Supporting Information

Polymer Brush-Based Optical Device with Multiple Responsivities

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1. Synthesis and Characterization

1.1 Materials

N-isopropylacrylamide (NIPAm) was purchased from TCI (Portland, Oregon) and purified by recrystallization from hexanes (ACS reagent grade, EMD, Gibbstown, NJ) before use. Copper(I) Bromide (Cu^IBr, 98%, Aldrich), was purified by adding it to 10% H_2SO_4 solution and followed by addition of saturated $NaHSO_3$ solution. After stirring for 5 min, the precipitated CuBr was separated by vacuum filtration, washed with acetic acid, anhydrous ethanol and ether, which finally yielded a white powder. Anhydrous ethanol (Brampton, Ontario) was processed by adding 3 Å molecular sieve. Acrylic acid (99%, Aldrich), 2-Bromo-2-methylpropionyl bromide (BiBB, 98%, Aldrich), 11-Mercapto-1-undecanol (97%, Aldrich), N,N,N',N',N"-pentamethyldiethyldiethylenetriamine (PMDETA, 99%, Aldrich), Dichloromethane (>99.8%, Aldrich) were used as received, without further purification. Milli-Q water with resistivity of 18 MΩ·cm was used. Glass microscope slides were purchased from Fisher. Chromium (99.999%) was purchased from ESPI (Ashland, OR) and Gold (99.99%) was purchased from MRCS Canada (Edmonton, AB, Canada)

1.2 Instrumentation

Characterization was performed using an imaging ellipsometer (Nano film ep4, Accurion, Germany), atomic force microscopy (Digital Instrument, Dimension 3100), and reflectance spectroscopy (Ocean optics, Dunedin). Metal layers were deposited using a Torr International Inc. model THEUPG thermal evaporation system (New Windsor, NY)

1.3 Surface-Initiated ATRP

1.3.1 ATRP initiator $(BrC(CH_3)_2COO(CH_2)_{10}S)_2$ Synthesis[1]

11-Mercapto-1-undecanol (1.02 g), 10% potassium hydrogen carbonate (5 mL) and dichloromethane (40 mL) were added to a round bottom flask and stirred for 30 min to mix well. Bromine (0.4 g) was added dropwise to the mixture with continuously stirring for another 30 min. The organic phase was separated and the aqueous phase was exacted with dichloromethane (15 mL x 2) twice. The organic phases were combined and dried by magnesium sulfate. After vacuum filtration, the solvent was collected and rotary evaporated, which gave a white solid. The crude disulfide was recrystallized from an ethanol/hexane solution. Recrystallized disulfide (0.55 g) and triethylamine (1.9 mL) were dissolved in dichloromethane (31.4 mL), which incubated in ice bath under N_2 environment. 2-Bromo-2-methylpropionyl bromide (0.42 mL) was added drop by drop to the mixture. After stirring for 1 hour, the solution was moved to room temperature and stirred for another 2 hours. The solution was exacted by 2M sodium carbonate and followed by saturated ammonium. The organic phase was dried by magnesium sulfate and was evaporated. The crude product was purified by column chromatography (hexane:ethyl acetate 13:1 V/V), which result in a pale yellow oil.

1.3.2 Preparation of PNIPAM brush

Microscope slides (1 inch x 1 inch) were washed copiously with ethanol and Milli-Q water. After dried with N_2 gas, they coated with an adhesive layer of chromium (2 nm) and followed by 50 nm thick of Au. The freshly prepared slides were immersed into 0.5 mM initiator solution (dissolved in anhydrous ethanol) and allowed to incubate for 3 h at room temperature. The initiator modified slides were rinsed with ethanol and dried by N_2 before use. NIPAm (6.9 g) was dissolved in water (68 mL) and degased with N_2 for 3 hours. PMDETA (216 µL) was added to methanol (20 mL) and degased with N_2 for 3 h. CuBr (31.15 mg) was added to methanol mixture under N_2 environment and was sonicated for 30 s. The microscope slide was added to a reaction vessel with N_2 purge. 17 mL degased NIPAM solution was transferred to this vessel by syringe, followed by 2 mL degased CuBr/PMDETA/methanol solution. The reaction time was varied from 5 min to 6 h. After the polymerization, the slides were removed from vessel, washed with copious amounts of methanol and water, and dried with nitrogen.

1.3.3 Preparation of pNIPAm-co-AAc brush

The procedure was similar as preparing pNIPAm brushes. Instead of using just

NIPAm in solution, acrylic acid (6 mL) was added. After then, 0.5 M sodium hydroxide was added to adjust the pH of the mixture close to 7.

2. Ellipsometry and Atomic Force Microscope Analysis

The thickness of NIPAm based brushes was measured by ellipsometry with angle of incidence (AOI) of 42° and multiple wavelengths were used to probe the sample (from 400 nm to 900 nm, 40 nm between each scan). Three spots were measured on each slide, and 3 areas of interest were selected from each spot to yield a total of 9 thickness measurements for each sample. The fitting parameters for NIPAm were refractive index (n) of 1.485 and absorption coefficient (k) of 0. The thicknesses of Au-brush-Au assemblies and the surface topology were also measured by AFM as shown in Figure S1. The polymerization time as a function of pNIPAm film thickness is shown in Figure S2.

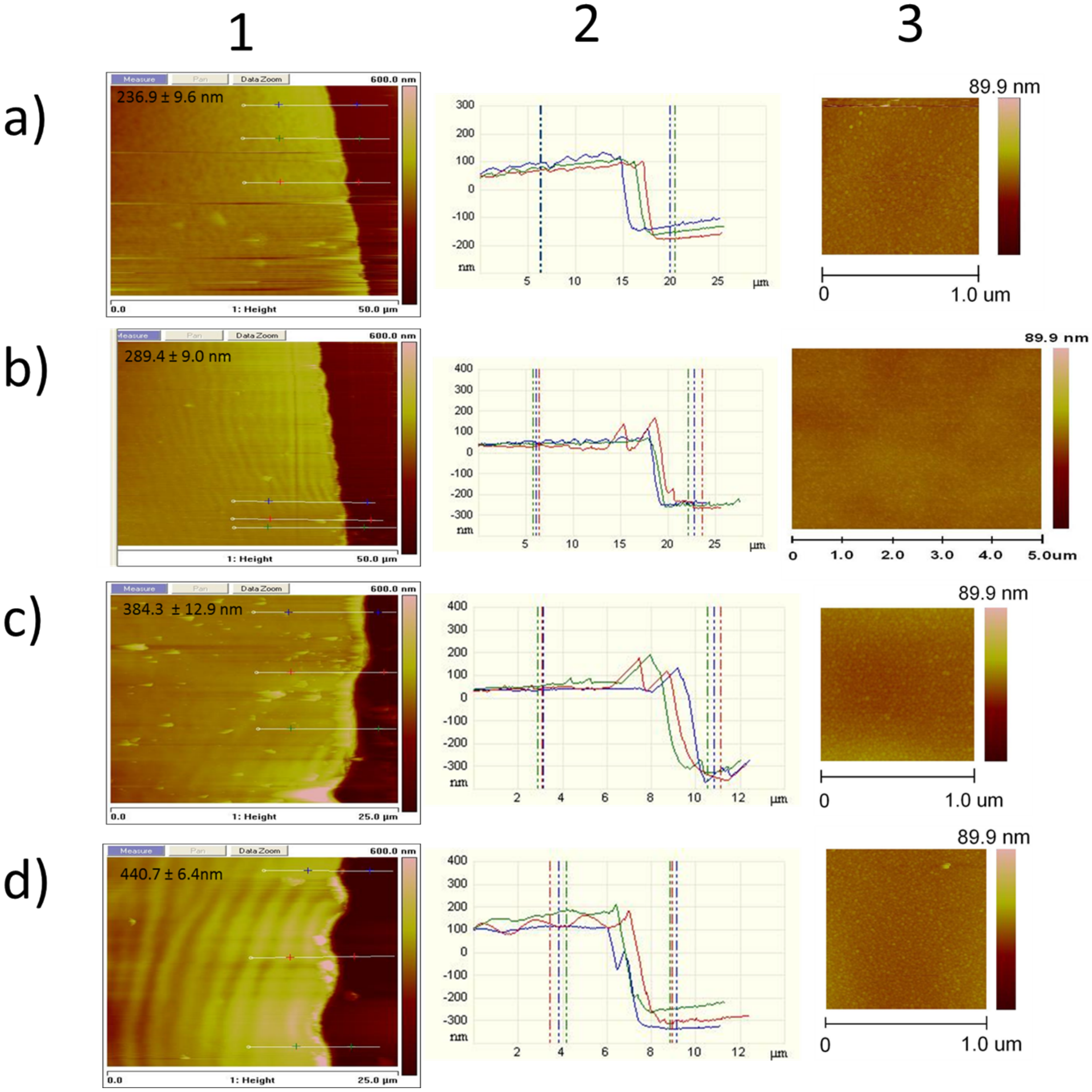

Figure S1. AFM images of pNIPAm brush-based devices. Column 1 are images acquired in air of a scratched portion of the device. The scratches were made with a razor blade. Column 2 are the line traces for the images in column 1. Column 3 shows the images of the films acquired away from the scratch.

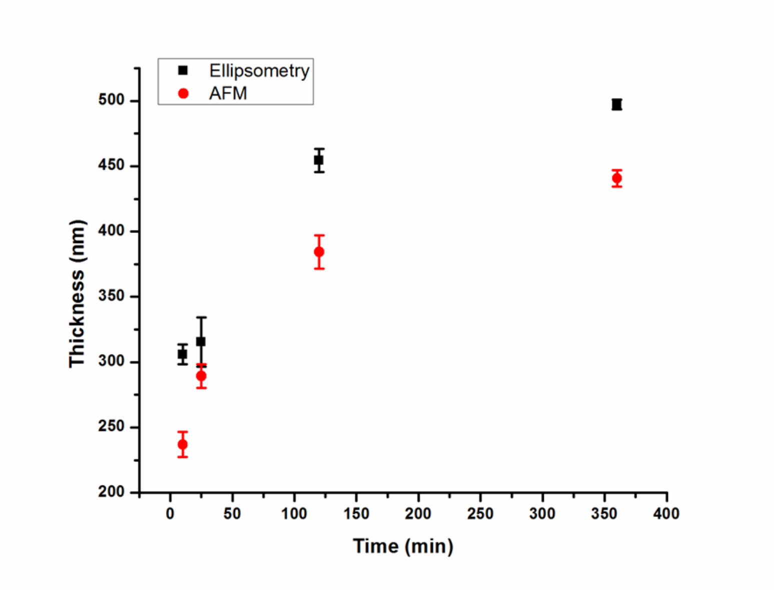

Figure S2. Brushes thicknesses as a function of polymerization time measured by (■) ellipsometry and (●) AFM.

3. Reproducibility of Device Response to pH and Temperature

Reflectance measurements were conducted in a temperature controlled chamber. The reflectance spectra were recorded using Ocean Optics Spectra Suite Spectroscopy Software. The temperature responsivity of three pNIPAm brush-based devices are shown in Figure S3. To evaluate the reproducibility of temperature response, the temperature was increased from 24 ^{o}C to 40 ^{o}C and followed by a decrease back to 24 ^{o}C for several runs. The reflectance spectrum wavelength shift with temperature variation is shown in Figure S4. For pH response reproducibility of pNIPAm-AAc brushes, the pH was changed from ~ 2.7 to ~ 6.2 and back to ~ 2.7 for several runs. The reflectance spectrum wavelength shift with pH change result is shown in Figure S5. The visible color change of the device due to temperature stimuli is shown in Figure S6 and Figure S7.

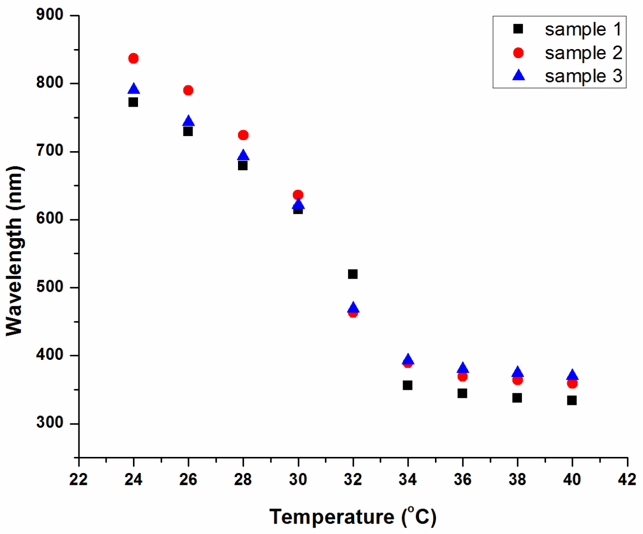

Figure S3. Temperature response of three separate pNIPAm brush-based devices.

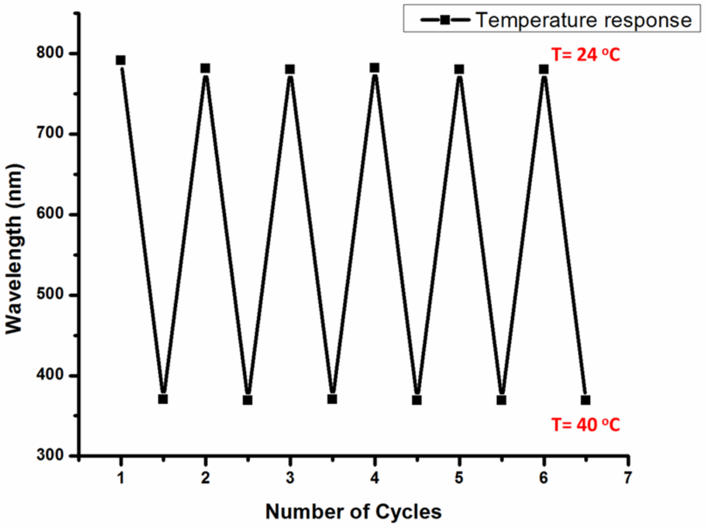

Figure S4. pNIPAm brush-based device response many temperature cycles, from 24 °C to 40 °C.

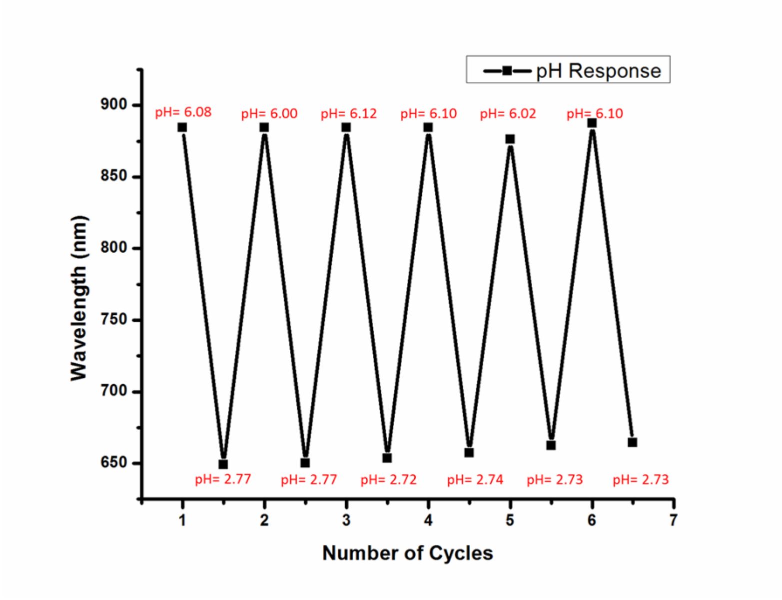

Figure S5. pNIPAm-co-AAc brush-based device response to pH cycling from pH ~2.7 to ~6.1.

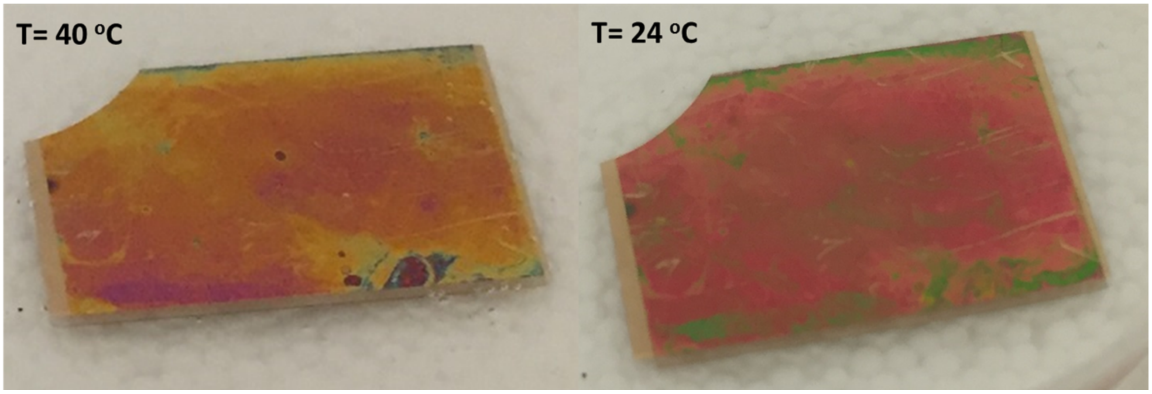

Figure S6. Photographs of a pNIPAm brush-based device in Milli-Q water at different temperature. The long edge is ~1 inch.

Reference

1. Shah, R. R.; Merreceyes, D.; Husemann, M.; Rees, I.; Abbott, N. L.; Hawker, C. J.; Hedrick, J. L., Using atom transfer radical polymerization to amplify monolayers of initiators patterned by microcontact printing into polymer brushes for pattern transfer. *Macromolecules* **2000,** *33* (2), 597-605