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Supporting Information

Unusually Fast and Large Actuation from Multilayer Polyelectrolyte Thin Films

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Experimental Section

Materials and Substrates

Branched polyethylenimine (PEI) (M_w 25,000 g/mol) and poly(acrylic acid) (PAA) (M_w=100,000 g/mol) were purchased from Sigma-Aldrich (Milwaukee, WI). Cationic waterborne polyurethane (PU) dispersion (SCR 20072, ~45 wt%) was provided by Lubrizol Co. (Avon Lake, OH). PEI, PAA, and PU aqueous solutions were prepared by diluting in deionized (DI) water (to 0.1, 0.2 and 10 wt%, respectively) and adjusting the pH (to 10, 4, and 6.5, respectively). Poly(ethylene terephthalate) (PET) film (ST505, Dupont-Teijin) was purchased from Tekra (New Berlin, WI), with a thickness of 51 μm, and used as the substrate to prepare free-standing membranes. Single-side-polished silicon wafers were purchased from University Wafer (South Boston, MA) and used as the substrate for thin film thickness and swelling ratio measurements.

Actuator Fabrication

A home-built robotic dipping system was used to prepare the multilayer membranes through alternating deposition of cationic PEI or PU and anionic PAA.[26] PET and silicon wafer substrates were cleaned by rinsing with DI water, methanol, and DI water again, followed by drying with compressed air. Silicon wafers were plasma treated with an ATTO plasma cleaner (Diener,

Germany) prior to use, while no surface treatment was performed on PET (to minimize adhesion). During the initial bilayer (BL) deposition, the substrates were dipped into the cationic (PEI or PU) and anionic (PAA) solutions for 5 min each, with 30 sec DI water rinsing and compressed air drying in between each deposition step. The remaining deposition cycles involved 1 min dipping in each solution. The stacked free-standing polymer actuator films were prepared through assembling a PU/PAA film on top of a PEI/PAA film, followed by removal from the PET substrate.

Actuator Characterization

Multilayer film thickness was measured by a 500 μL LiquidCell equipped α-SE ellipsometer (J.A Wollam Co., Inc., Lincoln, NE), using a previously reported method.[23] The thickness measurement was done on transparent multilayer films (less than 8 BL for both systems). A silicon wafer with ~25 nm thermal SiO_2 layer was used to calibrate the window effect prior to the measurement. Multilayer film thickness was initially measured under ambient conditions (23 °C, ~45% RH) as a function of the number of bilayers deposited. Deionized water and methanol were individually introduced into the liquid cell with a syringe. Silicon wafers were immersed in a given solution for 20 min before in-situ thickness measurement. Each reported thickness is the average of at least three measurements. The bending behavior of the actuator films was monitored by a CAM 200 contact angle goniometer (KSV Instruments, Ltd. Monroe, CT). The vapor detection ability of the multilayer polymer actuator was tested and demonstrated with a home-built system (Fig. 4).

Table S1. Thickness of each layer in the stacked multilayer actuator membranes.

Sample	PEI/PAA layer		PU/PAA layer	
	Number of BL	Thickness (um)	Number of BL	Thickness (um)
$(PEI/PAA)_1/(PU/PAA)_2$	55	10	84	20
$(PEI/PAA)_1/(PU/PAA)_1$	81	15	61	15
$(PEI/PAA)_1/(PU/PAA)_2$	110	20	42	10

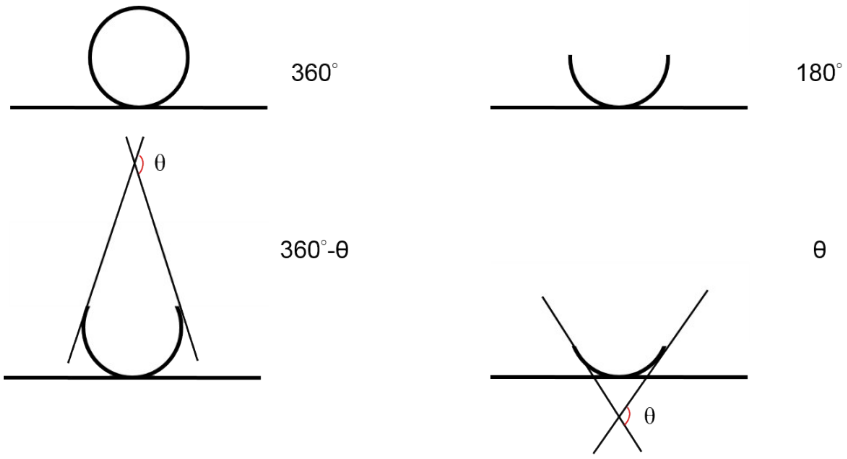

Figure S1. Schematic of bending curvature measurements in water and methanol vapor environments.