New responsive property of poly(ε-caprolactone) as the thermal switch from superhydrophobic to superhydrophilic†

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A reversible switch between superhydrophobicity at low temperature and superhydrophilicity at high temperature was fabricated by coating poly(ε-caprolactone) on a rough substrate, which resulted from the combination of the different adaptability of the polymer chain upon crystalline/amorphous phase transition and the optimized roughness.

Surfaces with responsive wettability have attracted much attention recently due to the great demand from micro-fluidic control, molecular separation, drug delivery, micro-device technology, *etc*.[1] Temperature change is a widely used environmental stimulus for responsive materials.[2] Up to now, most thermo-responsive surfaces have been those of polymers with a lower critical solution temperature (LCST). Wettability switching from superhydrophilicity to superhydrophobicity on increasing temperature has been demonstrated.[3] However, the inverse switching, which is from superhydrophobicity to superhydrophilicity on increasing temperature, is preferred in many cases. For example, such response of carriers for drug-delivery or bio-catalysts can promote drug permeability or reactant exchange upon local hyperthermia.[4] Grafting polymer chains with an upper critical solution temperature (UCST) could be an approach, but it is hampered by restricted choice and fabrication of polymer. Therefore, it is desirable and important to develop a facile method for such thermo-responsive surfaces.

In this study, we found that the rough surface of poly-(ε-caprolactone) (PCL) showed a thermo-response of switching from superhydrophobicity to superhydrophilicity upon temperature increase. The responsive property is considered to be achieved by taking advantage of the sharp change of polymer chain adaptability upon crystalline/amorphous phase transition. The films were fabricated by a simple solution process, which offers a versatile approach to adjust the switching range and temperature.

PCLs with different molecular weight (M_n = 2000 g/mol, 10 000 g/mol and 80 000 g/mol, namely PCL$_{2000}$, PCL$_{10\,000}$ and PCL$_{80\,000}$, respectively) were used in the experiment. The diluted PCL solution was pipetted onto silicon substrates,

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and dried thoroughly under vacuum at 120 °C (see experimental part in the ESI†). The polymer is crystalline at room temperature and its amorphous phase transition point is around 60 °C. The water contact angle (CA) changes at temperature below and above the phase transition temperatures are different depending on molecular weight.

The responsive wettability was first demonstrated on flat substrates. At room temperature, the CA on the PCL$_{2000}$ flat film declined after water droplet deposition on the surface. The CA on PCL$_{80\,000}$ film is quite stable at room temperature, but the CA response upon phase transition was less than 4°. However the PCL$_{10\,000}$ thin film exhibited a suitable CA switch between 88.1 ± 2.2° at 25 °C and 60.8 ± 1.3° at 60 °C (Fig. 1a).

Polymer phase transition causes many properties to change discontinuously, including surface tension.[6] It has been reported that during the liquid crystalline to isotropic phase transition, the interface tackiness can be changed as a result of chain re-conformation.[7] Nevertheless water has not been used as the test liquid in these studies. The PCL chain possesses groups with different polarities and shows good adhesion to substrates. The above observed thermo-response of the PCL surface should be attributed to the reorientation of the polymer chains at the surface (Fig. 1b). During the film formation, the hydrophobic groups are spontaneously enriched at the solid–air interface, therefore, the topmost surface are more
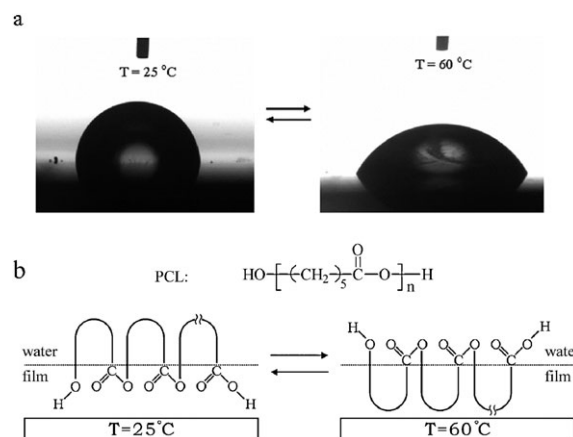
Fig. 1 Thermo-response of wettability on flat PCL$_{10\,000}$ surface. (a) Change of water drop profile when temperature was elevated from 25 °C to 60 °C. The water CA decreases from 88.1 ± 2.2° to 60.8 ± 1.3°. (b) Illustration of the proposed mechanism for the thermo-responsive PCL film. At room temperature (left), polymer chains are frozen by crystallisation; at the phase transition temperature (right), water can induce the reorientation of the hydrophobic/hydrophilic groups.

hydrophobic than the bulk.[8] The hydrophilic groups in the PCL chains are the end groups (COOH, OH), and the hydrophobic ones are $-(CH_2)_5-$ segments, while the ester groups are amphiphilic. At temperatures well below the crystalline/amorphous phase transition point, the PCL chains are frozen, thus water contact cannot induce the conformational change. When the phase transition temperature is reached, the polymer chains move much easily and water contact can readily induce the group reorientation. As a result, the hydrophilic end groups move to the water–PCL interface leading to the decrease of water CA.

The molecular weight related CA response suggests that the hydrophilic end groups (COOH, OH) play a important role in the wettability switching. The PCL with higher molecular weight possesses a lower ratio of hydrophilic end groups. The surface of $PCL_{80\,000}$ shows a lower response than that of $PCL_{10\,000}$, whereas the PCL_{2000} surface is more hydrophilic than the other two. On the other hand, the molecular weight also affects the mobility of polymer chains. The high ratio of end groups of PCL_{2000} gives high polymer chain mobility and low crystalline/amorphous phase transition temperature (Fig. S1†), which contributes to the decrease in the water CA at room temperature.

Enhanced wettability switching can be achieved by a suitable combination of the responsive materials and surface roughness.[5] Considering both response and stability, $PCL_{10\,000}$ was chosen for further experiment. To obtain the switch from superhydrophobic to superhydrophilic, surface roughness needs to be optimized.

In this study, the rough substrates are structured with cubic arrayed square pillars. They were introduced on flat silicon wafers by photolithography and an inductively coupled plasma deep-etching technique (See ESI†). The size of the square pillars are 10 μm × 10 μm in width, 30 μm in height, and the groove spacing varies from 10 μm to 60 μm. The responsive CA changes on all roughened surfaces were enhanced, though in different ranges, and the relationship between the groove spacing and the responding range is illustrated in Fig. 2a.

At room temperature, with increasing groove spacing from flat to 40 μm, the water CA increases gradually from 88.1 ± 2.2° to 166.9 ± 2.7°. Nevertheless, the water CA decreases on further increasing the groove spacing. As for surfaces with groove spacing of 50 and 60 μm, the water CA decreased to 135.3 ± 3.6° and 129.2 ± 2.4°, respectively. It is considered that when the groove spacing is smaller than 40 μm, only the top surface of the pillars can contact with water, and the air between the pillars kept is sealed as air pockets. This kind of contact is termed composite contact or Cassie state. With the increase in groove spacing, the air/solid area ratio increases. It decreases the composite surface tension, so the water CA increases.[9] When the groove spacing is larger than 40 μm, water can then drive away the air between the pillars and wet the surface beneath, thus contacting the surface in a wetting state or Wenzel state.

At the temperature around the phase transition point, the surface can be induced to be more hydrophilic. Assisted by capillary force, the droplets can wet the surface more than on a flat one.[10] Generally, the CAs decrease with increasing groove spacing. Water droplets once in a Cassie state can transfer to
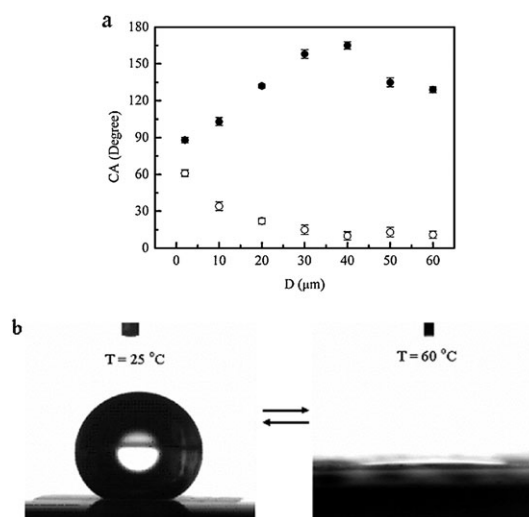

Fig. 2 (a) The relationships between the groove spacing and the water CA, at 25 °C (●) and at the $PCL_{10\,000}$ phase transitional temperature: 60 °C (○). D is the groove spacing between the nearest square pillars. (b) Switching of water CA between 166.9 ± 2.7° at 25 °C and 9.7 ± 1.8° at 60 °C on the surface with the groove spacing of 40 μm.

Wenzel state. The surface with groove spacing of 40 μm gives the largest CA responding range. As shown in Fig. 2b, the CA switched from superhydrophobic (CA = 166.9 ± 2.7° at 25 °C) to superhydrophilic (CA = 9.7 ± 1.8° at 60 °C).

The temperature dependence of water CA on flat and the rough surface (groove space = 40 μm) is shown in Fig. 3. The switching temperatures for both substrates are almost identical to the phase transitional point. The sharp CA change on the rough surface indicates that crystalline/amorphous phase transition may be a threshold that kinetically allows the polymer chains to respond to the environment.

We repeatedly cycled the temperature and recorded the water CA at 60 °C and 25 °C. As revealed in Fig. 4, the results show excellent reversible switching of water CA for at least 4 cycles.

In conclusion, the reversible switching between superhydrophobicity at low temperature and superhydrophilicity at high
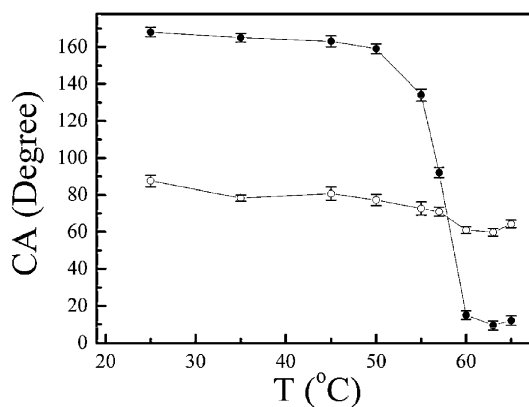
Fig. 3 Temperature (T) dependence of water CAs on $PCL_{10\,000}$ surfaces: flat (○) and rough surface with groove spacing of 40 μm (●).
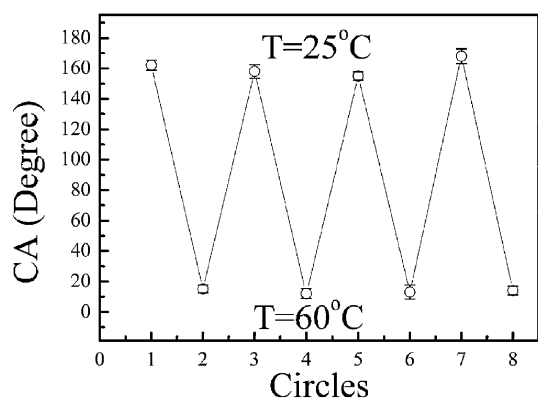
Fig. 4 The reversibility of the switching in 4 cycles. Half cycles: 60 °C; and integral cycles: 25 °C.

temperature has been demonstrated on a PCL rough surface. The wettability switch is achieved by a combination of optimized roughness and the remarkable change of polymer chain adaptability before and after the crystalline/amorphous phase transition. It is proposed that the hydrophilic end group ratio of the polymer chain plays an important role in the response. The surface is fabricated by a simple solution method, which can be broadened to a wide range of polymers and ready to be applied to many other smart systems.

Notes and references

1 T. P. Russell, *Science*, 2002, **297**, 964; I. Luzinov, S. Minko and V. V. Tsukruk, *Prog. Polym. Sci.*, 2004, **29**, 635; R. Langer and D. A. Tirrell, *Nature*, 2004, **428**, 487.
2 L. Feng, S. H. Li, Y. S. Li, H. J. Li, L. J. Zhang, Y. L. Song, B. Q. Liu, L. Jiang and D. B. Zhu, *Adv. Mater.*, 2002, **14**, 1857.
3 Z. B. Hu, Y. Y. Chen, C. J. Wang, Y. D. Zheng and Y. Li, *Nature*, 1998, **393**, 149; T. L. Sun, G. J. Wang, L. Feng, B. Q. Liu, Y. M. Ma, L. Jiang and D. B. Zhu, *Angew. Chem., Int. Ed.*, 2004, **43**, 357; M. S. Donovan, B. S. Sumerlin, A. B. Lowe and C. L. McCormick, *Macromolecules*, 2002, **35**, 8663.
4 S. Y. Lin, C. J. Ho and M. J. Li, *J. Control. Release*, 2001, **73**, 293; R. Dinarvand and M. J. Ansari, *Membrane Sci.*, 2003, **223**, 217.
5 X. J. Feng and L. Jiang, *Adv. Mater.*, 2006, **18**, 3063; S. T. Wang, Y. L. Song and L. Jiang, *J. Photochem. Photobiol. C*, 2007, **8**, 18; T. Onda, N. Shibuichi, N. Satoh and K. Tsuji, *Langmuir*, 1996, **12**, 2125; J. P. Youngblood and T. J. McCarthy, *Macromolecules*, 1999, **32**, 6800; T. L. Sun, L. Feng, X. F. Gao and L. Jiang, *Acc. Chem. Res.*, 2005, **38**, 644; E. A. Vogler, *Adv. Colloid Interface Sci.*, 1998, **74**, 69.
6 S. Wu, in *Polymer interfae and adhesion*, Marcel Dekker, Inc., New York, 1982.
7 G. de Crevoisier, P. Fabre, J. M. Corpart and L. Leibler, *Science*, 1999, **285**, 1246; K. Cho, J. H. Cho, S. Yoon, C. E. Park, J. C. Lee, S. H. Han, K. B. Lee and J. Koo, *Macromolecules*, 2003, **36**, 2009.
8 L. Feng, Y. L. Song, J. Zhai, B. Q. Liu, J. Xu, L. Jiang and D. B. Zhu, *Angew. Chem., Int. Ed.*, 2003, **42**, 800.
9 A. B. D. Cassie and S. Baxter, *Trans. Faraday Soc.*, 1944, **40**, 546; W. Chen, A. Y. Fadeev, M. C. Hsieh, D. Öner, J. Youngblood and T. J. McCarthy, *Langmuir*, 1999, **15**, 3395; T. J. McCarthy and D. Öner, *Langmuir*, 2000, **16**, 7777.
10 N. A. Patankar, *Langmuir*, 2003, **19**, 1249; N. A. Patankar, *Langmuir*, 2004, **20**, 7097; L. Barbieri, E. Wagner and P. Hoffmann, *Langmuir*, 2007, **23**, 1723; R. N. Wenzel, *Ind. Eng. Chem.*, 1936, **28**, 988; R. Wang, K. Hashimoto, A. Fujishima, M. Chikuni, E. Kojima, A. Kitamura, M. Shimohigoshi and T. Watanabe, *Nature*, 1997, **388**, 431; J. Bico, C. Tordeux and D. Quéré, *Europhys. Lett.*, 2001, **55**, 214; J. Bico, U. Thiele and D. Quéré, *Colloids Surf. A*, 2002, **206**, 41.