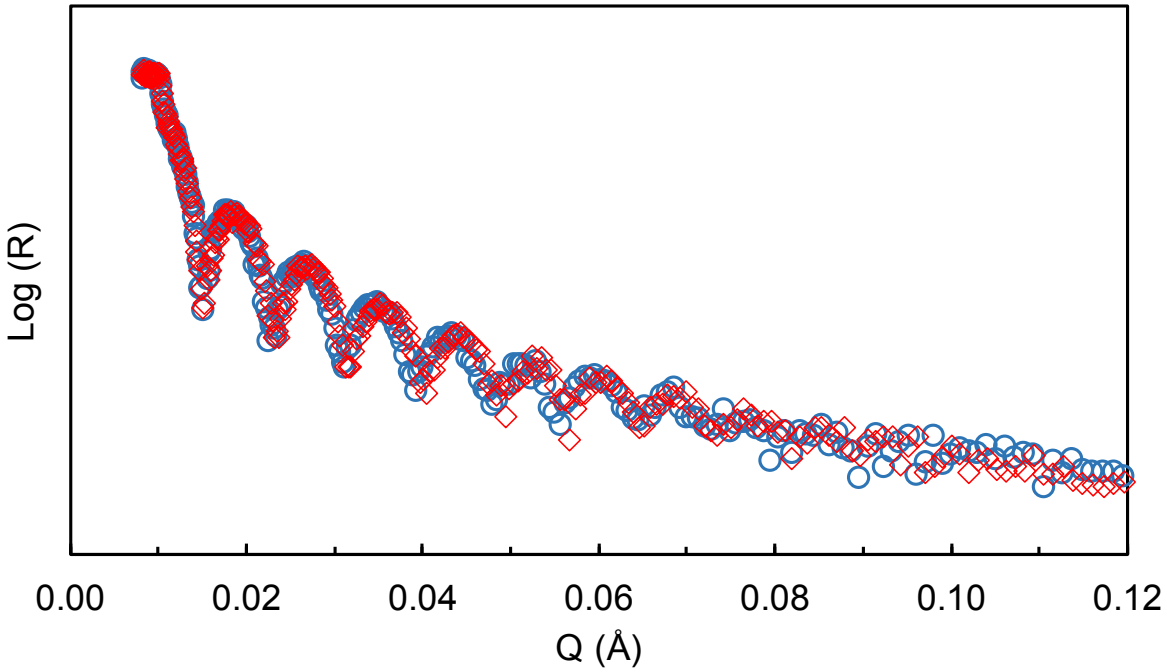

Figure S2. Neutron reflectivity profiles of $(PDADMA/PSS)_{10}^{*}$ (H) after 30 min and 4 h in vacuum. After 30 min: blue circles, and 4 h: red diamonds.

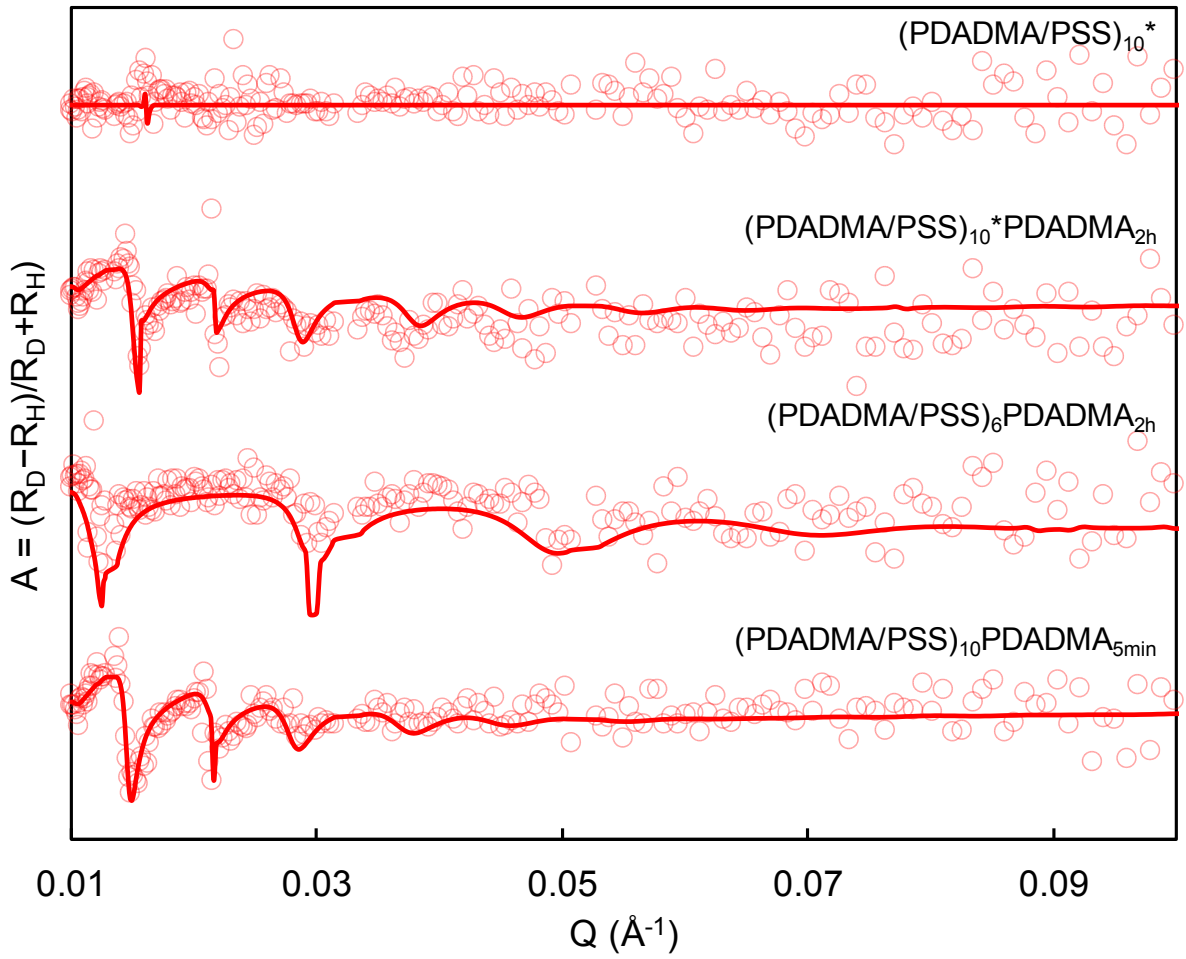

Figure S3. Asymmetry reflectivity profiles (markers) and fits (solid line) of $(PDADMA/PSS)_{10}$* (F2), $(PDADMA/PSS)_{10}$*$PDADMA_{2h}$ (F4), $(PDADMA/PSS)_6PDADMA_{2h}$ (F5), and $(PDADMA/PSS)_{10}PDADMA_{5min}$ (F6).

Table S4. Percent overcompensation (OC) and atomic composition of the upper slab only of overcharged films. The composition was determined using sulfate radiolabeling and half of the thicknesses obtained by ellipsometry directly (samples F1, F2) or indirectly (samples F3, F4, F5, and F6).

Film	Ion[a]	%OC[b]	C	H	O	N	S	D
F3	H	50	21.00	32.50	4.00	1.50	1.00	-
F3	D	50	21.00	31.00	4.00	1.50	1.00	1.50
F4	H	87	24.70	39.53	4.74	1.87	1.00	-
F4	D	87	24.70	36.92	4.74	1.87	1.00	2.61
F5	H	79	23.90	38.01	4.58	1.79	1.00	-
F5	D	79	23.90	35.64	4.58	1.79	1.00	2.37
F6	H	78	23.80	37.82	4.56	1.78	1.00	-
F6	D	78	23.80	35.48	4.56	1.78	1.00	2.34

*****represents cycling in 2.0 M NaCl and 10 mM PSS in 0.5 M NaCl.
[a]H: CH_3COO^-; D: CD_3COO^-.
[b]Percent overcompensation **only in the upper slab**.

Table S5. 50-50 fits parameters. Parameters, including the fraction of slab thicknesses, used to fit the NR data with the total amount of ions concentrated in the upper 50% of the material.

F.	Film slab	Ion[a]	Nb ($\times 10^{-6}$) (Å^{-2})	Density (g cm^{-3})	Calc. thick. (Å)[b]	Rough. (Å)	SiO_x thick. and rough. (Å)[c]	χ_H^2 of film	χ_D^2 of film	χ_{asym}^2	χ_{tot}^2
F3	Upper	H	1.14	1.20	449.8	149.7	1.8	17.99	37.13	5.43	20.18
		D	1.43								
	Lower	both	1.23	1.27	330.2	75.0					
F4	Upper	H	0.98	1.17	440.0	142.9	3.3	22.99	50.10	12.61	28.57
		D	1.43								
	Lower	both	1.23	1.27	270.0	71.0					
F5	Upper	H	1.03	1.17	207.8	107.5	7.5	7.26	5.50	6.90	6.56
		D	1.34								
	Lower	both	1.23	1.27	132.2	54.0					
F6	Upper	H	1.03	1.17	524.7	131.5	12.4	5.75	5.38	8.84	6.66
		D	1.40								
	Lower	both	1.23	1.27	335.3	66.0					

F. = Film.
[a]H: CH_3COO^-; D: CD_3COO^-.
[b]To obtain the calculated thickness:

- The excess molar volume ratio of exess (PDADMA/acetate) to the PEC (PDADMA/PSS) was calculated in the upper slab using the following equation:

$$\left(\frac{M_{PDADMA/acetate} \div density_{PDADMA/acetate}}{M_{PEC} \div density_{PEC}}\right) \times overcompensation\ fraction$$

with M_{PEC} = 309 g mol^{-1}, $M_{PDADMA/acetate}$ = 185 g mol^{-1}, d_{PEC} = 1.27 g cm^{-3}, $d_{PDADMA/acetate}$ = 1.05 g cm^{-3}, and the overcompensation fraction taken from Table S4 above.

- This ratio of excess was used as the thickness excess which was used to calculate the fraction of the upper versus lower slabs.
- The thicknesses of the upper versus lower slabs were calculated by multiplying the fractions by the dry ellipsometric thickness found in Table S2 above.

[c]Si roughness was the same as that of SiO_x. Si thickness was fixed at 100 Å.

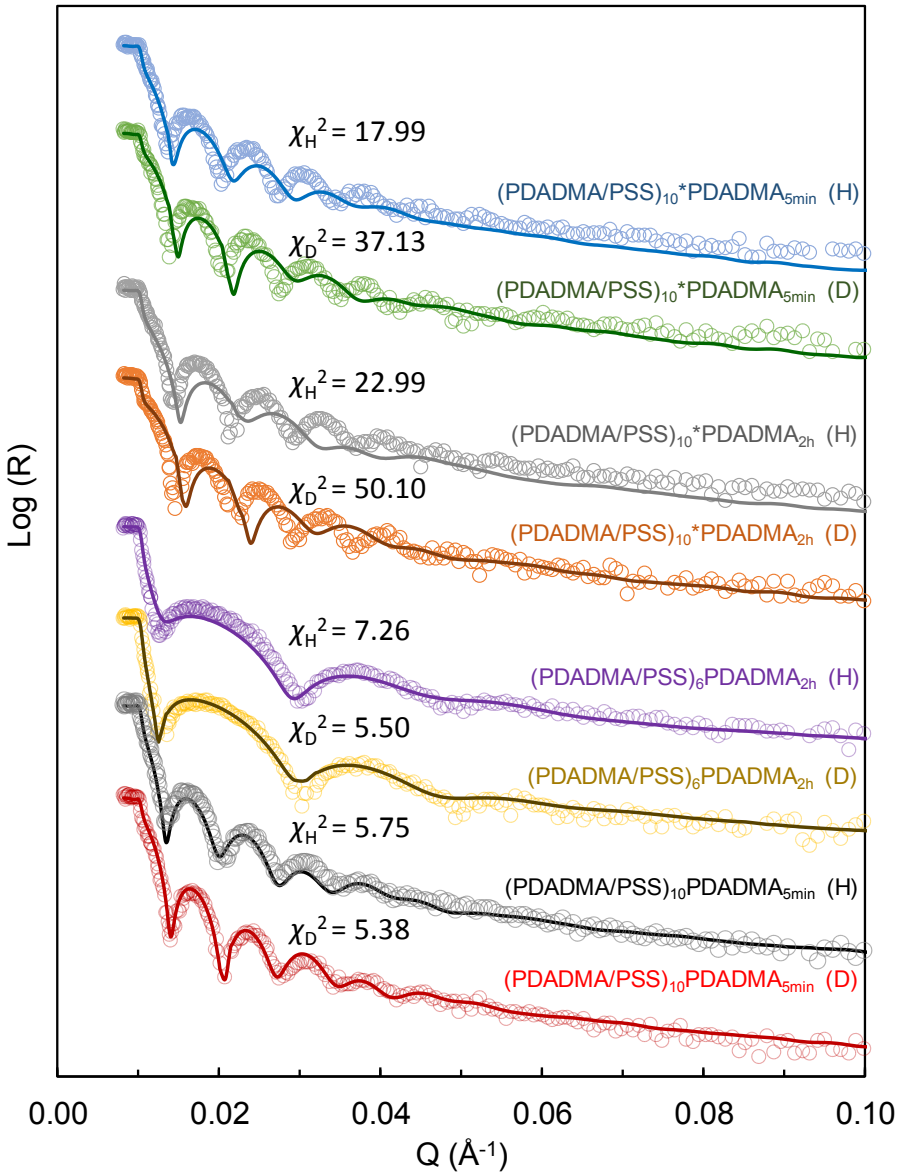

Figure S4. 50-50 slabs plots. A) Neutron reflectivity profiles (symbols) and fits (solid lines) of samples F3, F4, F5, and F6 labeled and analyzed in CH_3COO^- and CD_3COO^- respectively. Fits were based on concentrating all the excess ions in the top 50% of the film material.

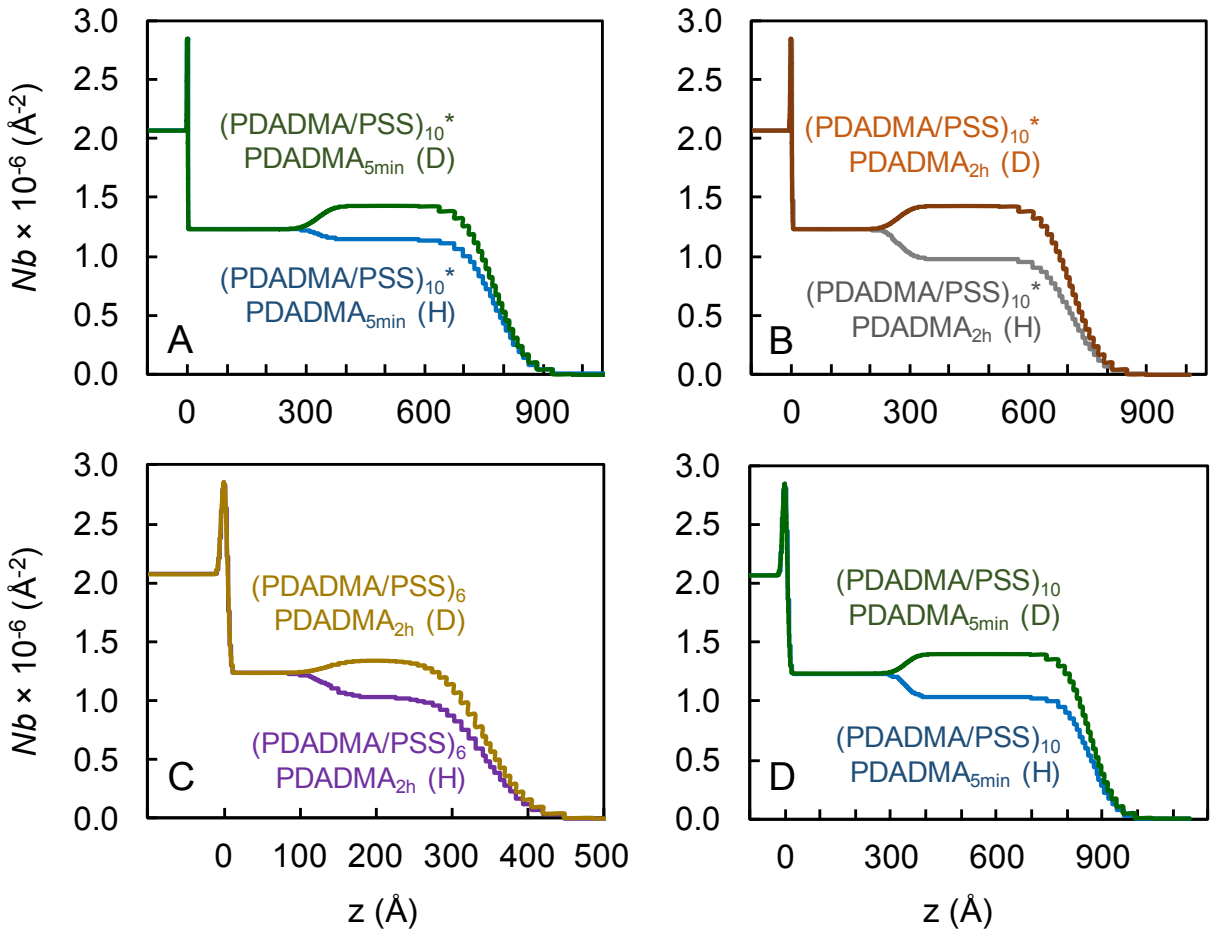

Figure S5. Scattering length density profiles for the 50-50 fits of A) F3, B) F4, C) F5 and D) F6 from the fits in Figure S4. The χ^2 values are shown on the plots in Figure S4 and in Table S5.