J|A|C|S
COMMUNICATIONS

Published on Web 04/01/2006

Highly Reversible and Multi-Stage Cantilever Actuation Driven by Polyelectrolyte Brushes

Feng Zhou,[†,‡] Wenmiao Shu,[†] Mark E. Welland,[†] and Wilhelm T S Huck*[,†,‡]

The Nanoscience Centre, University of Cambridge, 11 J.J. Thomson Avenue, Cambridge CB3 0FF, U.K., and Melville Laboratory for Polymer Synthesis, Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, U.K.

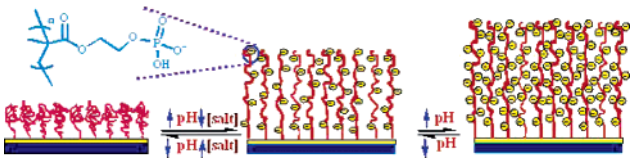
Received January 27, 2006; E-mail: wtsh2@cam.ac.uk

The bending of microcantilevers upon adsorption of polymers (DNA, proteins) or small molecules has great potential for the development of highly sensitive sensors and efficient nanoactuators.[1,2] For microcantilevers to be useful as actuators, precise positioning, reversibility, and large-scale bending are prerequisites.[3] Conventional modification by self-assembled monolayers (SAMs) usually generates small cantilever deflections.[4] By grafting polymers to the cantilever surface, a much wider range of responses can be achieved due to conformational changes in the polymer backbones,[5−7] and recently, the bending of pH responsive copolymer brush-coated AFM cantilevers was studied under different conditions.[8] However, reversible and multi-stage actuation of cantilevers remains a significant challenge. The use of polyelectrolytes and their collapse in response to salt has recently[9] emerged as a promising potential synthetic equivalent of one of the most powerful biological motors: the spasmoneme spring.[10] In this communication, we report the first example of polyelectrolyte brush-driven highly reversible actuation of cantilevers, expanding the range of triggers leading to mechanical actuation as well as providing new fundamental insights into polyelectrolyte brushes.

The brushes are selectively grown on one side of the cantilever via a sequential deposition of gold, "dummy" SAM, gold and brush growth (full details in Supporting Information). The cantilever was double side coated with gold film to minimize the consequences of temperature drift and the effects of changes in the electrical double layer. One side was modified with hexadecanethiol (HDT) as the internal calibration. The other side was grafted with around 20 nm polymethacryloyl ethylene phosphate (PMEP) via surface-initiated atomic transfer radical polymerization (SI-ATRP).[11] Careful calibrations were performed with cantilevers modified with inert HDT monolayer on both sides as a control experiment (Supporting Information). Non-brush-modified cantilevers exhibited negligible bending when switching between water and salt solution and solutions with different pH.

The conformational changes of the brushes in response to salt solution or pH are schematically shown in Scheme 1. PMEP can

Scheme 1. Schematic of Reversible Swollen/Collapse of PMEP Brush



be switched between three ionic states: fully protonated, monoprotonated/monobasic, and dipotassium salt/dibasic states, depending on pH.[11] Figure 1 displays the bending of brush-coated cantilevers when varying the pH of the solution between 1 and 13. In region I, the brushes are fully protonated, while in region III, they are fully deprotonated, and compressive stress is generated in both strongly acidic (pH < 2) and basic (pH > 8) environments. At pH < 2, the protonated brushes are no longer soluble and will collapse, generating a compressive surface stress since the "footprint" of the polymers is too small to accommodate the collapsing chain. This is consistent with previous reports that polymer brushes generate a compressive surface stress upon polymer collapse.[8]

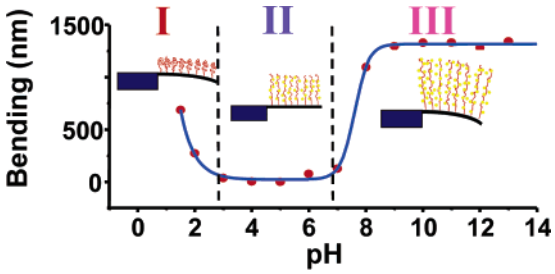


Figure 1. Observed bending of single-side PMEP brush-modified cantilever with changing pH and schematic illustration of brush conformation in different regimes.

At pH > 8, the PMEP brushes are fully deprotonated, and the electrostatic repulsion between charged polymer chains leads to the development of a large compressive stress. The maximum deflection of the cantilevers, up to micrometer scale (approximate 1300 nm), is found in this fully charged state. The large increase in compressive stress upon switching from monobasic to the fully deprotonated state is consistent with a significant swelling of the brushes, as corroborated by AFM imaging (Figure S2), when switching from pH 7 to pH 9. It should be noted that the cantilever deflections are highly reversible, and that the brushes can be cycled through a number of pH cycles. The magnitude and sensitivity of the response to salt depend strongly on the length of the brushes, the grafting density, and the degree of charging of the polymer.[13] We found no deflection for low (<10% initiator) grafting densities of brushes, and a full study on the influence of brush architecture is underway.

Figure 2a shows the reversible bending and return to equilibrium position of the brush-coated cantilever when switching between a 100 mM KCl solution and pure water, respectively. The response of the cantilever to changes of solution is very fast (30 s). The return to zero deflection upon addition of water is slow due to the slow diffusion of excess salt away from the brush layer. The compressive stress is generated by the brushes collapsing under the influence of the high salt environment; this situation is similar to the compressive stress generated at low pH (see above). The control experiments (black line) show that non-brush-modified cantilevers show no response to changes in salt concentration. Separate AFM

[†] The Nanoscience Centre.
[‡] Department of Chemistry.

10.1021/ja060649p CCC: $33.50

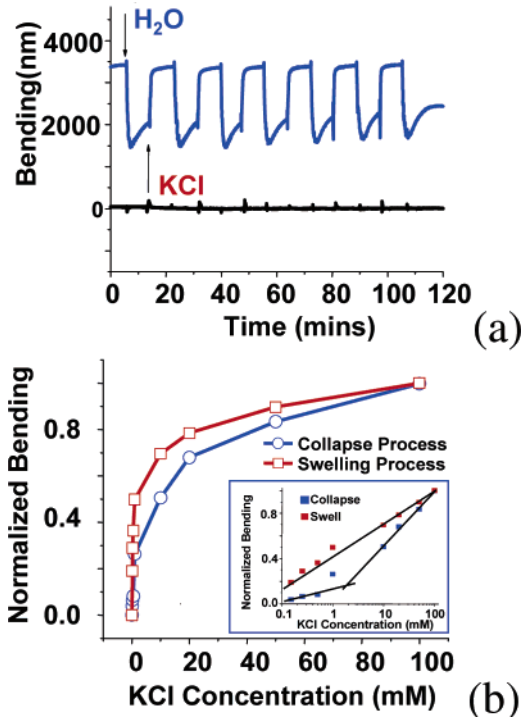


Figure 2. (a) Reversible cantilever bending (upper) and control cantilever (below) when switching between KCl solution and water. (b) Evolution of cantilever bending as a function of the concentration of salt solutions.

measurements verify the collapse of neutral PMEP brush under 0.1 mM KCl solution due to charge screening (Figure S3).

Control over the actual position of cantilever can be achieved by exposing the brush-coated cantilevers to different salt concentrations between 0 and 100 mM (Figure S4). By gradually increasing or decreasing the salt concentration, the actuation can be precisely manipulated in discrete multiple steps. By plotting the bending of the cantilever versus the salt concentration (Figure 2b), or to the logarithm of the salt concentration (inset), one can distinguish two distinct response regimes. At salt concentrations below 1 mM, the response is small (remaining below 10% of maximum bending amplitude), whereas at higher concentrations, a much larger response is observed. Conversely, when lowering the salt concentration, we see an approximately linear dependence of log[salt] versus normalized bending amplitude. Polyelectrolyte brush theory[12] predicts that for annealed brushes at low salt concentrations the brush heights (and therefore surface stress) first increase slightly due to the exchange between external cations and associated protons. At higher concentrations, charge screening is the dominant effect, leading to collapse of the brushes and generation of much more significant compressive stress. It should be noted that the *chemical nature* of the ions (valency, lipophilicity, etc.) also influences the collapse process,[13,14] opening up possibilities for selectivity. These results illustrate how the bending of cantilevers can be used to follow the conformational changes of polymer brushes in great detail and in real time.

The interfacial stress difference acting on the microcantilever surfaces can be calculated by applying Stoney's equation to the case of bending of cantilevers (see Supporting Information). The maximum surface stress generated by PMEP brush-modified cantilevers is calculated to be around 3 N/m. This is significantly larger than the stresses reported for the absorption of dodecanethiol on bare gold substrate (~0.2[4a] or ~0.5 N/m[4b]), DNA hybridization (5 mN/m[15]), or protein−protein interactions (200 mN/m[16]). Reversible nanoscale actuation (easily demonstrated here) was realized by Shu et.a1[17] using a DNA nanomotor, but with much lower surface stresses (~32 mN/m) compared with PMEP brushes, and requiring specific DNA sequences and complimentary strands. An estimate of the power density generated by these brushes is in the order of mW/kg (see Supporting Information for detailed calculation). This seems relatively small, but as a lower limit is very encouraging and similar to other polymer actuators.[9b]

In conclusion, we demonstrated for the first time the fast and reversible actuation of cantilevers driven by polyelectrolyte brushes that experience large conformation changes in response to the pH and electrolyte concentration. We prove the possibility of controlling the magnitude of cantilever bending by placing the brushes in different ionic strength solutions. The versatility of the chemical strategy followed to obtain these brushes allows the study of a wide range of parameters which could all govern bending behavior, including grafting density, chain length, nature of the polyelectrolyte brushes, salts used to collapse the brushes, and patterning of the brush layer to create nonbiaxial stresses. Even more importantly, we can use the highly sensitive and time-resolved measurements of cantilever bending as a means to probe the internal structure of the brushes and to reveal some of the processes occurring during brush collapse and stretching.

Acknowledgment. We thank the IRC in Nanotechnology and the EPSRC (G R/T11555/01) for financial support.

Supporting Information Available: Details of experiment method and cantilever calibration, AFM imaging of brush collapse, and bending curve as a function of salt concentration. Complete ref 6. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Lang, H. P.; Hegner, M.; Gerber, C. *Mater. Today* **2005**, *8*, 30. (b) Krecmer, P.; Moulin, A. M.; Stephenson, R. J.; Rayment, T.; Welland, M. E.; Elliott, S. R. *Science* **1997**, *277*, 1799.
(2) (a) Lahav, M.; Durkan, C.; Gabai, R.; Katz, E.; Willner, I.; Welland, M. E. *Angew. Chem., Int. Ed.* **2001**, *40*, 4095. (b) Berger, R.; Gerber, Ch.; Lang, H. P.; Cimzewski, J. K. *Microelectron. Eng.* **1997**, *35*, 373. (c) Thundat, T.; Oden, P. I.; Warmack, R. J. *Microscale Thermophys. Eng.* **1997**, *1*, 185.
(3) (a) Smela, E. *Adv. Mater.* **2003**, *15*, 481. (b) Fukushima, T.; Asaka, K.; Kosaka, A.; Aida, T. *Angew. Chem., Int. Ed.* **2005**, *44*, 2410.
(4) (a) Berger, R.; Delamarche, E.; Lang, H. P.; Gerber, C.; Gimzewski, J. K.; Meyer, E.; Güntherod, H. J. *Science* **1997**, *276*, 2021. (b) Godin, M.; Williams, P. J.; Tabard-Cossa, V.; Laroche, O.; Beaulieu, L. Y.; Lennox, R. B.; Grutter, P. *Langmuir* **2004**, *20*, 7090. (c) Yang, Y.; Ji, H. F.; Thundat, T. *J. Am. Chem. Soc.* **2003**, *125*, 1124.
(5) Bietsch, A.; Zhang, J.; Hegner, M.; Lang, H. P.; Gerber, C. *Nanotechnology* **2004**, *15*, 873.
(6) Ruehe, J.; et al. *Adv. Polym. Sci.* **2004**, *165*, 79.
(7) Bumbu, G. G.; Kircher, G.; Wolkenhauer, M.; Berger, R.; Gutmann, J. S. *Macromol. Chem. Phys.* **2004**, *205*, 1713.
(8) Abu-Lail, N. I.; Kaholek, M.; LaMattina, B.; Clark, R. L.; Zauscher, S. *Sens. Actuators, B* **2006**, *114*, 371.
(9) (a) Moya, S.; Azzaroni, O.; Farhan, T.; Osborne, V. L.; Huck, W. T. S. *Angew. Chem., Int. Ed.* **2005**, *44*, 4578. (b) Howse, J. R.; Topham, P.; Crook, C. J.; Gleeson, A. J.; Bras, W.; Jones, R. A. L.; Ryan, A. J. *Nano Lett.* **2006**, *6*, 73.
(10) Mahadevan, L.; Matsudaira, P. *Science* **2000**, *288*, 95.
(11) Zhou, F.; Huck, W. T. S. *Chem. Commun.* **2005**, 5999.
(12) (a) Pincus, P. *Macromolecules* **1991**, *24*, 2912. (b) Zhulina, E. B.; Birshtein, T. M.; Borisov, O. V. *Macromolecules* **1995**, *28*, 1491.
(13) Biesalski, M.; Johannsmann, D.; Ruehe, J. *J. Chem. Phys.* **2004**, *120*, 8807.
(14) Azzaroni, O.; Moya, S.; Farhan T.; Brown, A. A.; Huck, W. T. S. *Macromolecules* **2005**, *38*, 10192.
(15) (a) Wu, G.; Ji, H.; Hansen, K.; Thundat, T.; Datar, R.; Cote, R.; Hagan, M. F.; Chakraborty, A. K.; Majumdar, A. *Proc. Natl. Acad. Sci. U.S.A.* **2001**, *98*, 1560. (b) Fritz, J.; Baller, M. K.; Lang, H. P.; Rothuizen, H.; Vettiger, P.; Meyer, E.; Guntherodt, H.-J.; Gerber, Ch.; Gimzewski, J. K. *Science* **2000**, *288*, 316.
(16) (a) Dutta, P.; Tipple, C. A.; Lavrik, N. V.; Datskos, P. G.; Hofstetter, H.; Hofstetter, O.; Sepaniak, M. J. *Anal. Chem.* **2003**, *75*, 2342. (b) Moulin, A. M.; O'Shea, S. J.; Badley, R. A.; Doyle, P.; Welland, M. E. *Langmuir* **1999**, *15*, 8776.
(17) Shu, W.; Liu, D.; Watari, M.; Riener, C. K.; Strunz, T.; Welland, M. E.; Balasubramanian, S.; McKendry, R. *J. Am. Chem. Soc.* **2005**, *127*, 17054.

JA060649P