

ChemComm

Accepted Manuscript

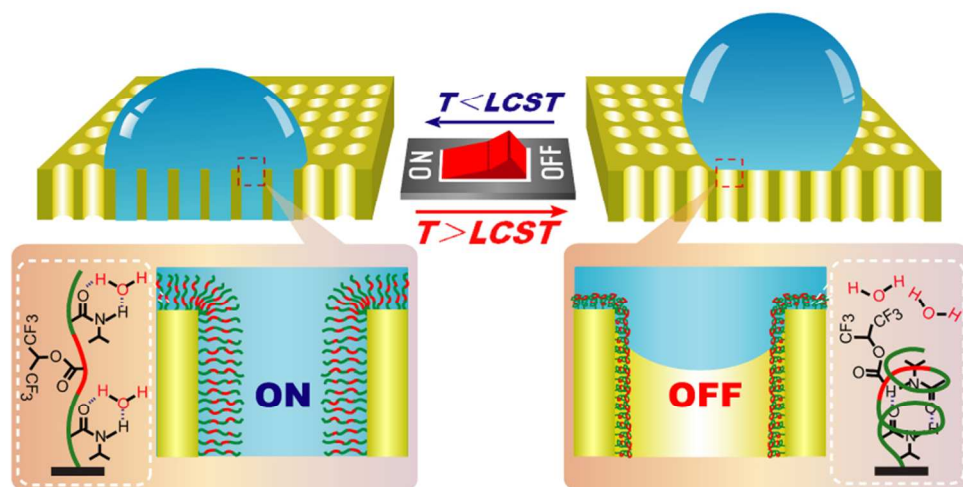


This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



A smart and reversible chemo-mechanical switch for controllable water transportation was developed by originally designing a thermally responsive block copolymer on capillary plate.
78x40mm (300 x 300 DPI)

COMMUNICATION

A Chemo-mechanical Switch for Controllable Water Transportation Based on Thermally Responsive Block Copolymer

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012Jianmin Yang, Mitsuaki Hida, Sifeng Mao, Hulin Zeng, Hizuru Nakajima and
Katsumi Uchiyama*

DOI: 10.1039/x0xx00000x

www.rsc.org/

A smart and reversible chemo-mechanical switch was developed by synthesis of a thermally responsive block copolymer brush poly(N-isopropylacrylamide-co-hexafluoroisopropyl acrylate) (P(NIPAAm-co-HFIPA)) on capillary plate. With the temperature changing around lower critical solution temperature (LCST), the designed chemo-mechanical switch exhibited excellent “ON-OFF” behavior for water transportation.

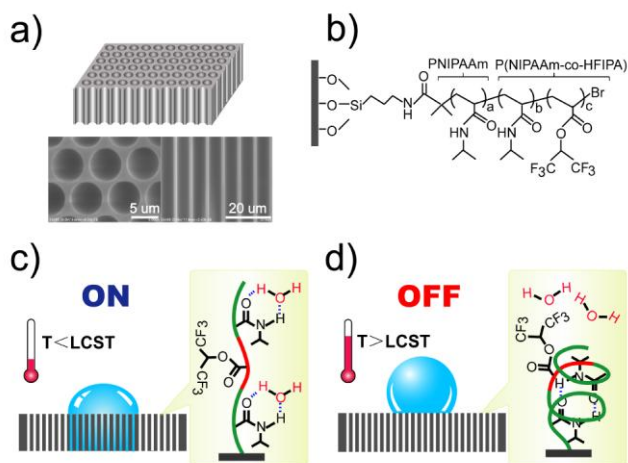
Smart switches, that can be modulated dynamically for controlling microfluidic transportation, have attracted considerable interest recently due to their great demand for use in microfluidic control, molecular separation, biological system, etc.¹ Stimuli-responsive polymers grafted onto micro/nano structured channels have frequently been utilized in developing such smart switches.² Stimuli-responsive polymers are a category of polymers that undergo a change in their conformation, surface energy, or charge state, triggered by an external stimulus.³ These stimuli may come from thermal,⁴ pH,⁵ light irradiation,⁶ electric field,⁷ or multiple factors.⁸

Poly(N-isopropylacrylamide) (PNIPAAm) is an excellent thermal responsive polymer with a lower critical solution temperature (LCST) in water of 32 °C. Its conformation shows a reversible transition between collapsed and swelling as the temperature around the LCST changes. A wide variety of approaches have been developed based on this specific property.⁹ Most studies have mainly focused on the use of PNIPAAm grafted on the substrates with special surface morphologies, such as a grooved substrate,¹⁰ and anodic aluminum oxide (AAO) membranes,¹¹ with the goal of achieving reversible switching between superhydrophilicity and superhydrophobicity by enhancing wettability. However, the design of a practical switching based on PNIPAAm for temperature controlling the transportation of an aqueous solution still remains challenging.¹²

In the current report, we report on the design and fabrication of a chemo-mechanical switch for controllable water transportation. We constructed this smart switch by integrating a NIPAAm-based thermally responsive block copolymer on a multi-capillary structured plate. Herein, the copolymer P(NIPAAm-co-HFIPA) was prepared using PNIPAAm, which governs the thermal properties, and HFIPA, which was used to adjust hydrophilicity and

hydrophobicity. The temperature dependences of water contact angle (CA) measurements on a flat glass plate demonstrated that the individual PNIPAAm brush was barely hydrophobic when the temperature was above the LCST,¹³ in which, the CA was $82.6 \pm 1.8^\circ$ (see Fig. S1, ESI†). According to the capillary effect,¹⁴ the water was easily driven into the capillary when the CA was smaller than 90° (see Fig. S2, ESI†). Thus, the HFIPA, which was water-resistant, was added to enhance the hydrophobicity of the surface with the objective of improving switch performance.

The chemo-mechanical switch was prepared as illustrated in Scheme 1. A capillary plate (1.0 mm thick) with a nominal pore size of 6.0 μm was used as a model platform (Scheme 1a). The copolymer P(NIPAAm-co-HFIPA) (Scheme 1b) was grafted onto the surface of the capillary plate by surface-initiated atom transfer radical polymerization (ATRP),¹⁵ and the entire polymerization process is described in detail in Part S2 and Fig. S3 (see ESI†). Energy-dispersive X-ray spectroscopy (EDX) was used to characterize the surface chemical composites of the capillary plate at each polymerization process. The results indicate that the copolymer brush was successfully grafted onto the capillary plate (see Fig. S4, ESI†). Water controllable transportation was realized by switchable surface energy and the conformation of the copolymer brush could be modulated with temperature, and the capillary effect was provided by the unique architectural structure of capillary plate. At the temperatures below the LCST, the surface of the capillary plate showed highly hydrophilic characteristics because of the dominant inter-molecular hydrogen bonding between the PNIPAAm chains and water molecules. As a result, water could easily penetrate through the capillary plate via the strong capillary effect induced by the microstructures (Scheme 1c). In contrast, at temperatures above the LCST, the surface of the capillary plate became hydrophobic because the intra-molecular hydrogen bonding between the C=O and N-H groups of the PNIPAAm chains results in a shrunken conformation, which makes it difficult for the hydrophilic C=O and N-H groups to interact with water molecules. Therefore, the dehydrated state of the copolymer chains and the large negative capillary effect made the switch impermeable to water, causing water to be retained on the surface (Scheme 1d).



Scheme 1 Schematic illustration of the (a) capillary plate, inset: SEM images of top view (left) and cross-sectional view (right), (b) structure of block copolymer chain, (c) switch at "ON" state, inset: conformation of copolymer chain, (d) switch at "OFF" state, inset: conformation of copolymer chain.

To improve the switch properties of the device, HFIPA was added to ensure the water CA above 90° at high temperature in order to achieve the "OFF" function. The effects of the ratio of HFIPA and the density of the copolymer affected on surface wettability was investigated on a flat glass plate. As shown in Fig. 1a, the water CAs measured at low temperature and high temperature gradually increased with increasing ratio of HFIPA. Therefore, 20% HFIPA was chosen as the optimum conditions which resulted in a CA of $92.3 \pm 1.7^\circ$ at 40°C and a CA of $74.5 \pm 1.3^\circ$ at 25°C . The density of the polymer brush on the substrate was controlled by the time used in amine functionalization. From X-ray photoelectron spectroscopy (XPS) characterization results, which are summarized in Table S1 (ESI[†]), it can be deduced the surface amination reached saturation after 4h. Herein, the high density of the polymer brush is defined as the time used for amine functionalization beyond 4h; while the time for amine functionalization below 2h classified as low density. As indicated from the results shown in Fig. 1b, a high density of copolymer brush was more suitable for modification. Regarding the capillary plate modified with P(NIPAAm-co-HFIPA), water CA experiments indicated that thermally responsive wettability was greatly enhanced by the rough surface. Fig. 1c-d shows photographs of water drop profile on a flat glass plate and the capillary plate at 20°C and 40°C , respectively. The water CA at 20°C decreased from 74.8° for a flat glass plate to 56.1° (capillary plate) as evidenced by the Wenzel equation (see Part S4 and Fig. S5, ESI[†]);¹⁶ whereas, at 40°C , the water CA increased from 94.3° (flat glass plate) to 118.7° (capillary plate) which can be explained by the Cassie and Baxter equation (see Part S4 and Fig. S5, ESI[†]).¹⁷

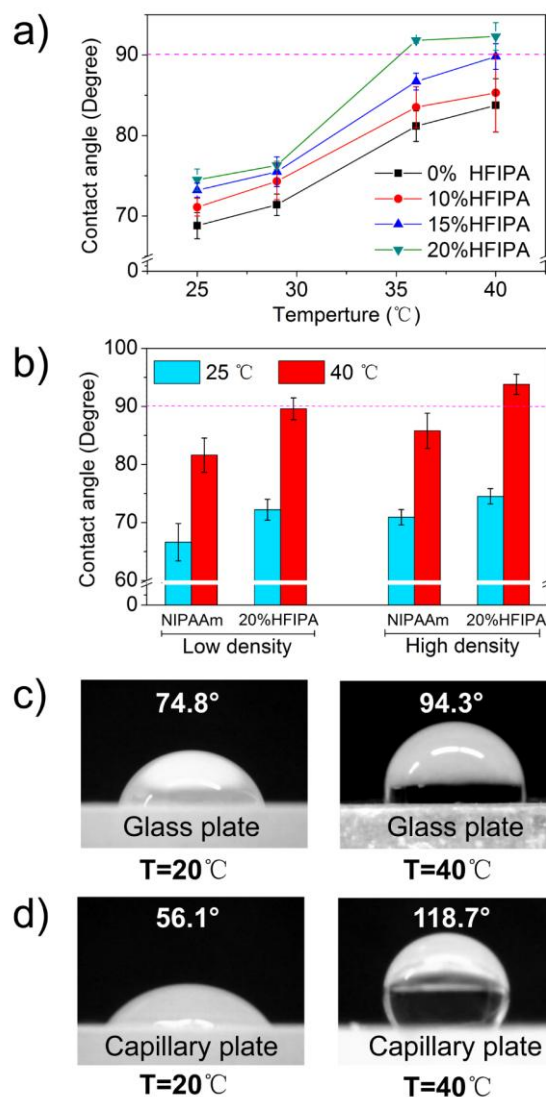


Fig. 1 Water CA on the flat glass substrate with (a) different HFIPA ratios and (b) different intensity of polymer. Photographs of water drop profile on (c) flat glass plate and (d) capillary plate at 20°C and 40°C , respectively.

To confirm the practical application of this switch for controllable water transportation, a transportation process was investigated with a starting temperature of 40°C , with a cooling down to 20°C . As shown in Fig. 2a, the capillary plate modified with a random order P(NIPAAm-co-HFIPA) brush fail to function as a switch within a short time, as anticipated. The water was retained on the surface after 10 min when the temperature was cooled to 20°C , and the corresponding CA changed from 118.2° to 113.3° . Further experiments indicated that the water penetrate through the capillary plate within nearly 22 min. This phenomenon can be attributed to the added hydrophobicity reagent HFIPA, which prolongs the time for transiting from intra-molecular hydrogen bonding to inter-molecular hydrogen bonding. To improve the switch properties, two new sequences of polymers were synthesized. One was the synthesis PNIPAAm first, followed by grafting the block copolymer P(NIPAAm-co-HFIPA) (Fig. 2b). The other sequence was the initially synthesized P(NIPAAm-co-HFIPA), which was then grafted on PNIPAAm (Fig. 2c). From the water transportation results, it can

be seen that both sequences can easily realize a switch function within 10 min when the temperature changes from 40 °C to 20 °C. However, the sequence b is slightly superior than sequence c for transportation modulation, the entire permeation transition cycle occurred within a shorter time (4.5±0.5 min). Therefore, a capillary plate with sequences of b polymer brush can be used for controllable water transportation with a high switch efficiency.

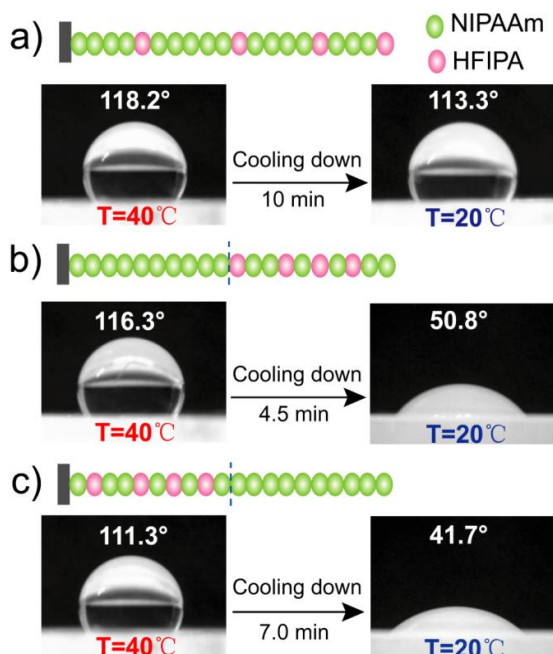


Fig. 2 The effect of block copolymer sequences on switching properties. (a) Random order of polymer. (b) First synthesis of PNIPAAm then grafted on P(NIPAAm-co-HFIPA). (c) Initial synthesis of P(NIPAAm-co-HFIPA) then grafted on PNIPAAm.

The temperature dependences of water CAs for P(NIPAAm-co-HFIPA) modified flat glass substrates and a capillary plate were studied in detail and results are shown in Fig. 3a. The findings indicate that the hydrophobic–hydrophilic transition temperature for flat glass substrates and the capillary plate were nearly identical. The LCST of the copolymer was about 30 °C, slightly lower than that for an individual PNIPAAm. This result confirms that the hydrophobic composition in the polymer were more conducive to intra-molecular hydrogen bond formation. Additionally, the thermally responsive wettability of the P(NIPAAm-co-HFIPA) modified capillary plate was greatly enhanced by the artificial structure, consistent with previous reports.^{10,11} Because of the thermally responsive switching between hydrophilicity and hydrophobicity was related to the surface chemical composition and surface roughness. The former provides the thermally responsive chemical change of the surface between hydrophilicity and hydrophobicity, and the latter enhances these properties.

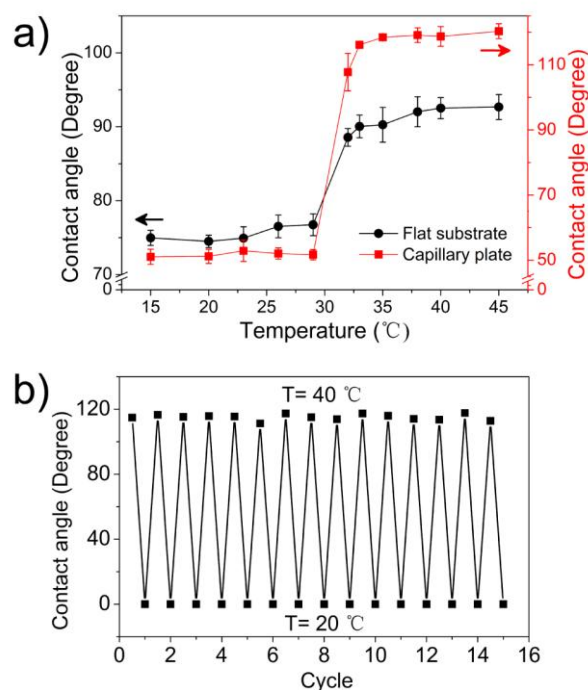


Fig. 3 (a) Temperature dependences of water CAs for P(NIPAAm-co-HFIPA) brush on a capillary plate and on a flat substrate. (b) Water CA measurements of the capillary plate modified with P(NIPAAm-co-HFIPA) were carried out alternately at 40 °C and 20 °C.

To study the reversibility and stability of switching, variations in the water CAs on a modified capillary plate when the temperature was repeatedly cycled from 40 °C to 20 °C was investigated. In these experiments, a filter paper was placed underneath of capillary plate. The water would be absorbed by the filter paper when it permeates to the bottom of the capillary plate. Therefore, the water CA was transiting to 0° at the "ON" state. It can be seen that the switch showed excellent responsiveness for more than 15 cycles (Fig. 3b). Meanwhile, a rapid transformation between "OFF" and "ON" occurred, as a single cycle lasts only a few minutes. The transportation process for a single cycle is shown in Fig. S7 (ESI†). Additionally, such a response persisted, even after the samples had been set aside for at least two months, without any special protection, indicating that the switch was mechanically and chemically stable.

In summary, we report on the development of a P(NIPAAm-co-HFIPA) block copolymer functionalized temperature-responsive switch for controllable water transportation. The ON/OFF state of the designed switching can be controlled by manipulating the temperature of the system. The system showed good water permeability at temperatures below 20 °C, and was water repellent at temperatures above 40 °C. The excellent controllability over aqueous solution transportation indicates that it has great potential for use in various important applications including intelligent microfluidic switching, water/oil separation, controllable drug release, and so on.

This work was financially supported by the High Technology Research Project by Tokyo Metropolitan Government.

Notes and references

Department of Applied Chemistry, Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University, Minamiohsawa,

COMMUNICATION

Hachioji, Tokyo 192-0397, Japan. Fax: +81-42-6772821; Tel: +81-42-6772835. E-mail: uchiyama-katsumi@tmu.ac.jp.

† Electronic Supplementary Information (ESI) available. Experimental procedures, EDX and XPS characterization data, images of water droplet transportation process. See DOI: 10.1039/c000000x/

- 1 (a) M. Tagliavacchi, O. Azzaroni and I. Szleifer, *J. Am. Chem. Soc.*, 2010, **132**, 12404; (b) X. Hou, W. Guo and L. Jiang, *Chem. Soc. Rev.*, 2011, **40**, 2385; (c) L. Ionov, N. Houbenov, A. Sidorenko, M. Stamm and S. Minko, *Adv. Funct. Mater.*, 2006, **16**, 1153. (d) E. K. Sackmann, A. L. Fulton and D. J. Beebe, *Nature*, 2014, **507**, 181.
- 2 (a) S. P. Adiga and D. W. Brenner, *Nano Lett.*, 2005, **5**, 2509; (b) M. Motornov, R. Sheparovych, E. Katz and S. Minko, *ACS Nano*, 2008, **2**, 41; (c) L. Cheng and D. Cao, *ACS Nano*, 2011, **5**, 1102.
- 3 T. P. Russell, *Science*, 2002, **297**, 964.
- 4 H. Ko, Z. Zhang, Y. L. Chueh, E. Saiz and A. Javey, *Angew. Chem. Int. Ed.*, 2010, **49**, 616.
- 5 G. H. Hwang, K. H. Min, H. J. Lee, H. Y. Nam, G. H. Choi, B. J. Kim, S. Y. Jeong and S. C. Lee, *Chem. Commun.*, 2014, **50**, 4351.
- 6 H. S. Lim, J. T. Han, D. Kwak, M. Jin and K. Cho, *J. Am. Chem. Soc.*, 2006, **128**, 14458.
- 7 J. Lahann, S. Mitragotri, T. N. Tran, H. Kaido, J. Sundaram, I. S. Choi, S. Hoffer, G. A. Somorjai and R. Langer, *Science*, 2003, **299**, 371.
- 8 (a) J. Zhou, G. Wang, J. Hu, X. Lu and J. Li, *Chem. Commun.*, 2006, 4820; (b) F. Xia, H. Ge, Y. Hou, T. Sun, L. Chen, G. Zhang and L. Jiang, *Adv. Mater.*, 2007, **19**, 2520.
- 9 (a) M. Szuwarzyński, L. Zaraska, G. D. Sulka and S. Zapotoczny, *Chem. Mater.*, 2013, **25**, 514; (b) E. Amstad, S. H. Kim and D. A. Weitz, *Angew. Chem. Int. Ed.*, 2012, **51**, 12499; (c) H. Ye, C. L. Randall, T. G. Leong, D. A. Slanac, E. K. Call and D. H. Gracias, *Angew. Chem. Int. Ed.*, 2007, **46**, 4991; (d) Y. Iwasaki, M. Sakiyama, S. Fujii and S. Yusa, *Chem. Commun.*, 2013, **49**, 7824; (e) 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 and A. Javey, *Nano Lett.*, 2011, **11**, 3239.
- 10 T. Sun, G. Wang, L. Feng, B. Liu, Y. Ma, L. Jiang and D. Zhu, *Angew. Chem. Int. Ed.*, 2004, **43**, 357.
- 11 Q. Fu, G. V. R. Rao, S. B. Basame, D. J. Keller, K. Artyushkova, J. E. Fulghum and G. P. López, *J. Am. Chem. Soc.*, 2004, **126**, 8904.
- 12 (a) J. Huang, X. Wang, X. Chen and X. Yu, *J. Appl. Polym. Sci.*, 2003, **89**, 3180; (b) T. Peng, and Y. L. Cheng, *J. Appl. Polym. Sci.*, 1998, **70**, 2133. (c) W. Song, F. Xia, Y. Bai, F. Liu, T. Sun and L. Jiang, *Langmuir*, 2007, **23**, 327.
- 13 R. Pelton, *J. Colloid Interface Sci.*, 2010, **348**, 673.
- 14 (a) J. P. Youngblood and T. J. McCarthy, *Macromolecules*, 1999, **32**, 6800; (b) B. Liu and F. F. Lange, *J. Colloid Interface Sci.*, 2006, **298**, 899; (c) D. Tian, X. Zhang, X. Wang, J. Zhai and L. Jiang, *Phys. Chem. Chem. Phys.*, 2011, **13**, 14606.
- 15 (a) T. Zhao, F. Q. Nie and L. Jiang, *J. Mater. Chem.*, 2010, **20**, 2176; (b) A. Chhabra, R. R. Kanapuram, T. J. Kim, J. Geng, A. K. da Silva, C. W. Bielawski, and C. H. Hidrovo, *Langmuir*, 2013, **29**, 8116.
- 16 R. N. Wenzel, *Ind. Eng. Chem.*, 1936, **28**, 988.
- 17 A. B. D. Cassie, and S. Baxter, *Trans. Faraday Soc.*, 1944, **40**, 546.