Supporting Information for the Manuscript:

Nonlinear Layer-by-Layer Films: Effects of Chain Diffusivity on Film Structure and Swelling

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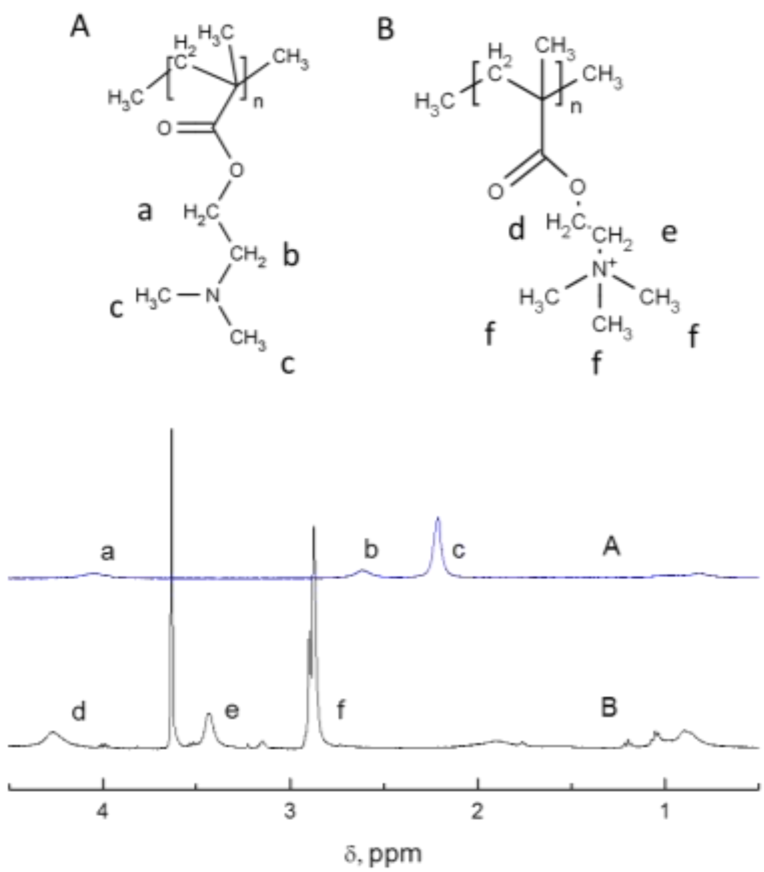

Fig. S1. ^{1}H-NMR spectra of *h*PDMAEMA before quaternization (A) and after complete quaternization and conversion to *h*QPC (B) measured in D_2O at pH 9.

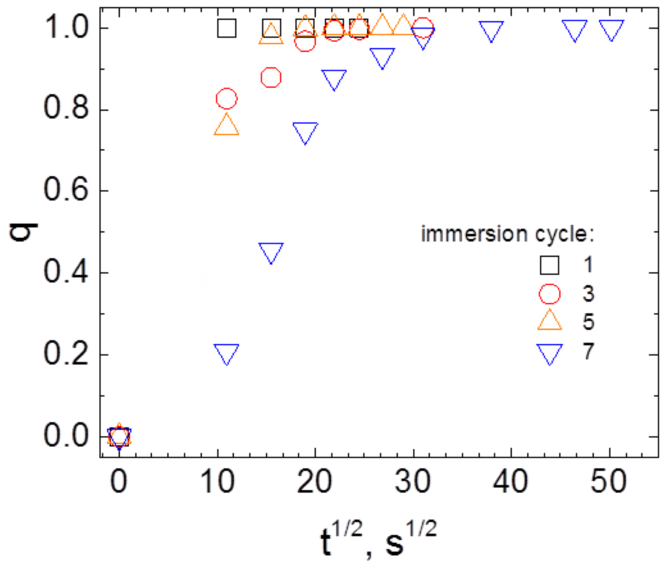

Fig S2. The kinetics of PMAA uptake by the film during 1st, 3rd, 5th and 7th layer deposition steps.

Table S1. Model parameters for $(PMAA/QPC)_4(dPMAA/QPC)(PMAA/QPC)_4$ film constructed using a 4 min per layer deposition time.

Layer	***Nb*** **(Å^{-2})**	***d*** **(Å)**	$\boldsymbol{\sigma_{int}}$ **(Å)**
H-stack	6.430E-07	457.0	47.6
d-stack	2.330E-06	143.4	66.8
H-stack	6.430E-07	478.3	57.2
BPEI	2.500E-07	29.8	29.8
SiO2	3.200E-06	18.0	5.0
Si	2.070E-06	100.0	5.0

Table S2. Model parameters for $(PMAA/QPC)_4$(QPC/dPMAA)$(PMAA/QPC)_4$ film constructed using a 8 min per layer deposition time.

Layer	***Nb*** **(Å^{-2})**	***d*** **(Å)**	σ_{int} **(Å)**
H-stack	6.430E-07	477.4	139.0
D-stack	2.405E-06	260.0	166.0
H-stack	6.443E-07	404.0	118.8
BPEI	2.500E-07	75.0	75.0
SiO2	3.200E-06	18.0	5.0
Si	2.070E-06	100.0	5.0

Table S3. Model parameters for $(PMAA/QPC)_3$ (dPMAA/QPC)$(PMAA/QPC)_2$ film constructed using a 24 min per layer deposition time.

Layer	***Nb*** **(Å^{-2})**	***d*** **(Å)**	σ_{int} **(Å)**
H-stack	6.430E-07	206.8	89.9
D-stack	2.136E-06	351.9	119.9
H-stack	6.430E-07	328.2	93.7
BPEI	2.500E-07	24.1	24.1
SiO2	3.200E-06	19.5	5.0
Si	2.070E-06	100.0	5.0

Table S4. Model parameters for $(PMAA/QPC)_4$(PMAA/dQPC)$(PMAA/QPC)_4$ film constructed using a 4 min per layer deposition time.

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Layer	***Nb*** **(Å^{-2})**	***d*** **(Å)**	σ_{int} **(Å)**
H-stack	6.430E-07	471.5	241.4
d-stack	2.260E-06	167.4	127.9
H-stack	6.430E-07	281.7	113.5
BPEI	2.500E-07	20.7	20.7
SiO2	3.200E-06	39.9	5.0
Si	2.070E-06	100.0	8.0

Table S5. Model parameters for $(PMAA/QPC)_4(PMAA/dQPC)(PMAA/QPC)_4$ film constructed using a 8 min per layer deposition time.

Layer	***Nb*** **(Å^{-2})**	***d*** **(Å)**	**σ_{int} (Å)**
H-stack	6.430E-07	753.3	80.8
d-stack	2.522E-06	266.1	158.0
H-stack	6.430E-07	368.6	165.3
BPEI	4.850E-07	48.0	17.6
SiO2	3.200E-06	19.0	3.0
Si	2.070E-06	100.0	3.0

Table S6. Model parameters for $(PMAA/QPC)_3(PMAA/dQPC)(PMAA/QPC)_2$ film constructed using a 24 min per layer deposition time.

Layer	***Nb*** **(Å^{-2})**	***d*** **(Å)**	**σ_{int} (Å)**
H-stack	6.430E-07	162.9	162.9
d-stack	2.080E-06	905.9	160.0
H-stack	6.430E-07	25.5	25.5
BPEI	1.100E-07	85.4	85
SiO2	3.200E-06	33.6	3.0
Si	2.070E-06	100.0	3.0

Table S7. Model parameters for $(PMAA/QPC)_4(PMAA/dQPC)(PMAA/QPC)_4$ film constructed using a 8 min per layer deposition time after 30 min exposure to a 0.01 M phosphate buffer.

Layer	***Nb*** **(Å^{-2})**	***d*** **(Å)**	**σ_{int} (Å)**
H-stack	6.430E-07	753.3	80.8
d-stack	2.522E-06	266.0	148.4
H-stack	6.430E-07	382.4	165.3
BPEI	4.850E-07	48.0	17.6
SiO2	3.200E-06	19.0	3.0
Si	2.070E-06	100.0	3.0

Table S8. Model parameters for $(PMAA/QPC)_4$(dPMAA/QPC)$(PMAA/QPC)_4$ film constructed using a 8 min per layer deposition time after 30 min exposure to a 0.01 M phosphate buffer.

Layer	***Nb*** **(Å^{-2})**	***d*** **(Å)**	**σ_{int} (Å)**
H-stack	6.430E-07	477.0	159.0
d-stack	2.405E-06	260.0	160.0
H-stack	6.443E-07	410.0	125.0
BPEI	2.500E-07	75.0	75.0
SiO2	3.200E-06	18.0	5.0
Si	2.070E-06	100.0	5.0

Table S9. Model parameters for $(PMAA/QPC)_4$(PMAA/dQPC)$(PMAA/QPC)_4$ film constructed using a 8 min per layer deposition time after 210 min exposure to a 0.01 M phosphate buffer.

Layer	***Nb*** **(Å^{-2})**	***d*** **(Å)**	**σ_{int} (Å)**
H-stack	6.430E-07	753.3	78.0
d-stack	2.522E-06	266.0	167.0
H-stack	6.430E-07	366.7	165.3
BPEI	4.850E-07	48.0	17.6
SiO2	3.200E-06	19.0	3.0
Si	2.070E-06	100.0	3.0

Table S10. Model parameters for $(PMAA/QPC)_4$(dPMAA/QPC)$(PMAA/QPC)_4$ film constructed using a 8 min per layer deposition time after 210 min exposure to a 0.01 M phosphate buffer.

Layer	***Nb*** **(Å^{-2})**	***d*** **(Å)**	**σ_{int} (Å)**
H-stack	6.430E-07	477.0	159.0
d-stack	2.405E-06	260.0	145.0
H-stack	6.443E-07	410.0	125.0
BPEI	2.500E-07	75.0	75.0
SiO2	3.200E-06	18.0	5.0
Si	2.070E-06	100.0	5.0

Table S11. Model parameters for hydrogenated $(PMAA/QPC)_6$ film constructed using a 8 min per layer deposition time.

Layer	*Nb* (Å^{-2})	*d* (Å)	σ_{int} (Å)
H-Block	6.430E-07	1002.0	120.0
BPEI	3.790E-07	28.0	5.0
SiO2	3.200E-06	19.0	10.0
Si	2.070E-06	100.0	19.0

Table S12. Model parameters for hydrogenated $(PMAA/QPC)_6$ film constructed using a 8 min per layer deposition time after 4 min exposure to a 0.2 mg/ml dQPC solution.

Layer	*Nb* (Å^{-2})	*d* (Å)	σ_{int} (Å)
D-block	7.000E-07	430.5	85.0
H-block	6.430E-07	556.6	180.0
BPEI	4.500E-07	73.5	62.5
SiO2	3.400E-06	16.0	5.0
Si	2.070E-06	100.0	5.0

Table S13. Model parameters for hydrogenated $(PMAA/QPC)_6$ film constructed using a 8 min per layer deposition time after 8 min exposure to a 0.2 mg/ml dQPC solution.

Layer	*Nb* (Å^{-2})	*d* (Å)	σ_{int} (Å)
D-block	8.000E-07	589.7	100.8
H-block	6.430E-07	419.7	177.7
BPEI	5.000E-07	67.9	67.0
SiO2	3.400E-06	16.0	5.0
Si	2.070E-06	100.0	5.0

Table S14. Model parameters for hydrogenated $(PMAA/QPC)_6$ film constructed using a 8 min per layer deposition time after 24 min exposure to a 0.2 mg/ml dQPC solution.

Layer	***Nb*** **(Å^{-2})**	***d*** **(Å)**	**σ_{int} (Å)**
D-block	1.080E-06	660.0	155.0
H-block	6.430E-07	352.0	325.9
BPEI	2.700E-07	75.0	62.5
SiO2	3.400E-06	16.0	5.0
Si	2.070E-06	100.0	5.0

Table S15. Model parameters for hydrogenated $(PMAA/QPC)_6$ film constructed using a 8 min per layer deposition time after 48 min exposure to a 0.2 mg/ml dQPC solution.

Layer	***Nb*** **(Å^{-2})**	***d*** **(Å)**	**σ_{int} (Å)**
D-block	1.490E-06	1027.0	192.4
H-block	6.430E-07	68.8	88.6
BPEI	2.700E-07	75.0	62.5
SiO2	3.400E-06	16.0	5.0
Si	2.070E-06	100.0	5.0

Table S16. Model parameters for hydrogenated $(PMAA/QPC)_6$ film constructed using a 8 min per layer deposition time after 96 min exposure to a 0.2 mg/ml dQPC solution.

Layer	***Nb*** **(Å^{-2})**	***d*** **(Å)**	**σ_{int} (Å)**
D-block	1.500E-06	1048.0	201.4
H-block	6.430E-07	75.0	64.2
BPEI	2.390E-07	75.0	62.5
SiO2	3.400E-06	16.0	5.0
Si	2.070E-06	100.0	5.0

Table 17. Model parameters for hydrogenated $(PMAA/QPC)_6$ film constructed using a 8 min per layer deposition time after 192 min exposure to a 0.2 mg/ml dQPC solution.

Layer	***Nb*** **(Å^{-2})**	***d*** **(Å)**	**σ_{int} (Å)**
D-block	1.642E-06	1102.0	202.0
H-block	6.430E-07	69.4	69.4
BPEI	2.390E-07	75.0	62.5
SiO2	3.400E-06	16.0	5.0
Si	2.070E-06	100.0	5.0

Table S18. SLD values calculated for the PEM components.

	QPC	PMAA	QPC	dPMAA	dQPC	PMAA	H_2O
SLD, Å^{-2}	4.71E-07	1.10E-06	4.71E-07	5.11E-06	6.36E-06	1.10E-06	-5.60E-07

Table S19. Mass ratios calculated for the corresponding SLD values.

Exposure time, min	QPC mass ratio	PMAA mass ratio	dQPC mass ratio	Water content	SLD of D-containing block, Å^{-2}
0	0.460	0.439	0.000	0.101	6.43E-07
4	0.458	0.431	0.010	0.101	7.00E-07
8	0.451	0.424	0.023	0.101	7.70E-07
24	0.436	0.414	0.049	0.101	9.12E-07
48	0.417	0.363	0.118	0.101	1.29E-06
96	0.383	0.361	0.154	0.101	1.50E-06
192	0.364	0.356	0.178	0.101	1.64E-06
394	0.361	0.333	0.205	0.101	1.78E-06