Polymer Actuation

DOI: 10.1002/ange.201303475

Polymer-Based Muscle Expansion and Contraction**

*Molla R. Islam, Xue Li, Keady Smyth, and Michael J. Serpe**

Polymer-based stimuli-responsive polymers and materials have been of considerable interest for many years owing to their ability to convert a chemical or physical stimulus into an observable change in a system. Hydrogel-based thin films, assemblies, and particles (microgels and nanogels) have been designed to respond to a variety of stimuli for a number of potential applications in tissue engineering, artificial muscles, valves, and actuators.[1–9] Hydrogels are of particular interest owing to their mechanical properties, chemical diversity, and hydration properties, which allow them to interface well with biological systems. Recently, responsive hydrogels and polymer-based thin films have been developed as programmable soft matter or motors by exploiting conformational changes of the polymer that affects the system.[4,6] Of specific interest to the investigation here are responsive polymer-based systems that are able to do work, that is, lift a mass.[10–12] These systems, often referred to as artificial muscles, have been the subject of intense research owing to their potential to control movements in mechanical motors.[10–13] One of the most well studied responsive polymers to date is poly(*N*-isopropylacrylamide) (pNIPAm), which shows random-coil-to-globule transition at temperatures below 32 °C.[14,15]

Charged pNIPAm-based microgels have been synthesized and used for various applications.[16–18] By far, the most common chemical functionality added to pNIPAm-based microgels is acrylic acid (AAc). AAc is a weak acid, having a pK_a of approximately 4.25, therefore at pH > 4.25 the AAc groups are deprotonated, thus making the microgels negatively charged (polyanionic), while they are neutral at pH < 4.25 owing to AAc protonation. At high pH values the microgels swell because of the charge–charge (Coulombic) repulsion in the polymer network of the microgel.

Herein we present a pNIPAm-microgel-based device that is able to do work and lift masses many times the mass of the device, in response to simple changes in the humidity of its environment. The device is constructed by depositing a monolayer of poly(*N*-isopropylacrylamide)-*co*-acrylic acid, pNIPAm-*co*-AAc microgels on an Au-coated substrate. Once deposited, the microgels form a homogenous layer, with the thickness defined by their diameter in solution. The pNIPAm-*co*-AAc microgels used herein had a solution diameter of (1548 ± 69) nm (measured using differential interference contrast microscopy); the films typically have a thickness of approximately 0.5 of the solution diameter.[19] Subsequently, a solution containing oppositely charged poly(diallyldimethylammonium chloride) (pDADMAC) is added to the microgel-coated substrate and allowed to dry. The pDADMAC solution had a pH of 6.55, which rendered the microgel layer polyanionic. The pDADMAC layer contracts when it dries, owing to water evaporation enhancing hydrophobic interactions between the pDADMAC chains. Since the electrostatic interactions between pDADMAC and the microgels, and the interaction between microgels and the Au layer, are strong, the substrate bends when the polymer dries (Figure 1).

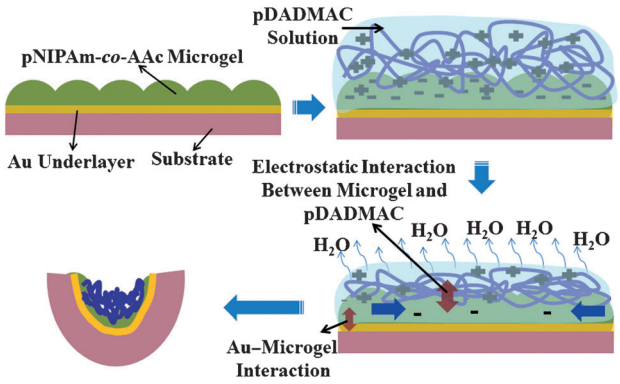

Figure 1. A flexible plastic substrate (transparency film) was coated with an Au/Cr layer. Cr acts as an adhesion layer such that the Au adheres to the plastic. PNIPAm-*co*-AAc microgels were deposited on this substrate, to yield a monolithic monolayer of microgels on the Au. Addition of a pDADMAC solution renders the pNIPAm-*co*-AAc microgel negatively charged owing to the deprotonation of AAc moieties in the microgel initiating the electrostatic interaction between the microgels and polyelectrolyte. Upon drying, the pDADMAC layer contracts bending the substrate owing to the strong interactions between the microgels and pDADMAC and the microgels and Au.

When this process is conducted using a standard microscope glass coverslip as the substrate, the bending forces are so strong that the coverslip is shattered. This is shown in Figure 2a along with the results for control experiments conducted by drying the pDADMAC solution on bare glass and unmodified Au-coated glass substrates. When the pDADMAC solution is dried on an Au-coated glass substrate, with microgels painted on the Au, the glass substrate bends so much that the glass shatters (Figure 2a). This was repeated many times, which showed that 80% of the Au-coated microgel-painted substrates shattered after drying. When

[*] Dr. M. R. Islam, X. Li, K. Smyth, Prof. Dr. M. J. Serpe
Department of Chemistry, University of Alberta
Edmonton, Alberta, T6G 2G2 (Canada)
E-mail: michael.serpe@ualberta.ca

[**] M.J.S. acknowledges funding from the University of Alberta (the Department of Chemistry and the Faculty of Science), the Natural Science and Engineering Research Council (NSERC), the Canada Foundation for Innovation (CFI), the Alberta Advanced Education & Technology Small Equipment Grants Program (AET/SEGP) and Grand Challenges Canada. M.J.S. acknowledges Mark McDermott for the use of the thermal evaporator.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201303475.

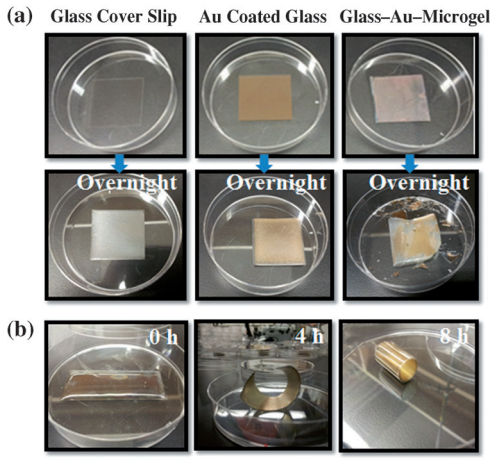

Figure 2. Electrostatic interaction and substrate bending mediated by pDADMAC drying. In each case, a fixed amount of pDADMAC solution was added and dried at ambient condition. a) (left column) bare glass cover slip, (middle column) Au-coated glass and (right column) microgel painted on Au-coated glass. b) Flexible Au-coated substrate with microgels deposited bends and eventually curls upon drying over 8 h.

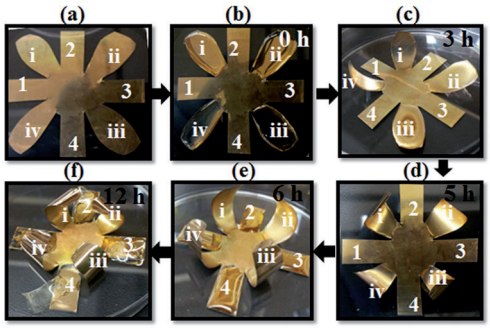

Figure 3. A specially cut Au-coated plastic substrate, with the Au containing pNIPAm-based microgels. Arms i–iv were exposed to the pDADMAC solution while Arms 1–4 were exposed to the PSS solution. The arms that were exposed to pDADMAC clearly bend upon solution drying, while the PSS arms are unresponsive to drying. Drying of the pDADMAC solution took place over 6 h. After this time, (e) the PSS solution was added to the arms and allowed to dry overnight.

the same experiment is conducted on a bare glass substrate, no bending is observed, while slight bending, and even occasional substrate cracking (ca. 20% of the samples) takes place on Au-coated glass substrates without microgels present. When a microgel-modified, Au-coated plastic substrate (simple transparency slide) is exposed to pDADMAC, and the pDADMAC solution is allowed to dry, the plastic substrate can curl up significantly into a tight scroll structure (Figure 2b). In all the cases above, we hypothesize that the microgels serve as glue that allows the contraction of the pDADMAC layer to be translated to the substrate below. Our previous studies have shown that the microgel–Au interaction is extremely strong. Furthermore, we have shown that there are multiple, electrostatic interactions between pDADMAC and the charged microgels.[17] Therefore, the contraction of the pDADMAC layer upon drying can be translated to the solid substrate through its interaction with the microgels, and the microgels transfer the contraction to the Au-coated surface, thereby pulling the sides of the substrate up. Depositing Cr as an adhesion layer between the Au and the substrate strengthens the Au–substrate bond. Drying pDADMAC on an Au-coated substrate without the microgels present does not yield a strong enough bond to the surface to allow for consistent substrate bending/breaking. Similarly, simply drying microgels on a surface does not bend the substrate, because when the microgels dry, there are no long-range interactions between them, hence they dry "locally" without long-range deformations that are translated to the substrate.

To further prove our hypothesis that the electrostatic interactions between the microgels and the pDADMAC lead to the observed bending, we designed a flexible substrate with numerous arms. The arms were coated with Au and painted with pNIPAm-*co*-AAc microgels and alternate arms were exposed to the same pDADMAC solution used above while keeping the other arms empty (Figure 3). The arms exposed to the pDADMAC solution curled up (Figure 3). When the empty arms were exposed to polyanionic poly(sodium 4-styrenesulfonate) (PSS) solution (20%) and dried at ambient condition, they did not bend at all. This proves that the polyanionic PSS deposited on the polyanionic microgels cannot yield the necessary interactions with the microgels bound to the Au-coated substrate to bend the plastic substrate. Furthermore, this experiment shows that by controlling the shape of the flexible substrate, we are able to devise complex constructs, in this case a "hand" capable of grasping an object.

If our above hypothesis is correct, and the bending of the substrates is a result of the dehydration-mediated contraction of the pDADMAC layer, the process should be reversible upon rehydration of the devices (Figure S1 in the Supporting Information). To illustrate this, we introduced our device to a humidity chamber (Figure 4), which allowed for atmospheric temperature and humidity to be controlled and maintained.

The device was connected to a string, which was extended out of the chamber top. Initially, under low humidity, the

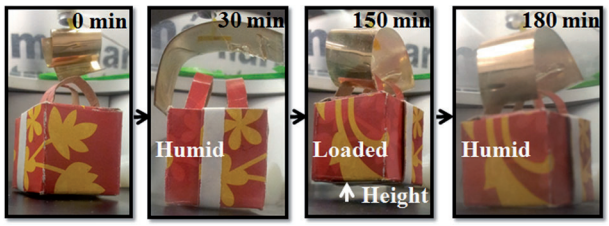

Figure 4. The curled substrate was hung from a string into a humidity chamber (0 min). The humidity of the environment was then increased to 80%, and the device uncurled, which was then lowered close to a box (30 min). The humidity was reduced to 10% and the substrate recurled, grasping the box. While maintaining this humidity, the box was lifted off the chamber surface (150 min). A subsequent increase in the humidity allowed the device to reopen, and drop the box (180 min). Here, the masses of the device and the box were 0.2 g and 4.8 g, respectively.

device was fully closed (Figure 4) but opened up after the humidity of the environment was increased to 80%. The open arm was then lowered to a box that was in the chamber, and the humidity was subsequently decreased to 10%. After this decrease, and waiting (ca. 2.0 h), the device curled back up, but in this case it clamped onto the box. To illustrate the strength of the clamping, the box was lifted off the chamber's bottom surface. Finally, the humidity was increased to 70%, which caused the device to open again, thus dropping the box. The mass of the box was 4.8 g, while that of the polymer-based device was only 0.2 g. That is, the mass of the box was 24 times the mass of the device.

We further studied whether the device can be used as an artificial muscle to lift weight and release it in response to humidity. To do this we loaded paper clips onto a curled substrate and exposed the setup to a humid environment (Figure 5). Paperclips (used as weights) were hung off the end

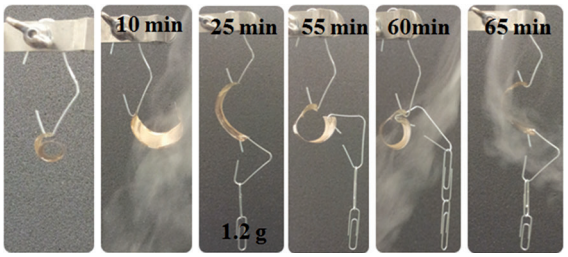

Figure 5. Use of the polymer-based devices as artificial muscles. A small curled substrate was hung from an arm and cycled between low and high humidity. In this case, the device was able to recontract and curl up with a mass of 1.2 g. A complete data set is shown in Figure S2 in the Supporting Information).

of the device, and the device opened up upon increasing the humidity and curled back up when the humidity was decreased. This is similar to an arm curling a mass, but in this case, the mass that is being lifted is 14 times the mass of the device. Given that a human arm is approximately 6.5% of the total mass of the human body, this is equivalent to a 75 kg human with a single arm that is capable of lifting 68.3 kgs.

Finally, we showed that dried substrates can resist opening when a force is applied to them. This is illustrated in Figure 6, where weights were hung from the end of a suspended device showing that even with 52.50 g hanging from the end of the dried device it is not significantly unwound. Using the same numbers as above for the mass of a human arm, this is equivalent to a 75 kg human that has an arm capable of resisting a force of 1280 kgs pulling on the arm.

In conclusion, we found that polyelectrolyte-mediated crosslinking of microgels painted on Au-coated substrates are able to actuate, and act as muscles or arms in response to humidity. These arms are able to lift relatively large masses, and resist forces many times its own mass. Given this, we strongly believe that this device can be further developed to optimize its capability as artificial arm. This study is very promising to realize responsive-polymer-based materials for applications in soft robotics and artificial muscles.

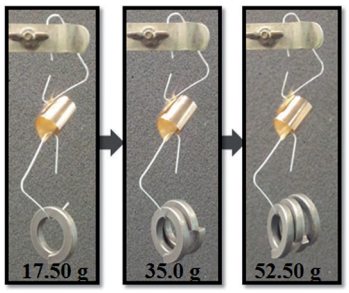

Figure 6. A dry polymer-based device resisting uncurling as masses are hung from the end of the device.

Experimental Section

Microgel synthesis: Microgels composed of poly(*N*-isopropylacrylamide)-*co*-acrylic acid (pNIPAm-*co*-AAc) were synthesized through temperature-ramp, surfactant-free, free-radical precipitation polymerization as described previously.[17–19] The monomer mixture, with a total concentration of 154 mM, was comprised of 85% (mole/mole) NIPAm, 10% AAc, and 5% *N*,*N*-methylenebisacrylamide (BIS) as the crosslinker. NIPAm (17.0 mmol), and BIS (1.0 mmol) were dissolved in deionized water (100 mL) with stirring in a beaker. The mixture was filtered through a 0.2 μm filter affixed to a 20 mL syringe into a 200 mL 3-neck round-bottom flask. The beaker was rinsed with deionized water (25 mL) and then filtered into the NIPAm/BIS solution. The flask was then equipped with a temperature probe, a condenser, and a N_2 gas inlet. The solution was bubbled with N_2 gas for approximately 1.5 h, while stirring at a rate of 450 rpm, allowing the temperature to reach 45 °C. AAc (2.0 mmol) was then added to the heated mixture with a micropipette in one aliquot. An aqueous solution of ammonium persulfate (APS; 0.078 M, 5 mL) was delivered to the reaction flask with a transfer pipet to initiate the reaction. Immediately following initiation, a temperature ramp of 45 to 65 °C was applied to the solution at a rate of 30 °C h^{-1}. The reaction was allowed to proceed overnight at 65 °C. After polymerization, the reaction mixture was allowed to cool to room temperature and filtered through glass wool to remove any large aggregates. The coagulum was rinsed with deionized water and filtered. Aliquots of these microgels (12 mL) were centrifuged at a speed of approximately 8500 relative centrifugal force (rcf) at 23 °C for approximately 40 min to produce a pellet at the bottom of the centrifuge tube. The supernatant was removed from the pellet of microgels, and the pellet was then resuspended to the original volume (12 mL) by using deionized (DI) water. This process was repeated until the microgels were cleaned a total of six times to remove any unreacted monomer and/or linear polymer from the microgel solution.

Fabrication of Au-coated substrate: Briefly, 25 × 25 mm precleaned glass coverslips or transparent flexible plastic sheets were rinsed with DI water and ethanol and dried with N_2 gas, and a 2 nm layer of Cr followed by 15 nm or 50 nm of Au were thermally evaporated onto them at a rate of ca. 0.2 Å s^{-1} and ca. 0.1 Å s^{-1}, respectively, by using a Torr International Inc. model THEUPG thermal evaporation system (New Windsor, NY). The Cr acts as adhesion layer to hold the Au layer on the glass/plastic. The Au-coated glass substrates were annealed at 250 °C for 3 h and then cooled to room temperature prior to use. An aliquot of about 12 mL of previously purified microgel solution was centrifuged for 30 min at 23 °C at approximately 8500 rcf to pack the microgels into a pellet at the bottom of the tube. After removal of the supernatant solution, the microgel pellet was vortexed and placed onto a hot plate at 30 °C. A previously coated Cr/Au substrate was rinsed with ethanol, dried with N_2, and then placed onto hot plate (Corning, NY) set to 30 °C. An aliquot (40 μL for each 25 × 25 mm area) of the concentrated microgels was put onto the substrate and then spread toward each edges by using the side of a micropipette tip. The substrate was

rotated by 90°, and the microgel solution was spread again. The spreading and rotation continued until the microgel solution became too viscous to spread owing to drying. The microgel solution was allowed to dry completely on the substrate for 2 h with the hot plate temperature set to 35 °C. After 2 h, the dry film was rinsed copiously with DI water to remove any excess microgels not bound directly to the Au. The microgel-painted substrate was then placed into a DI water bath and allowed to incubate overnight on a hot plate set to approximately 30 °C. Following this step, the substrate was again rinsed with DI water to further remove any microgels not bound directly to the Au substrate surface. The microgel-painted Au-coated substrate was dried with N_2 gas and used for the experiment.

Bending experiment: Au-coated microgel-painted substrates were placed in a Petri dish. A specific amount (1.5 mL) of pDADMAC solution (20 % in water) was spread onto the microgel layer. The whole setup was undisturbed and dried at ambient temperature. After the complete drying of the film, the humidity response was tested either in a humidity chamber or in air. The box-load-and-release experiment was done in a humidity chamber (Rame-Hart Instrument Co., NJ, USA) and the paper-clip experiment was done in air. In both cases an Air-O-Swiss AOS 7145 Cool Mist Ultrasonic humidifier (manufactured by Swiss Pure Air) was used.

Received: April 24, 2013
Revised: June 4, 2013
Published online: July 4, 2013

Keywords: charged microgels · electrostatic interactions · mechanical deformation · polyelectrolytes · polymers

[1] A. Lendlein, H. Y. Jiang, O. Junger, R. Langer, *Nature* **2005**, *434*, 879.
[2] D. J. Beebe, J. S. Moore, J. M. Bauer, Q. Yu, R. H. Liu, C. Devadoss, B.-H. Jo, *Nature* **2000**, *404*, 588.
[3] T. P. Russell, *Science* **2002**, *297*, 964.
[4] M. Ma, L. Guo, D. G. Anderson, R. Langer, *Science* **2013**, *339*, 186.
[5] Y. Osada, A. Matsuda, *Nature* **1995**, *376*, 219.
[6] Z. L. Wu, M. Moshe, J. Greener, H. Therien-Aubin, Z. Nie, E. Sharon, E. Kumacheva, *Nat. Commun.* **2013**, *4*, 1586.
[7] K. Liu, C. Cheng, Z. Cheng, K. Wang, R. Ramesh, J. Wu, *Nano Lett.* **2012**, *12*, 6302.
[8] X. Zhang, C. L. Pint, M. H. Lee, B. E. Schubert, A. Jamshidi, K. Takei, H. Ko, A. Gillies, R. Bardhan, J. J. Urban, M. Wu, R. Fearing, A. Javey, *Nano Lett.* **2011**, *11*, 3239.
[9] E. Wang, M. S. Desai, S.-W. Lee, *Nano Lett.* **2013**, *13*, 2826.
[10] M. Yamada, M. Kondo, J.-I. Mamiya, Y. Yu, M. Kinoshita, C. J. Barrett, T. Ikeda, *Angew. Chem.* **2008**, *120*, 5064; *Angew. Chem. Int. Ed.* **2008**, *47*, 4986.
[11] J. C. Nawroth, H. Lee, A. W. Feinberg, C. M. Ripplinger, M. L. McCain, A. Grosberg, J. O. Dabiri, K. K. Parker, *Nat. Biotechnol.* **2012**, *30*, 792.
[12] Y. Takashima, S. Hatanaka, M. Otsubo, M. Nakahata, T. Kakuta, A. Hashidzume, H. Yamaguchi, A. Harada, *Nat. Commun.* **2012**, *3*, 1270.
[13] M. D. Lima, N. Li, M. Jung de Andrade, S. Fang, J. Oh, G. M. Spinks, M. E. Kozlov, C. S. Haines, D. Suh, J. Foroughi, S. J. Kim, Y. Chen, T. Ware, M. K. Shin, L. D. Machado, A. F. Fonseca, J. D. W. Madden, W. E. Voit, D. S. Galvão, R. H. Baughman, *Science* **2012**, *338*, 928.
[14] C. Wu, S. Zhou, *Macromolecules* **1995**, *28*, 8381.
[15] C. Wu, X. Wang, *Phys. Rev. Lett.* **1998**, *80*, 4902.
[16] M. J. Serpe, K. A. Yarmey, C. M. Nolan, L. A. Lyon, *Biomacromolecules* **2005**, *6*, 408.
[17] M. R. Islam, M. J. Serpe, *Macromolecules* **2013**, *46*, 1599.
[18] M. R. Islam, M. J. Serpe, *Chem. Commun.* **2013**, *49*, 2646.
[19] C. D. Sorrell, M. J. Serpe, *Adv. Mater.* **2011**, *23*, 4088.

