Patterned, Oscillating, pH-Responsive Actuation Of Polymeric Microstructures In Fluid

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INTRODUCTION

Responsive and reversibly actuating surfaces have attracted significant attention recently due to their promising applications including microfluidic mixing, particle propulsion and fluid transport, capture and release systems, and antifouling[1,2,3]. Here, we build upon our previous work on humidity-responsive actuation of high-aspect-ratio polymeric structures[4] and alter the system to be sensitive to pH by using an acrylic acid-co-acrylamide hydrogel with a volume transition at pH?4.2. Actuating surfaces remain submerged making them more ideal for fluidic applications such as propulsion. Indeed, polymeric actuators embedded in the pH-responsive hydrogel can be patterned within microfluidic channels and put in motion by flow of acid and base or by reversible electrochemically generated pH gradients. We observe and describe unusual non-linear waves created in the surface-attached hydrogels that experience dynamic creasing upon swelling which exerts anisotropic forces on the embedded microstructures resulting in patterned micropost deflections. These clear micropost patterns can then be used as a powerful visualization tool of gel structure and topography.

EXPERIMENTAL

Sample preparation and characterization. Acrylamide (AAm), acrylic acid (AAc), *N,N*'-methylenebisacrylamide (bis-AAm), ammonium persulfate (APS), glycidyl methacrylate (GMA), and (tridecafluoro-1,1,2,2-tetrahydrooctyl) triethoxy silane were purchased from Sigma-Aldrich (St. Louis, MO). Polydimethylsiloxane (PDMS) (Dow-Sylgard 184) was purchased from Ellsworth (Germantown, WI) and UVO-114 was purchased from Epoxy Technology (Billercia, MA). All the chemicals were used as received.

Replication of silicon master structures in PDMS, and the subsequent polymer replication of those structures, was done via methods described previously[4]. pH responsive acrylamide-co-acrylic acid hydrogel precursor solution was placed on the polymer replica micropost surface and then the confining layer was placed face down over the posts and held clamped together by binder clips. The hydrogel was cured in an oven at 40°C for 90 minutes and then the sample was placed in

deionized water at room temperature for 45 minutes to swell the hydrogel before unclipping the slides and separating the post and confining surface. Samples were placed in a solution in which the pH was altered to above and below $pK_{a,AAc}$ via various methods demonstrate actuation. Optical imaging and video recording was done on an Olympus IX71 inverted microscope using StreamPix v.3 software and QImaging EXi Blue and Evolution VF cameras.

Generation of reversible pH gradients. Sulfuric acid (H_2SO_4, 95-98%), sodium sulfate (Na_2SO_4), and bromophenol blue indicator were purchased from Sigma-Aldrich and used as received.

10 ml of an electrolyte solution of (0.01 M Na_2SO_4, $1x10^{-4}$ M H_2SO_4, bromophenol blue indicator in deionized water) was placed in a petri dish (55 mm diameter, 15 mm height). Platinum electrodes (100 Å titanium, 100 nm platinum sputter coated on a glass slide) were placed vertically in solution at a distance of 3 cm apart and 15 V was applied to the electrodes with a DC power supply (Hewlett Packard, Model E3611A) and the input polarity was quickly reversed manually.

Fabrication of micro-channels. Channels 2mm wide of various lengths were cut in double sided Kapton tape (thickness ?70μm) and PDMS (10:1 prepolymer: hardener) was partially cured at 70°C and used to seal the top of the channel. Polyethylene tubing and a syringe were used to inject 1M HCl and 1M NaOH with bromophenol blue.

RESULTS

Actuation was demonstrated via addition of acid and base, through flow of acid and base in microfluidic channels, and by reversible electrochemically generated pH gradients. Interesting dynamic creasing patterns were observed in the gel and are easily visualized by micropost gradient deflection. The slow and gradual pH change allowed by electrochemical pH gradient generation allows for the visualization of a sharp actuation gradient upon sudden contraction of the hydrogel (Figure 1).

Figure 1. Electrochemical setup and images of actuation

CONCLUSIONS

We have successfully demonstrated the controlled actuation of polymer microposts driven by the volume phase transition of AAc-co-AAm hydrogel in open and closed systems in response to electrochemically generated and reversible pH gradients as well as flow in microfluidic channels. Reversible actuation is achievable while the sample is continuously submerged and it can be controlled remotely by the application of an electric field. This actuation was achieved by altering the responsiveness of the acrylamide hydrogel utilized in our previously reported actuation system and

speaks to the versatility and robustness of a responsive gel driven polymer actuator. Additionally, since the polymeric microposts are flexible, actuation has been accomplished by a pH responsive hydrogel which has a swelling ratio lower than a humidity responsive hydrogel. Other stimuli-responsive materials that have minimal swelling ratios could still be useful for integration into this system. We are further examining the use of a wide range of other responsive hydrogels and smart materials in this actuation system such as gels which are self-oscillating, or responsive to temperature or light, that could potentially be incorporated to tailor the actuation for various purposes.

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