Supporting Information for the Manuscript:

Molecular Weight Dependence of Polymer Chain Mobility within Multilayer Films

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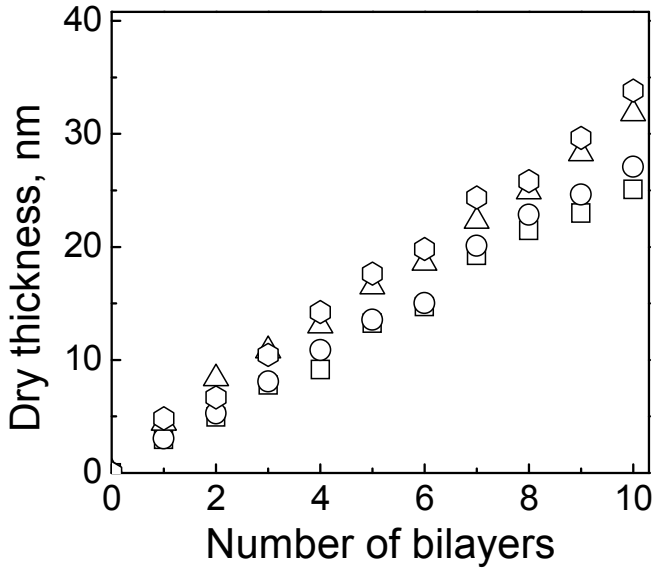

Figure S1. Ellipsometric thickness of PC/PMAA multilayers as a function of bilayer number for $PMAA_{7k}$ (squares), $PMAA_{25k}$ (circles), $PMAA_{110k}$ (triangles) and $PMAA_{480k}$ (hexagons). M_w of PC is 30 kDa. The deposition of the films was carried out in 0.01 M pH 4.5 phosphate buffer solutions at 25 °C.

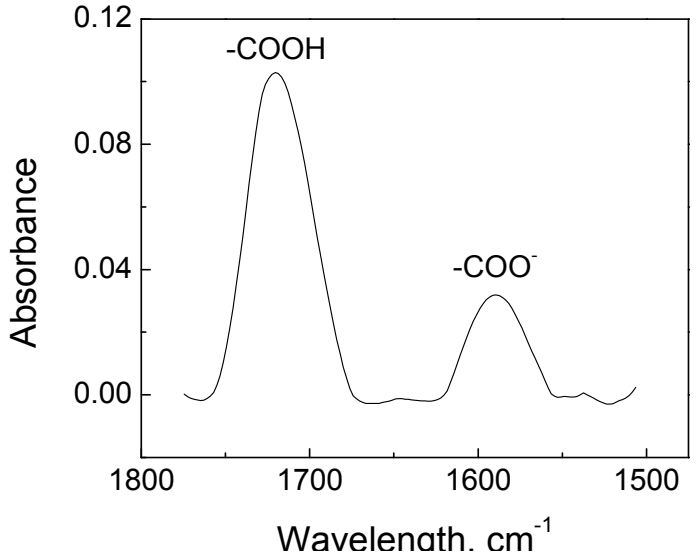

Figure S2. A representative FTIR spectrum of a 50-bilayer PC/PMAA$_{110k}$ multilayer film deposited in 0.01 M pH 4.5 phosphate buffer solutions at 25 °C. Ionization degree of PMAA, calculated as described elsewhere,[1] was 27%.

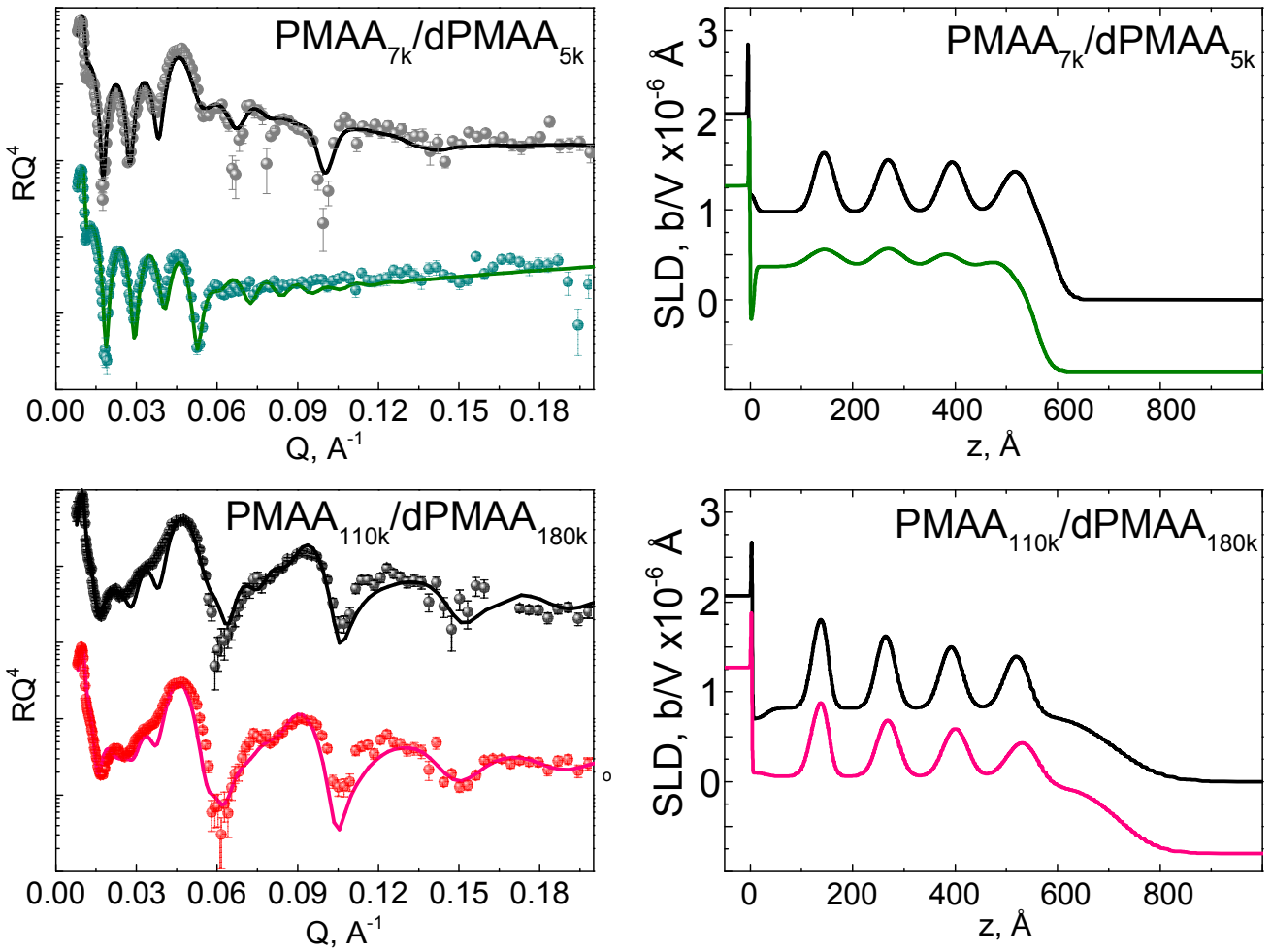

Figure S3. Neutron reflectivity data (plotted as R×Q4 to enhance small features) (left) and corresponding fitted scattering length density profiles (right) for dry $[(PC/PMAA)_4/(PC/dPMAA)]_4/(PC/PMAA)_4$ PEMs for $PMAA_{7k}/dPMAA_{5k}$ and $PMAA_{110k}/dPMAA_{180k}$ samples, after annealing for 54 h in 0.01 M phosphate buffer with no-salt and in 0.6 M NaCl solutions (indicated as black and colored symbols and lines, respectively).

Table S1. Average values and standard deviations for dry ellipsometric thicknesses of bilayers within PC/PMAA films.

Multilayer films	PC/PMAA			
M_w of PMAA	7,000	25,000	110,000	480,000
$d_{bilayer}$ (nm)	2.5 ± 0.2	2.7 ± 0.3	3.2 ± 0.3	3.3 ± 0.3

Table S2. Average lateral diffusion coefficients $D_{//}$ and standard deviations for PMAA*s within PC/PMAA PEMs obtained from FRAP results in Fig. 1.

C_{NaCl}	$D_{//}$ of PMAA* ($\times 10^{-15}$ cm^2/s)			
	$PMAA_{7k}$	$PMAA_{25k}$	$PMAA_{110k}$	$PMAA_{480k}$
0.6 M	82.6 ± 15.0	27.7 ± 4.2	6.2 ± 0.9	1.5 ± 0.1

Table S3. Model parameters for a 24-bilayer PC/$PMAA_{7k}$ film with $dPMAA_{5k}$ in every 5th bilayer.

Layer	***Nb* (Å^{-2})**	***d* (Å)**	***σ* (Å)**
$(PC/PMAA)_4$	8.50E-07	50.0	50.0
dPMAA	1.58E-06	52.0	52.0
$(PC/PMAA)_4$	9.80E-07	76.0	50.0
dPMAA	1.66E-06	46.0	41.0
$(PC/PMAA)_4$	9.80E-07	80.5	41.0
dPMAA	1.71E-06	43.0	40.0
$(PC/PMAA)_4$	9.80E-07	84.5	40.0
dPMAA	1.80E-06	38.0	35.0

$(PC/PMAA)_4$	9.80E-07	115.0	35.0
BPEI	1.18E-06	13.0	13.0
SiO2	3.20E-06	2.0	2.0
Si	2.07E-06	100.0	2.0

Table S4. Model parameters for a 24-bilayer $PC/PMAA_{7k}$ film with $dPMAA_{5k}$ in every 5th bilayer after annealing in 0.6M NaCl for 54 hours.

Layer	***Nb* (Å^{-2})**	***d* (Å)**	***σ* (Å)**
$(PC/PMAA)_4$	9.00E-07	50.0	50.0
dPMAA	1.25E-06	52.0	52.0
$(PC/PMAA)_4$	1.10E-06	55.0	51.0
dPMAA	1.35E-06	51.0	51.0
$(PC/PMAA)_4$	1.10E-06	63.0	51.0
dPMAA	1.38E-06	51.0	51.0
$(PC/PMAA)_4$	1.15E-06	71.0	51.0
dPMAA	1.38E-06	51.0	51.0
$(PC/PMAA)_4$	1.20E-06	110.0	51.0
BPEI	5.50E-07	8.0	8.0
SiO2	3.20E-06	2.0	2.0
Si	2.07E-06	100.0	2.0

Table S5. Model parameters for a 24-bilayer $PC/PMAA_{25k}$ film with $dPMAA_{40k}$ in every 5th bilayer.

Layer	***Nb* (Å^{-2})**	***d* (Å)**	***σ* (Å)**
$(PC/PMAA)_4$	6.50E-07	160.0	160.0
dPMAA	1.50E-06	55.0	55.0

$(PC/PMAA)_4$	9.80E-07	81.5	55.0
dPMAA	1.68E-06	44.0	44.0
$(PC/PMAA)_4$	9.80E-07	89.5	44.0
dPMAA	1.79E-06	39.0	39.0
$(PC/PMAA)_4$	9.80E-07	94.5	39.0
dPMAA	1.94E-06	34.0	22.0
$(PC/PMAA)_4$	9.80E-07	89.0	34.0
BPEI	9.00E-07	40.0	34.0
SiO2	3.00E-06	5.0	2.0
Si	2.07E-06	100.0	2.0

Table S6. Model parameters for a 24-bilayer $PC/PMAA_{25k}$ film with $dPMAA_{40k}$ in every 5th bilayer after annealing in 0.6M NaCl for 84 hours.

Layer	***Nb* (Å^{-2})**	***d* (Å)**	***σ* (Å)**
$(PC/PMAA)_4$	8.50E-07	150.0	150.0
dPMAA	1.44E-06	60.0	55.0
$(PC/PMAA)_4$	1.00E-06	74.5	55.0
dPMAA	1.53E-06	53.0	53.0
$(PC/PMAA)_4$	1.00E-06	82.0	53.0
dPMAA	1.66E-06	45.0	45.0
$(PC/PMAA)_4$	1.00E-06	89.5	39.0
dPMAA	1.82E-06	38.0	34.0
$(PC/PMAA)_4$	1.00E-06	90.0	38.0
BPEI	9.00E-07	34.0	34.0
SiO2	3.00E-06	2.0	2.0
Si	2.07E-06	100.0	2.0

Table S7. Model parameters for a 24-bilayer PC/PMAA$_{110k}$ film with dPMAA$_{180k}$ in every 5th bilayer.

Layer	*Nb* (Å^{-2})	*d* (Å)	**σ (Å)**
(PC/PMAA)$_4$	7.50E-07	170.0	170.0
dPMAA	1.59E-06	45.0	45.0
(PC/PMAA)$_4$	8.20E-07	85.5	45.0
dPMAA	1.71E-06	40.0	40.0
(PC/PMAA)$_4$	8.20E-07	89.5	40.0
dPMAA	1.80E-06	37.0	37.0
(PC/PMAA)$_4$	8.20E-07	93.0	37.0
dPMAA	1.95E-06	33.0	22.0
(PC/PMAA)$_4$	8.20E-07	88.0	30.0
BPEI	7.00E-07	28.0	28.0
SiO2	3.00E-06	2.0	2.0
Si	2.07E-06	100.0	2.0

Table S8. Model parameters for a 24-bilayer PC/PMAA$_{110k}$ film with dPMAA$_{180k}$ in every 5th bilayer after annealing in 0.6M NaCl for 84 hours.

Layer	*Nb* (Å^{-2})	*d* (Å)	**σ (Å)**
(PC/PMAA)$_4$	7.50E-07	160.0	140.0
dPMAA	1.36E-06	55.0	55.0
(PC/PMAA)$_4$	8.60E-07	82.5	55.0
dPMAA	1.55E-06	44.0	44.0
(PC/PMAA)$_4$	8.60E-07	90.5	44.0
dPMAA	1.68E-06	39.0	39.0
(PC/PMAA)$_4$	8.60E-07	95.5	39.0
dPMAA	1.84E-06	34.0	24.0

$(PC/PMAA)_4$	8.60E-07	88.0	34.0
BPEI	9.00E-07	28.0	28.0
SiO2	3.00E-06	2.0	2.0
Si	2.07E-06	100.0	2.0

Preparation of Alexa Fluor® 488-labeled PMAA (PMAA*). Labeling of PMAA with Alexa Fluor® 488 was performed in 0.1 M phosphate buffer at pH 5 as described elsewhere.[2] 5 μL (6.34×10^{-4} mmol) of PMAA solution, 1 mg (5.20×10^{-3} mmol) of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride and 1.2 mg (5.50×10^{-3} mmol) of N-hydroxysulfosuccinimide sodium salt were mixed in 0.1 M phosphate buffer at pH 5. The solution was continuously stirred for one hour, followed by an addition of 25 μL (4.38×10^{-4} mmol) of Alexa Fluor® 488 dihydrazide in 0.1 M phosphate buffer at pH 5. The reaction was allowed to proceed overnight. The solution was then diluted with 0.1 M phosphate buffer solution at pH 7 and dialyzed against 0.01 M phosphate buffer at pH 7 with 0.1 M NaCl for 72 hours, and then against Milli-Q water for 48 hours. The molecular weight cutoff of the dialysis tubing was 5,000 for $PMAA_{7k}$ and 10,000 for $PMAA_{25k,}$ $PMAA_{110k}$ and $PMAA_{480k}$, respectively. The dialysis was terminated when no fluorescence was detected in the outer dialysis water (measured by fluorometry at excitation wavelength 488 nm).

Polymer Synthesis and Characterization. Poly(2-(dimethylamino)ethyl methacrylate) (PC) homopolymer was synthesized by atom transfer radical polymerization (ATRP) as previously described[3,4]. DMA, ethyl 2-bromoisobutyrate (EBiB), CuBr and 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) were mixed in 8 mL of 2-propanol, with a molar ratio of 150:1:1:2, respectively. The solution was stirred continuously in an argon atmosphere at room temperature for 12 h. The polymerization was terminated with liquid nitrogen and the solution diluted

with THF. The copper salts was purified by passage through a basic aluminum oxide column. The polymer was precipitated in cold hexane and then dried in a vacuum oven at 25 °C overnight. Gel permeation chromatography (GPC) study of PC was performed in THF with polystyrene (PS) as standard samples. M_w and PDI of PC homopolymer was determined as 30 kDa and 1.10, respectively. M_w of PC was also confirmed by ^{1}H-NMR result.

Fluorescence Recovery after Photobleaching. The effect of molecular weight on the diffusion coefficient of PMAA* within PC/PMAA multilayer films was determined using a homemade FRAP setup with design and optics described in earlier publications.[2,5,6]. Briefly, the 488 nm wavelength light beam from a Spectra-Physics Stabilite 2017 laser is spatially filtered and expanded three times, attenuated 100 times, reflected from a Chroma Q505LP dichroic mirror and illuminates the back aperture of an Olympus 60x plan apochromat infinity-corrected oil immersion objective with the numerical aperture (N.A.) of 1.45. The fluorescent signal collected from the sample by the same objective passes through the dichroic mirror, is reflected from a Thorlabs BB1-E02 broadband dielectric mirror, and then filtered by a Chroma HQ535/50 narrow band filter and a spatial filter with a 10 cm focal length through a 15 μm pinhole. This provides an effective optical system magnification of 37.5x, and allows the sample volume lateral size behind the pinhole to be 0.4 μm. The exact value of a bleaching spot radius (0.205 μm) was determined experimentally by FCS using a calibration solution of Alexa 488 Fluor® with a known value of the diffusion coefficient. The FRAP instrument was equipped with a programmable computer-controlled shutter in order to control measurements in the required time intervals.

PC/PMAA PEMs were prepared by LbL assembly within home-built glass cuvettes. A surface priming layer was prepared by injecting BPEI solution at pH 9 into the cells for 15 min, followed by rinsing with Milli-Q water. Alternative depositions of polyelectrolytes were controlled at pH 4.5 and room temperature with two 1 min 0.01 M phosphate buffer rinsing cycles between the 15 min polymer deposition steps. 60 μl of 0.6 M NaCl solutions were added into glass cells with deposited films and

sealed with parafilm. A spot in the films was bleached for 1 minute by a focused laser at 1 mW. After the bleaching process, the fluorescence intensity of multilayer films in the bleached zone was recorded every 2 - 60 min (depending on the observed recovery kinetics and a time program) at 1 μW. Since the recovering time required for fluorescence intensity of films in all experiments was much longer than the bleaching time (≥6 hours vs. 1 minute), a contribution of molecular motion during bleaching to the fluorescence intensity recovery profile was negligible. All FRAP measurements were performed at room temperature in 0.01 M phosphate buffer solutions at pH 4.5.

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