

Polyelectrolyte multilayer-like films from layer-by-layer processing of protected polyampholytic block copolymers

Materials

All materials were commercial materials and were used as received unless otherwise indicated.

Experimental Procedures

General Information

Number and weight-average molecular weights, M_n and M_w respectively, and dispersity values, \mathcal{D} , for the non-nitrogen-containing block polymers were measured by gel permeation chromatography (GPC) on a Waters alliance system equipped with a refractive index detector. Samples were dissolved in high performance liquid chromatography (HPLC) grade tetrahydrofuran (THF) at a concentration of approximately 1 mg/mL and injected through four Shodex columns (KF805, KF804, KF803 and KF802). A flow rate of 1 mL/min and temperature of 35 °C were maintained. The columns were calibrated with narrow molecular weight PS standards (EasiCal PS-2, Polymer Laboratories, Inc.). For nitrogen-containing block copolymers, molecular weights were estimated from the M_w of the nitrogen-free blocks and the composition from ^1H NMR spectroscopy.

^1H nuclear magnetic resonance (NMR) spectroscopy was done on a Varian INOVA 400 MHz NMR spectrometer. Deuterated tetrahydrofuran was used for all NMR spectra. A delay time of 10 seconds was used to ensure complete relaxation of protons for quantitative integrations. Chemical shifts were reported relative to tetramethylsilane (TMS).

Film thicknesses were measured using a NanoSpec/AFT 2100 Film Thickness Measurement tool. The thickness of the films were determined from the interference of a white light passed through a diffraction grating with measurements taken at 81 different points across the wafer. A standard program called "Polyimide on Silicon" was used to analyze the component wavelengths (380-780 nm) to determine the film thickness.

Synthesis of PDMAEMA-*b*-PtBMA

Dimethyl 2,2'-azobis(2-methylpropionate) (0.101 g), tert-butylmethacrylate (tBMA, 20.000 g), 2-cyanopropan-2-yl benzodithioate (CPBD, 0.389 g), ethyl acetate (20 mL) and a magnetic stir bar were loaded into a 250 mL glass bottle. The mixture was deoxygenated by N_2 gas for 1 h and then the flask was placed in a heat block at 70 °C for

24 h. After the reaction, the flask was cooled, ethyl acetate was evaporated by keeping the bottle open for 2 h and bubbling N₂. The reaction mixture was then dissolved in 60 mL tetrahydrofuran (THF) and precipitated into 1 L methanol/water mixture (9:1 v/v). The precipitate was collected and re-precipitated. The resulting poly(*t*-butylmethacrylate) (PtBMA) was collected and dried in a vacuum oven at room temperature overnight. The resulting PtBMA had $M_n = 10.5$ kg/mol and $\mathcal{D} = 1.09$.

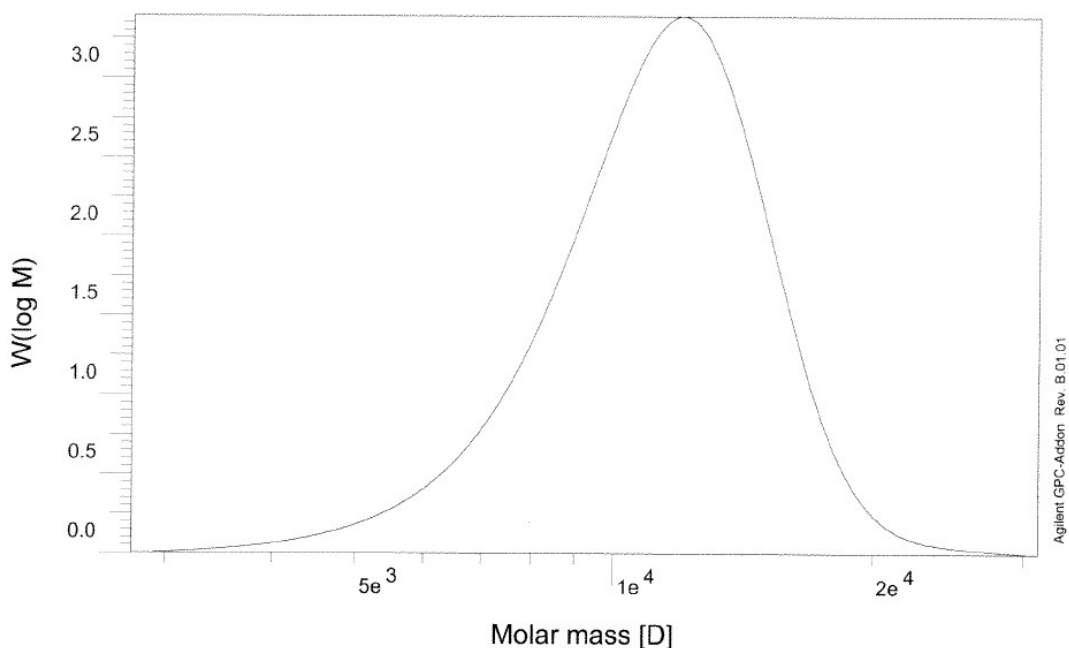


Figure S1. GPC spectra of PtBMA macroinitiator.

Using the above PtBMA as a macroinitiator, 2-(dimethylamino)ethyl methacrylate (DMAEMA) monomers were polymerized using a similar procedure set forth above. 3.000 g of PtBMA, 3.315g of DMAEMA, 0.065g of dimethyl 2,2'-azobis(2-methylpropionate) and a magnetic stir bar were loaded into a 50 mL reactor. Ethyl acetate (6 mL) was deoxygenated and added to the reactor in a glove box. The reactor was then sealed with a septum and placed in a heat block at 70°C for 24 h. After the reaction, the flask was cooled, ethyl acetate was evaporated by keeping the bottle open for 2 h and bubbling N₂. The reaction mixture was then dissolved in 60 mL of THF and precipitated into 1 L methanol/water mixture (9:1 v/v). The precipitate was collected and re-precipitated. The polymer was collected and dried in a vacuum oven at room temperature overnight. The resulting PDMAEMA-*b*-PtBMA had an estimated total $M_n = 24$ kg/mol and 54 mol% PDMAEMA (57 wt%) by ¹H NMR and is reported as 13k-11k referring to the M_n 's of the *t*BMA and DMAEMA blocks, respectively.

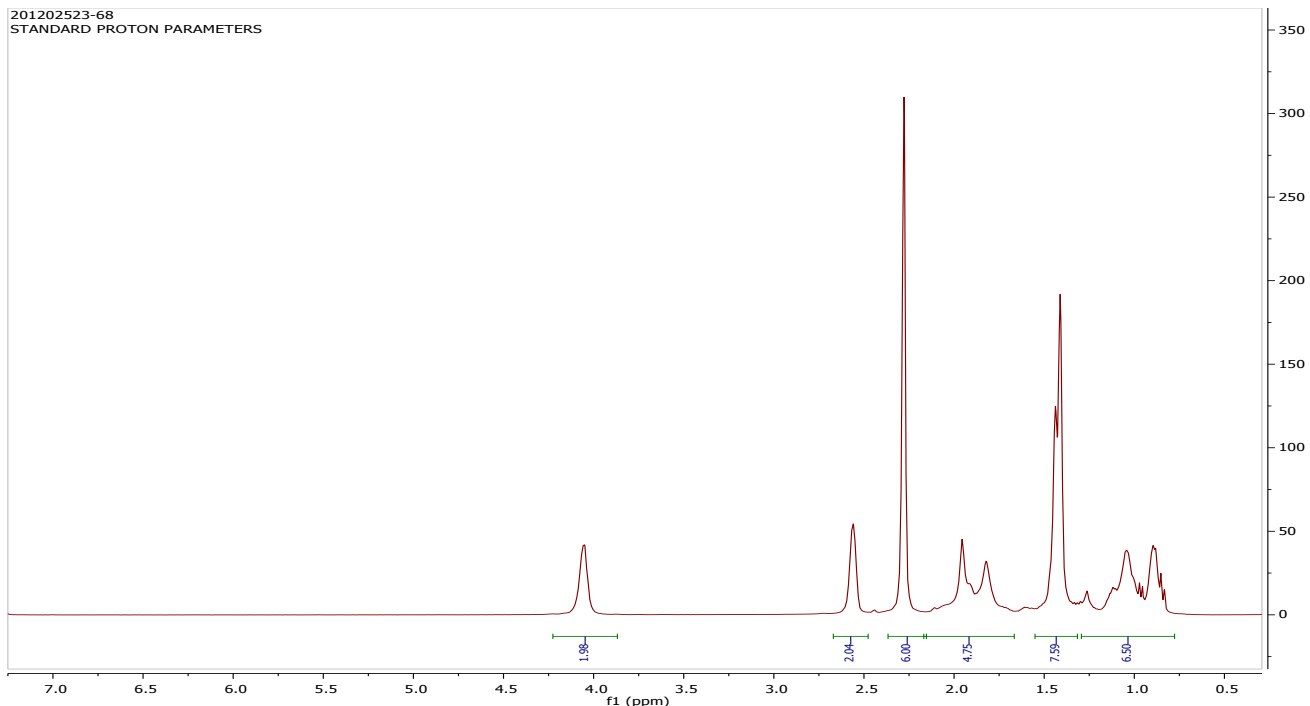


Figure S2. ¹H NMR spectra of PDMAEMA-*b*-PtBMA in CDCl₃. The mole % of tBMA was calculated based on the ¹H integration ratio of -N(CH₃)₂ (δ 2.15-2.37 ppm) and tBMA (δ 1.32-1.55 ppm).

Synthesis of PDMAEMA-*b*-PAdMA-*b*-PtBMA

Dimethyl 2,2'-azobis(2-methylpropionate) (0.043 g), tBMA (10.0 g), 2-cyanopropan-2-yl benzodithioate (CPBD, 0.341 g), PGMEA (17.5 g) and a magnetic stir bar were loaded into a 200 mL air-free flask. The mixture was freeze-pump-thawed three times with liquid N₂ and the flask was then placed in a heat block at 70 °C for 16 h. After the reaction, the flask was cooled and the reaction mixture was then precipitated into 500 mL methanol. The precipitate was collected and re-precipitated. The polymer was collected and dried in a vacuum oven at 50 °C overnight. The resulting poly(*t*-butyl methacrylate) macroinitiator (PtBMA-MI) had an $M_n = 4.8$ kg/mol and $\mathcal{D} = 1.2$, as evidenced by the GPC trace shown in Figure S3.

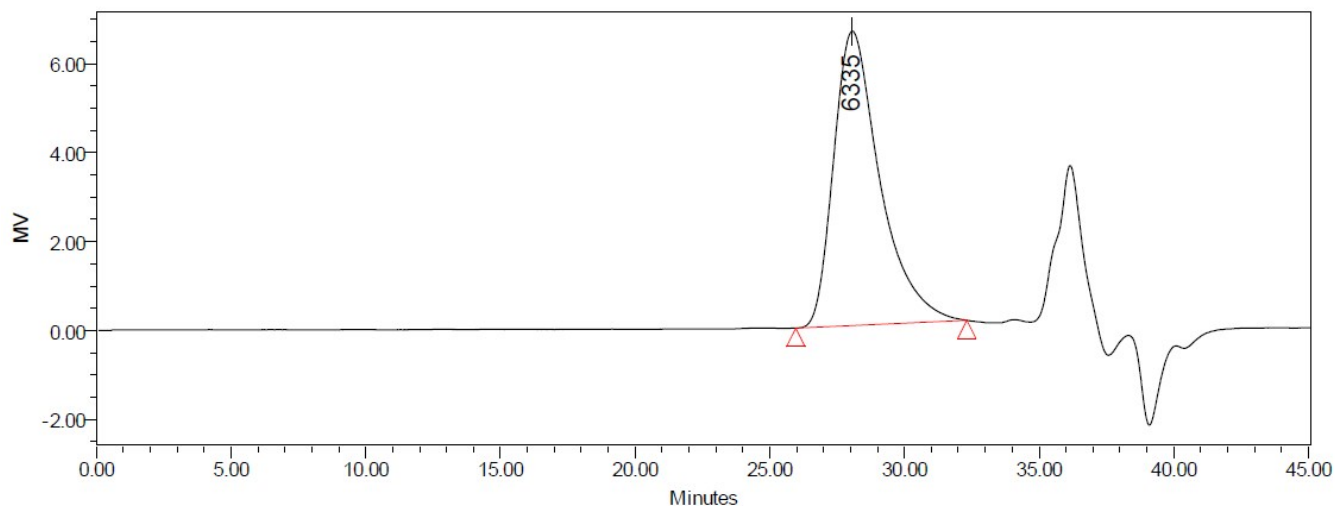


Figure S3. GPC trace of PtBMA-MI.

The resulting PtBMA-MI (2.0 g), adamantyl methacrylate (AdMA, 13.3 g), dimethyl 2,2'-azobis(2-methylpropionate) (0.014 g), PGMEA (15.5 g) and a magnetic stir bar were loaded into a 200 mL air-free reactor. The mixture was freeze-pump-thawed three times with liquid N₂ and the flask was then placed in a heat block at 70 °C for 16 h. After the reaction, the flask was cooled. The reaction mixture was then precipitated into 500 mL methanol, and the precipitate was collected and re-precipitated. The polymer was collected and dried in a vacuum oven at 50 °C overnight. The resulting poly(t-butyl methacrylate)-b-poly(adamantyl methacrylate) macroinitiator (PtBMA-b-PAdMA-MI) had an $M_n = 15.2$ kg/mol and $\mathcal{D} = 1.18$, as evidenced by the GPC trace shown in Figure S4.

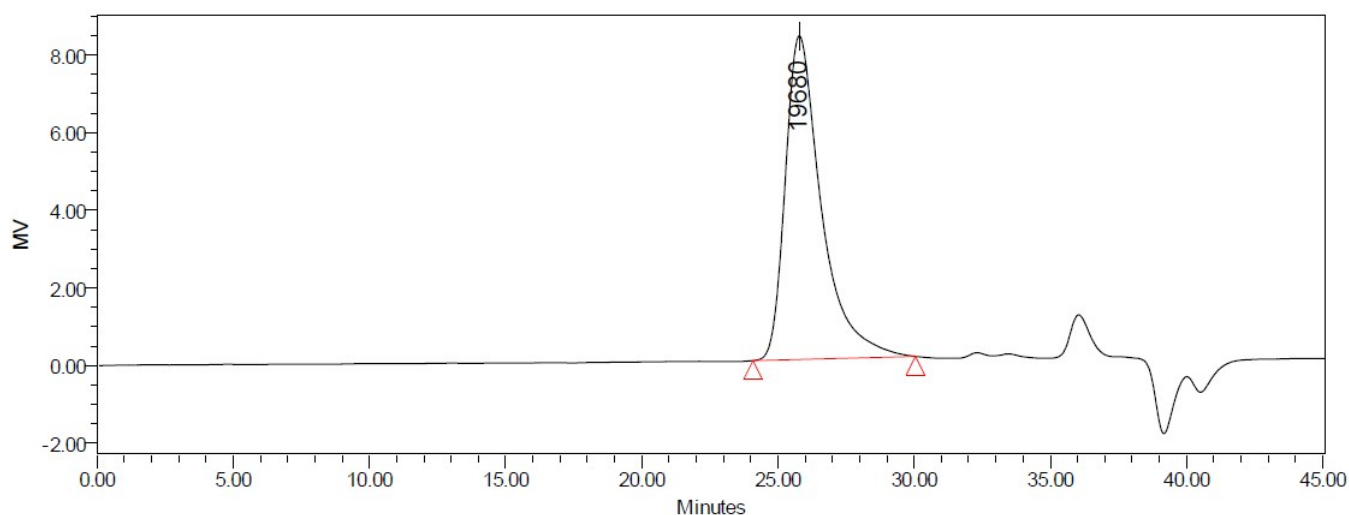


Figure S4. GPC trace of PtBMA-b-PAdMA-MI.

The resulting PtBMA-b-PAdMA-MI (7.0 g), DMAEMA (2.1 g), dimethyl 2,2'-azobis(2-methylpropionate) (0.008 g), PGMEA (26.72 g) and a magnetic stir bar were loaded into a 200 mL air-free reactor. The mixture was freeze-

pump-thawed three times with liquid N₂ and the flask was then placed in a heat block at 70 °C for 16 h. After the reaction, the flask was cooled and the reaction mixture was precipitated into 500 mL methanol. The precipitate was collected and re-precipitated. The polymer was collected and dried in a vacuum oven at 50 °C overnight. The resulting poly(t-butyl methacrylate)-b-poly(adamantyl methacrylate)-b-poly(dimethylaminoethyl methacrylate) (PtBMA-b-PAdMA-b-PDMAEMA) had an estimated total $M_n = 20$ kg/mol and 22 wt% PDMAEMA by ¹H NMR and is reported as 5k-10k-5k referring to the M_n 's of the tBMA, AdMA, and DMAEMA blocks, respectively. The ¹H NMR spectra of the final triblock is shown in Figure S5.

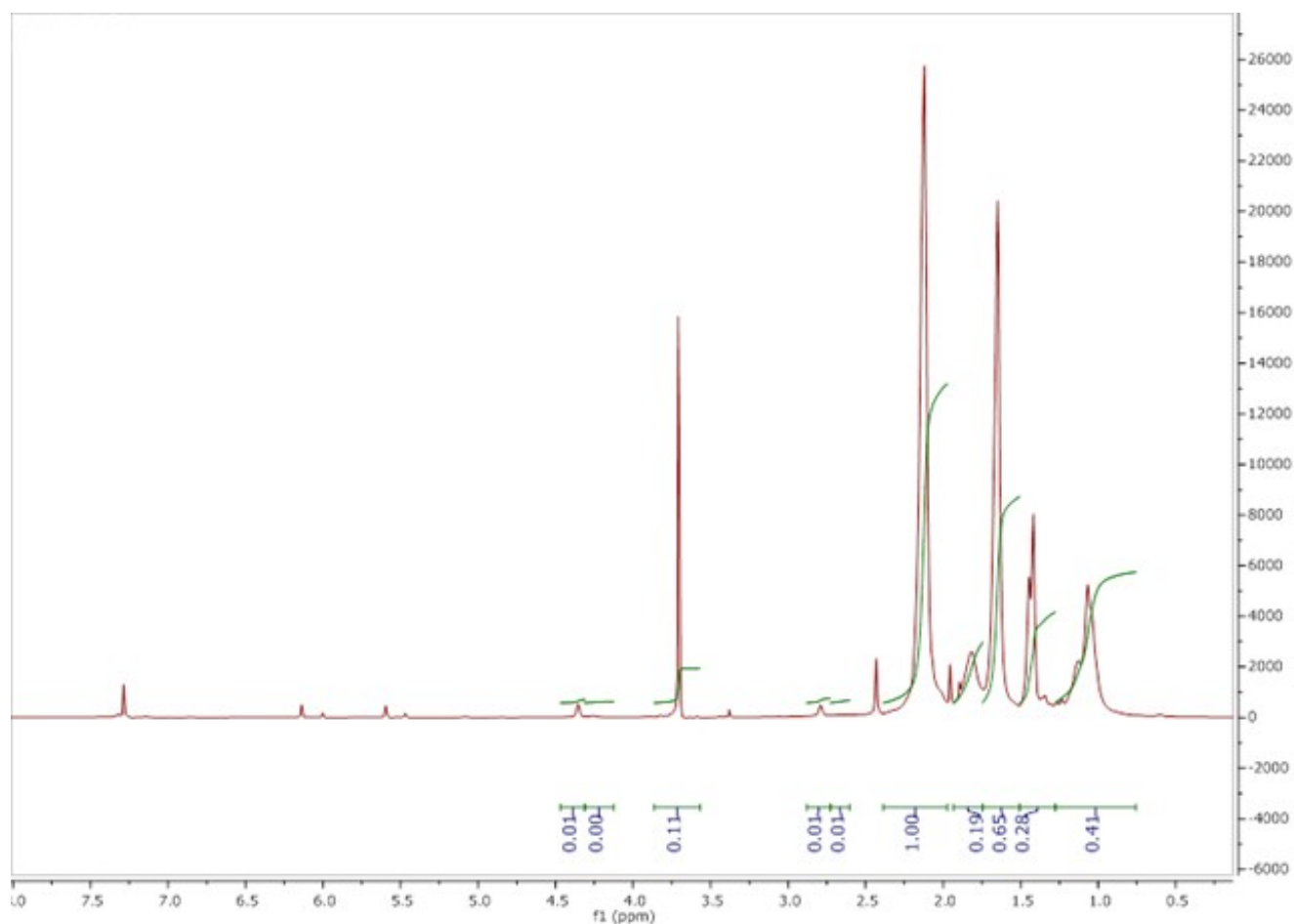


Figure S5. ¹H NMR spectra of the final triblock PtBMA-b-PAdMA-b-PDMAEMA.

General procedure for film deposition

Wafer processing was conducted on 8" silicon wafers with native oxide coating using a TEL CLEAN TRACK™ LITHIUS.TM. i+ coater/developer. All films were formed using spin coating at 1500 rpm for 1 min unless otherwise noted. A model polyanionic surface was first prepared by coating a random copolymer of n-butylmethacrylate (40%) and methacrylic acid (60%) (P(nBMA-r-MAA)) in 4-methyl-2-pentanol (2 wt%) to give a film with thickness of 54 nm after a bake at 90°C for 1 min to remove residual solvent. Process conditions for the

steps and thickness results demonstrating sequential film growth are summarized in Table 1. All coatings For Layer 1 (See Layer 1, Process A in Table 1), a n-butylacetate (nBA) solution of 1 wt% of the block copolymer PDMAEMA-b-PtBMA was then overcoated on the film (initial thickness ~ 50 nm), baked at 110 °C, and rinsed with nBA to remove excess material, and film thickness was recorded. To begin Step 2, the film stack was then coated with a 2 wt% isobutyl isobutyrate (IBIB) solution of p-toluenesulfonic acid (pTSA) (20 wt% of total solids) and a random copolymer of n-butylmethacrylate (25%) and isobutylmethacrylate (75%) (P(nBMA-r-iBMA) (80 wt% of total solids). The combined stack was then baked at 150 °C, and the acid layer was removed by rinsing with IBIB, and thickness was again measured. The nBA solution of PDMAEMA-b-PtBMA was again overcoated on the film, baked at 110°C, and rinsed with nBA to remove excess material, and film thickness was recorded. This alternating process of acid treatment material (Step B) followed by block copolymer (Step A) is then repeated to give the desired number of layers and film growth.

Atomic force microscopy

The silicon wafer was secured to the AFM stage via the stage vacuum system. The AFM images of the coatings were captured at ambient temperature by using a Bruker FastScan Icon AFM system operated in tapping mode with a FastScan-A probe. The probe has a spring constant of ~18 N/m and a resonant frequency in the vicinity of 1.4 MHz. An imaging frequency of 2 Hz was used with a set point ratio of ~0.8.

Table S1. Film thickness from control experiments without acid-catalyzed deprotection.

Layer Number		0	1	2	3
Diblock	h (nm)	54.2 (0.1)	57.1 (0.1)	57.6 (0.1)	58.2 (0.2)
	Δ_h^a (nm)		2.9	0.5	0.6
	Σ_h^b (nm)		2.9	3.4	4.0
Triblock	h (nm)	54.2 (0.1)	57.1 (0.1)	57.6 (0.1)	58.2 (0.2)
	Δ_h (nm)		2.8	0.5	0.6
	Σ_h (nm)		2.8	3.3	3.9

^a Δ_h is the difference in thickness of the BCP coated film minus the thickness of the previous film; ^b Σ_h is the total thickness growth after successive layer depositions.

Fourier transform infrared spectroscopy

The Nicolet 6700 FT-IR (Fourier transform infrared) Spectrometer was used to collect IR spectra from 400 cm^{-1} to 4000 cm^{-1} with a data interval of 1 cm^{-1} . Each sample was compressed against the diamond with a consistent

force to ensure good contact between sample and ART crystal. IR analysis was performed on the first BCP layer, after deprotection, and after deposition of a second BCP layer. IR intensity changes of the C-H stretch at 2900 cm^{-1} and of the C=O stretch at 1700 cm^{-1} were closely monitored to follow deprotection and reintroduction of the t-butyl protecting group.

Contact angle measurement

Water contact angle measurements were taken on a Dataphysics OCA20 contact angle system. 2.5 μL droplets of ultrapure water (18.2M Ω -cm) were deposited on the surface and drop shape image captured. The drop shape horizon was fitted with a circle algorithm to extract the contact angle with the substrate. The measurement was repeated 5 times on each sample to gather statistics across the sample.