On-Demand Liquid Transportation Using Bioinspired Omniphobic Lubricated Surfaces Based on Self-Organized Honeycomb and Pincushion Films

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In this work, on-demand control of liquids is realized by using elastic, patterned omniphobic surfaces. This paves the way for novel microfluidics, as well as liquid harvesting, transportation, and manipulation technologies. Inspired by the lubricating properties of pitcher plants, microstructured 1,2-polybutadiene honeycomb and pincushion films obtained by self-organization are fluorinated by the ene-thiol reaction and infused with fluorinated lubricant to obtain omniphobic liquid-repellent surfaces. Unlike conventional bioinspired omniphobic surfaces, the liquid repellency of the fabricated surface can be programmed by changing the surface microstructures via patterning of the film. Furthermore, the elasticity of the omniphobic film is suitable for controlling the repellency through external stimuli. The method presented here for the fabrication of lubricant-infused omniphobic microstructured surfaces is also simple, cost-effective, and can be scaled for large area fabrication.

1. Introduction

Surfaces that repel both high and low surface tension liquids are the subject of intense research, both in science and industry. Traditionally, materials with self-cleaning,[1] antifouling,[3] drag reduction,[4] and corrosion prevention[5] properties, and stain-free clothing and spill-resistant wear[2] are fabricated by using superhydrophobic and superomniphobic materials, famously inspired by self-cleaning lotus leaves. Although liquid-repellent surfaces based on the lotus leaf model have advanced, several challenges, such as the loss of the repellency under high pressure and upon destruction of the microstructures, have remained unsolved and have hindered the practical use of such surfaces.

Inspired by the surface of carnivorous pitcher plants, Aizenberg and co-workers reported the possible fabrication of a highly liquid-repellent surface, by infusing the surface microstructures with a liquid lubricant (slippery liquid-infused surfaces (SLIPS)).[6–12] In contrast to lotus leaves, the liquid infused surface requires a fluid/fluid interface between the lubricant and the immiscible liquid to be repelled. For a stable repellency, the interfacial energy of the lubricant layer on the surface has to be smaller than that of the liquid to be repelled. Furthermore, the microstructures are required to retain the lubricant through capillary force. Superomniphobic SLIPS can be obtained by the infusion of the microstructures with fluorinated lubricants, which are immiscible with most liquids. Because the interfacial tension between the fluorinated lubricant and the surface must be reduced to maintain this layer of lubricant stably, fluorinated surfaces are also required. Additionally, microstructures on the surface must be on a micrometer scale to match the capillary length of the fluorinated lubricant.

Controlling and inducing the movement of liquid spatiotemporally on a surface has attracted interest from science and industry, because it paves the way for novel microfluidic systems,[13,14] and liquid harvesting, transportation, and manipulation technologies.[15–20] It has been reported that by changing the repellency of a surface, the movement of liquids on the surface can be allowed or stopped. In conventional techniques, the movement of a liquid on a surface is mainly controlled by manipulating the interfacial energy between the surface and the liquid[21] through changing the chemical properties of a surface via chemical,[22] electrochemical,[23,24] or photochemical[25] methods. However, the surface structure is also an important factor that affects the wetting behavior of a liquid on a surface. The repellency toward liquids can be tuned by controlling the surface structure, and thus the movement of liquid on a surface can be programmed and controlled.

The next generation of SLIPS is expected to have tunable, programmed repellency for an on-demand transportation and manipulation of liquid along their surfaces. Two strategies can be adapted to create a system for effective spatio-temporal on-demand transport of liquid. The first strategy is to introduce a nonrepellent surface spatially in a mainly liquid-repellent surface. For example, in surface tension confined microfluidics,[26] a nonrepellent pattern area in a repellent plane works as an anchoring point for the liquid and restricts its movement. The second strategy is to control the movement of the liquid temporally by changing the microstructure via an external stimulus. Therefore, a fabrication method for a microstructured surface

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DOI: 10.1002/adfm.201501020

is needed that fulfills the SLIPS requirement, that can be patterned, and the wettability of which can be changed in response to external stimulus.

The breath figure method for fabricating microstructured surfaces has been an area of extensive research because it enables the one-step fabrication of highly ordered honeycomb structures by self-organization. Honeycomb-like porous structures (HC) can easily be obtained by using water droplets as templates through casting a polymer solution in humid conditions.[27–32] By simply peeling off the top layer of the HC film, pincushion-like structures (PC) can also be obtained.[34] This method has several advantages compared with traditional microfabrication methods, including easy fabrication on meter scale areas,[35] high controllability of pore size from the sub-micrometer to micrometer-scale, fabrication on non-flat surfaces,[36] and a wide variety of hydrophobic and hydrophilic[31,34,37,42,44] polymers that are suitable for the fabrication method.

In particular, HC and PC films made of 1,2-polybutadiene (PB), which is a synthetic rubber widely used in industry, are robust and elastic. These properties allow the microstructures to change form under external stimuli, such as stretching and releasing. In addition, the PB HC and PC film can also be patterned by cross-linking the PB under UV irradiation.[38,39] Finally, the surface chemistry of the PB films can be changed by the ene-thiol click reaction, which is a universal, highly efficient method for the functionalization of vinyl groups by the free-radical addition of thiols onto double bonds.[40,41] The reaction of a fluorinated thiol reagent with PB can convert the microstructured surfaces into low surface energy materials that can stably contain the fluorinated lubricant on their surfaces. These three features make microstructured PB well suited for the fabrication of SLIPS that can control the movement of liquids on demand.

In this paper, we report the fabrication of omniphobic SLIPS by the fluorination of 1,2-polybutadiene HC and PC films by using the ene-thiol reaction and the infusion of fluorinated lubricant. Furthermore, we also investigate the application of the SLIPS to an on-demand liquid transportation system.

2. Results and Discussion

2.1. Fabrication of Fluorinated HC and PC Films

HC films were prepared by depositing a 5 g L^{-1} chloroform solution of PB and Polymer 1 (PB:Polymer 1 = 10:1 w/w) on a glass substrate or polyethylene terephthalate substrate of size 10 × 30 cm under a flow of humid air (relative humidity ≈90%, velocity of 130 L min^{-1}) and ambient temperature (**Figure 1**).[33,35] PC films were prepared by peeling off the top layer of the HC film using a sheet of adhesive tape.[34] The HC and PC structures were examined by scanning electron microscopy (SEM). The SEM image (**Figure 2**a) clearly shows hexagonally arranged 5–6 µm micropores in a highly ordered HC film.

By peeling off the top layer with adhesive tape (Figure 2b), each pillar was broken at its center and a highly ordered PC film with a pillar height of 2–3 µm was obtained. The minimum distance between two adjacent pillars was 7–8 µm. According to our calculations, the capillary length (capillary length = surface tension of liquid/(density × gravitational acceleration)$^{1/2}$) of the fluorinated lubricant was 950 µm. Thus, each of the films had a size in the order of several micrometers, which is an order of magnitude smaller than the capillary length of the fluorinated lubricant.

The surface chemistry of the PB HC film was analyzed by Fourier transform infrared (FT-IR) after the ene-thiol reaction. The FT-IR spectra showed a C–F vibration at 1203 cm^{-1} on the PB HC film after the ene-thiol reaction (Figure 2c), whereas no such peak was observed on the untreated PB HC film.

^{1}H-NMR (400 MHz, $CDCl_3$) of the film after the ene-thiol reaction contained a chemical shift at δ_H 2.8–2.9 (m, CH_2–S–CH_2–CH_2–C_6F_{13}) suggesting it was successful (Figure S4, Supporting Information). To evaluate the surface chemistry of the microstructured films after the ene-thiol reaction, the contact

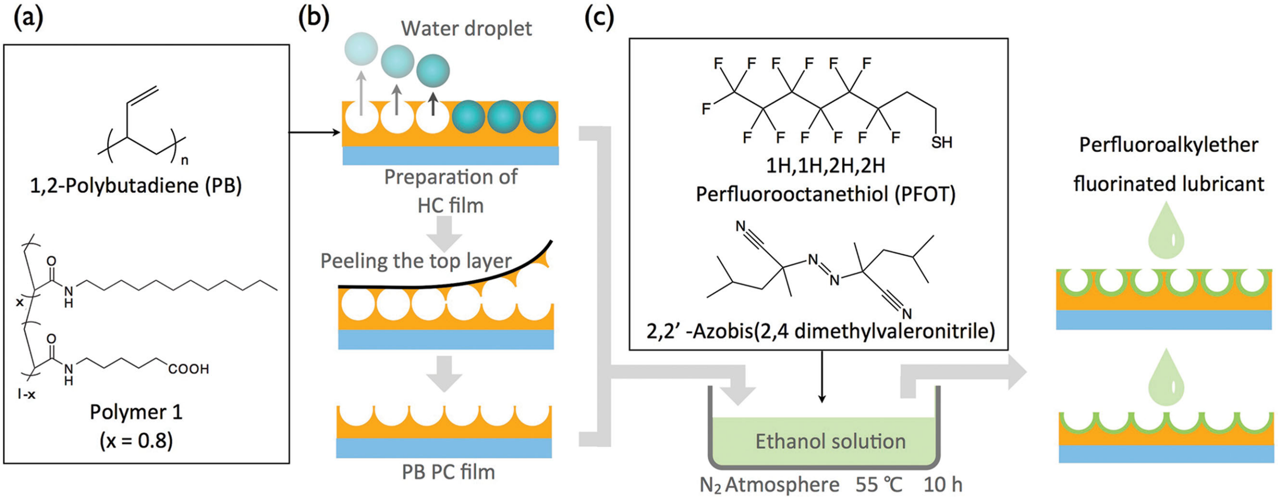

Figure 1. a) Structures of PB and Polymer 1 and b) schematic of the fabrication process of HC and PC films. c) The obtained PB HC and PC films were immersed in ethanol solution of PFOT and ADV in a N_2 atmosphere at 55 °C for 10 h.

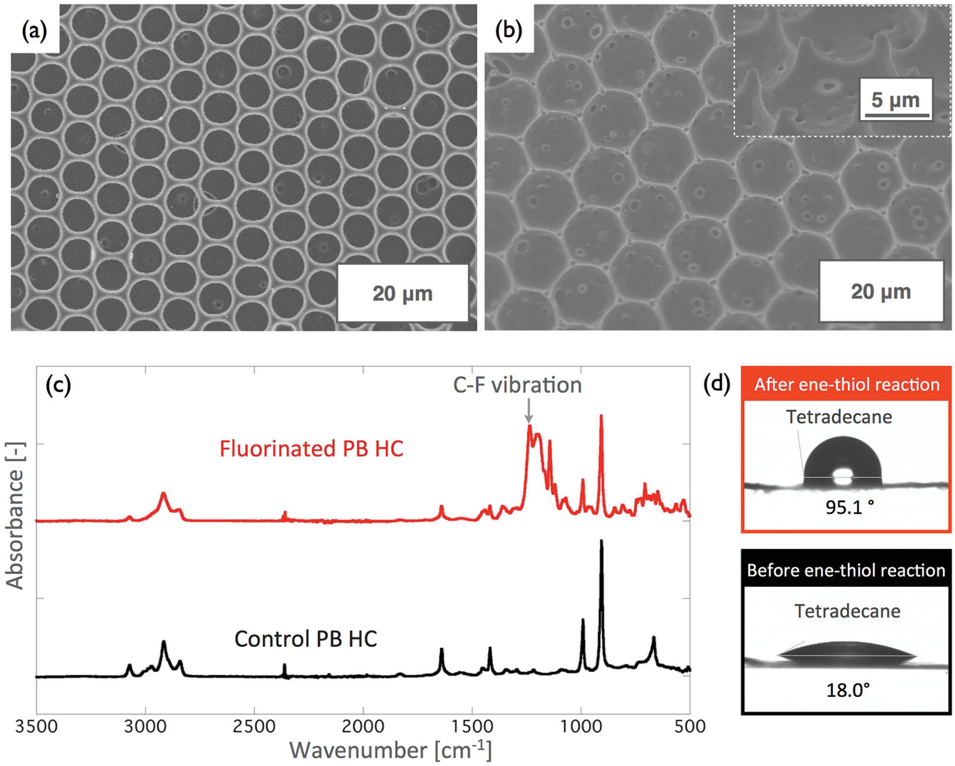

Figure 2. HC film obtained by casting a chloroform solutions of PB and Polymer 1 (weight ratio PB:Polymer 1 = 10:1) on a PET film under humid conditions at ambient temperature. a) SEM image of HC film surface after fluorinated treatment. b) SEM image and tilted image of the PC film surface obtained by peeling the top layer. c) FT-IR spectrum of a PB HC film before (black) and after (red) the ene-thiol reaction, obtained in the ATR mode. d) Contact angle of a tetradecane droplet (0.5 µL) on a PB HC film before (black) and after (red) the reaction.

angles of tetradecane (0.5 µL), which normally wets PB because of its low surface tension, on the PB HC film before and after the reaction were measured. The contact angles on the HC film before the reaction was 18.0° and it increased to 95.1° after, suggesting that the surface of the PB film was fluorinated by the ene-thiol click reaction (Figure 2d).

2.2. Measurement of the Liquid Repellency of the Lubricant-Infused PB HC and PC Film

The liquid repellency of the lubricant-infused fluorinated PC and HC film was investigated. Each of the films was inclined by 7.5°, and 15 µL droplets of water (high surface tension) and tetradecane (low surface tension) were released on the lubricant-infused HC and PC film.

Figure 3a,b shows pinning of the water and tetradecane droplet on the lubricant-infused HC film. In contrast, both liquids were repelled by the lubricant-infused PC film (see Movie S1, Supporting Information). The differences in the repellency of these two types of films were investigated by observing the lubricant layer on each of the films after casting the liquid droplets. The optical microscopy images of the lubricant-infused HC film, the lubricant on the upper layer was displaced, leaving a naked fluorinated PB surface in contact with the liquid (Figure S7, Supporting Information). This displacement of the lubricant was not observed for the PC film. Because of the high surface ratio of the polymer surface that is in contact with the liquid to be repelled, pinning of the liquid is likely to occur in the uncovered region of the HC film.

These results show that the PC structure is most suited for creating the required liquid-repellent surface. We measured the contact angle hysteresis and sliding angle of different liquids on the lubricant-infused PC film to investigate the repellency of the film in detail. We defined the sliding angle as the angle at which the gravitational force that pulls the liquid droplet downward equals the adhesion force of the liquid on the surface, causing the liquid to start sliding along the surface. The contact angle hysteresis is defined as the difference between the advancing angle and receding angle of the liquid droplet at the sliding angle.

Droplets of water, ethylene glycol, tetradecane, and paraffin oil (10 µL each) were cast on the film. The contact angle hysteresis (left axis, blue plot) and sliding angle (right axis, red plot) of different liquids are plotted according to the surface tension in Figure 3b. A very low sliding angle was observed for each of the liquid droplets (water: 5.4°, ethylene glycol: 3.9°, tetradecane: 3.3°) as well as a very low contact angle hysteresis (water: 1.9°, ethylene glycol: 4.6, tetradecane: 2.0°). For lotus leaf-inspired liquid-repellent surfaces, the reported sliding angle for liquid-repellent surfaces are <5°. Consequently, our results demonstrate the high liquid repellency of the fluorinated lubricant-infused PC film.

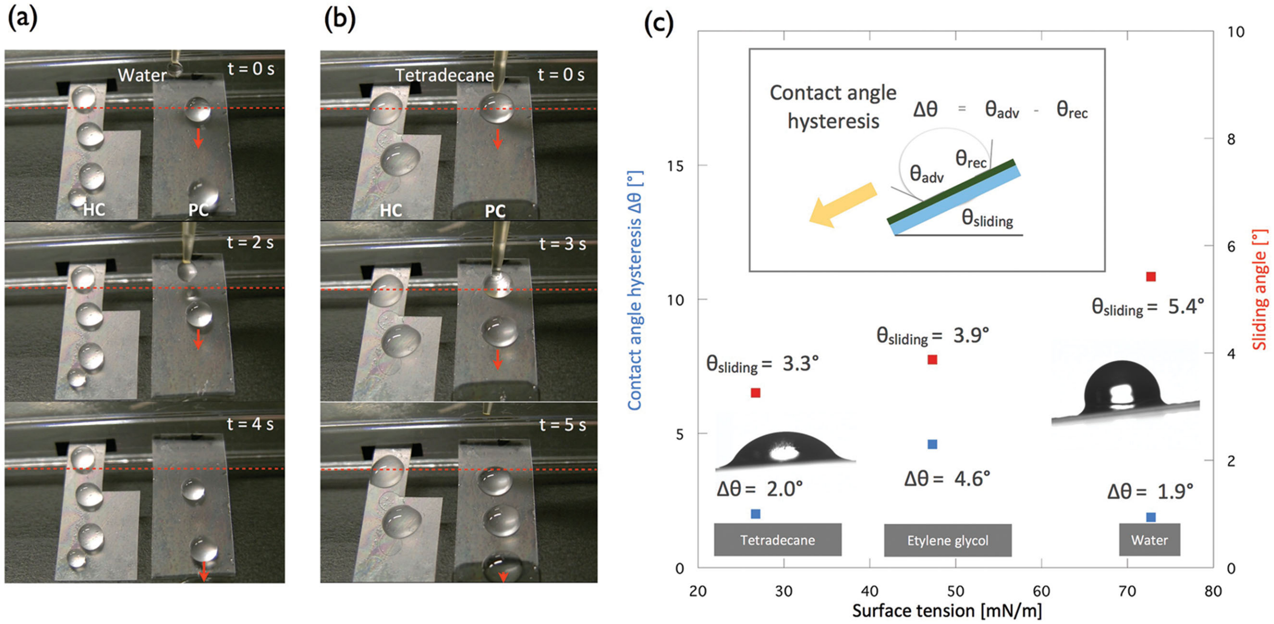

Figure 3. Liquid repellency of lubricant-infused HC and PC films tested with a) water and b) tetradecane droplets (10 µL). c) Contact angle hysteresis and sliding angle of different liquids on the lubricant-infused PC.

2.3. Patterning of PB HC and PC Films

We suggest that by creating a hybrid microstructured surface composed of HC and PC areas, the movement of the liquid on the hybrid plane can be controlled and programmed beforehand.[43] The HC area on the surface is expected to function as a pinning site. Therefore, by creating a linear HC area surrounded by a PC area, after fluorination of the film and infusion of the lubricant, the HC area should function as a guide that restricts the movement of the liquid droplet. This paves the way for a new method for creating programmable liquid-infused 2D microfluidics.[24,26]

However, in the fabrication of the 2D microfluidics, HC structures must be finely incorporated into a plane mostly consisting of PC structures. Therefore, a method for leaving micro areas of HC is required because the current method we used for PC fabrication based on peeling the upper layer of the HC is not sufficiently accurate for micropatterning. We have previously reported that a PC structure can be obtained from a HC structure by ultrasonicating the film (**Figure** 4a). However, for this method, the HC film material must be stiff enough for the pillars in the HC structure to break and produce a PC structure (Figure 4b). For example, a HC film made of polystyrene, which is a high elastic modulus polymer, is converted into a PC film after ultrasonication in water. However, for low elastic modulus polymers, the HC structure is maintained, even after the ultrasonication. Our research team has reported recently that a PB HC film can be cross-linked by UV irradiation.[38,39] By performing the UV irradiation under nitrogen, it was expected that the elastic modulus of the film could be controlled by regulating the irradiation site and time on the PB film. By applying a photomask during the irradiation process, it was expected that the PB HC film could be patterned along the same plane. The elastic modulus of the nonmasked area of the PB HC should increase because of the cross-linking of the polymer, whereas the masked area retains its low elastic modulus. As shown in the Figure S8, Supporting Information, we found that a PC structure formed on rigid region (e.g., PS) after ultrasonication treatment though soft PB region remained. Since the stiffness of UV-irradiated region increased with increasing UV irradiation time,[39] a PC structure was formed on UV-irradiated region of PB HC film (see Figure S8, Supporting Information).

To leave a micro area of HC in a PC film, we combined the photopatterning of the PB HC using a mask, followed by ultrasonication in water. We expected that the masked areas would remain as HC because of their low elastic modulus, whereas the nonmasked areas would cross-link and be converted to PC upon ultrasonication.

The fluorinated PB HC was irradiated with UV light (λ = 365 nm) for 90 min under nitrogen. The film was partly masked with a 500 µm wide silicon plate. The film was then introduced to a bath filled with water and ultrasonicated for 10 min. The film was dried in a vacuum oven at ambient temperature, and then infused with fluorinated lubricant.

Figure 4b shows an optical image of the film after ultrasonication in water. HC, which was slightly whiter than the PC that surrounded it, remained where the film was masked, whereas the unmasked area was converted to a PC structure. A magnified image of the HC and PC structure is shown in Figure 4c. The HC structure remained intact where the film was masked and the boundary between the PC and HC structures was clear.

The concept of the HC structure as a liquid guide in the liquid-repellent surface was tested (see Movie S2, Supporting Information). After the film was infused with the lubricant, it was inclined by 21° and 30 µL water droplets were cast (Figure 4d,e). The water droplet rolled straight down when cast

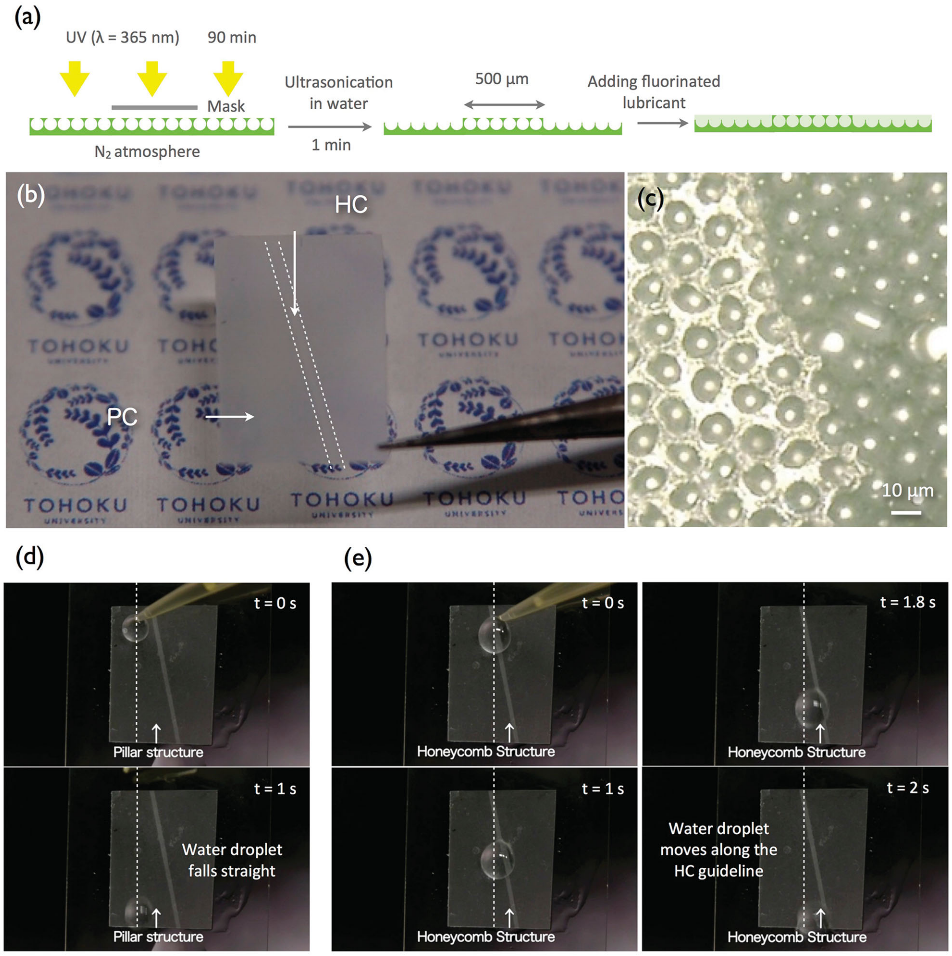

Figure 4. a) Schematic of the experimental procedure for the fabrication of patterned liquid-repellent surface. Image of b) the patterned film and c) the magnified image. The HC structure remained where the film was unexposed to UV. d,e) The difference in the adhesion in PC area and HC area. d) The water droplet falls straight in PC area. e) In contrast, the water droplet cast on the HC guide moves along the guide.

on the lubricated PC surface (Figure 4d). However, when the water droplet was cast on the HC guide, it moved along the line, suggesting that the partial pinning of the liquid droplet is an effective method for guiding and restricting the movement of a liquid on a repellent surface (Figure 4e).

2.4. Controlling the Liquid Repellency

Next, we exploited the elastomeric property of the microstructured PB film to control the liquid repellency by mechanical strain induced on the lubricant-infused film (**Figure 5**). The clamp holding the lubricant infused PC film was inclined by 30° and a water droplet (15 μL) was cast on the film. The behavior of the water droplet is shown in Figure 4. First, the water droplet slid on the surface of the film when the film was at its initial length. Upon stretching the film, the sliding speed of the water droplet decreased gradually. The water droplet completely stopped moving when the film was stretched to about twice its initial length and remained pinned to the surface of the film. As soon as the strain was released, the droplet restarted moving along the film. A similar slip-stop movement was also observed with tetradecane.

To investigate the nature of this stretching induced pinning of liquid droplet on lubricant-infused PC film, surface SEM images of the film in the initial state and in the stretched state were taken (Figure S10 and Movie S3, Supporting Information). In the unstretched film, the tips of the PC structures were partly above the surface of the lubricant. However, when the film was stretched to twice its initial length the entire PC structures were above the lubricant surface. This explains the observed high adhesion of the water droplet to the stretched film. By stretching the film, the height of the lubricant decreased in response to the increase of the surface area, resulting in the total exposure of the PC structures above the lubricant surface. Consequently, the emerging PC structures acted as pinning sites for the liquid droplets. Finally, when the strain was released, the PC structures were reimmersed under the lubricant surface, causing the liquid droplet to be mostly in contact with the lubricant layer and to slide over the film surface. Moreover, top parts of PCs were not fluorinated since PC films prepared after fluorination by en-thiol reaction of HC

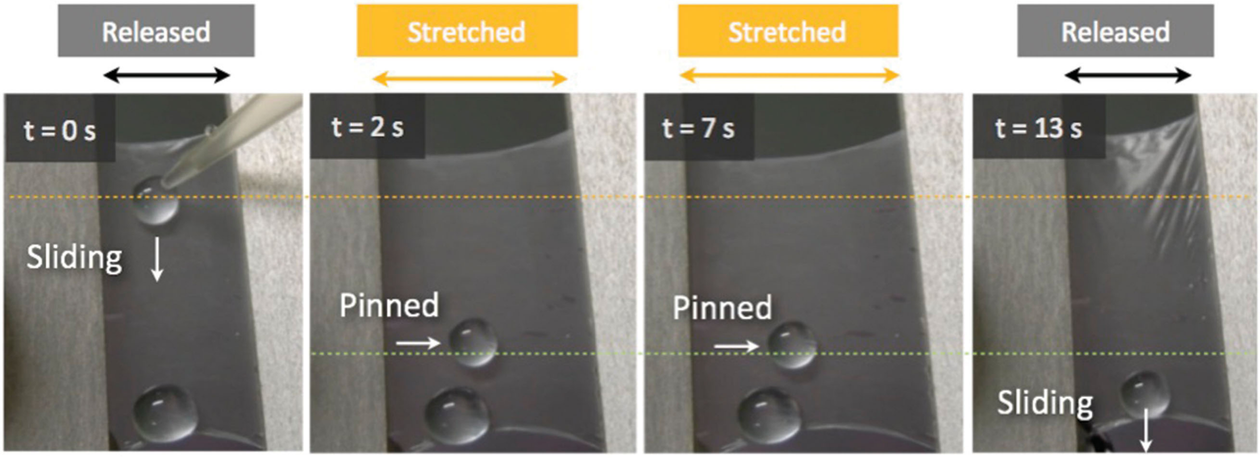

Figure 5. The film was set on a pair of arms with clips connected to a home-made uniaxial stretcher. A water droplet (15 μL) was cast on the lubricant-infused film and the pinning of the droplet was observed upon stretching of the film.

films. The surface wettability of top parts of PCs was same as hydrocarbon PB, which had lower water repellency than fluorinated one, the water droplets easily trapped.

3. Conclusion

High liquid repellency was observed in the fluorinated lubricant-infused PC film, after PB was fluorinated by the ene-thiol reaction and infused with a perfluoroalkylether lubricant. Both high and low surface tension liquids showed very low contact angle hysteresis and sliding angle when cast on the substrate. However, the adhesion of liquids was observed for the lubricant-infused HC film. The difference in the adhesion force between the liquid and the different substrates was discussed. We then used this difference in the repellency to create a surface with hybrid PC and HC structure. A combination of UV patterning of the PB HC film and ultrasonication of the treated film underwater incorporated a microscale HC area into a PC plane. After infusing the film with a fluorinated lubricant, we were able to create a HC guide for liquid droplets in a slippery PC plane and to program the movement of a liquid droplet on the surface.

Furthermore, the elastomeric properties of PB were used for the on-demand control of liquid repellency of the lubricant-infused PC film. By stretching and releasing the elastomer film, we were able to control the height of the lubricant layer and control the ratio of the underlying pincushion structure that appears above the lubricant surface. Pinning of the liquid droplet was observed when the elastomeric film was stretched, and sliding was observed when the film was released to its original length. This novel material with on-demand tunable repellency paves the way for active microfluidics, and novel liquid harvesting, transport, and manipulation technologies.

4. Experimental Section

Preparation of the HC and PC Films: 1,2-Polybutadiene ($\bar{M}_w$ = 250 000 g mol^{-1}; Figure 1a) and chloroform were purchased from JSR Co, Ltd. (Tokyo, Japan) and Wako Chemicals Inc. (Osaka, Japan), respectively. An amphiphilic copolymer (Polymer 1; $\bar{M}_w$ = 40 000 g mol^{-1}; Figure 1a) was synthesized by copolymerizing *N*-dodecylacrylamide and 6-acylamidehexanoic acid.[33,35] HC films were prepared by depositing a 5 g L^{-1} chloroform solution of PB and Polymer 1 (PB:Polymer 1 = 10:1 w/w) on a glass substrate or polyethylene terephthalate substrate of size 10 × 30 cm under a flow of humid air (relative humidity ≈90%, velocity of 130 L min^{-1}) and ambient temperature.[33,35] PC films were prepared by peeling off the top layer of the HC film using a sheet of adhesive tape.[34]

Fluorination of the HC and PC Films by the Ene-thiol Reaction: The PB HC and PC films were treated with a fluorinated reagent by using the ene-thiol click reaction between the thiol-terminated molecule 1H,1H,2H,2H-perfluorooctanethiol (PFOT) and the vinyl group of the PB (Figure S1, Supporting Information). The film was immersed in an ethanol solution containing 20 g L^{-1} PFOT (30 mL) with a catalytic amount of 2,2′-azobis(2,4 dimethylvaleronitrile) as a radical initiator under nitrogen for 10 h at 55 °C.

Characterization of PB HC and PC Film after the Ene-thiol Reaction: We observed the surface structures of the treated HC and PC films by field-emission scanning electron microscopy (SEM; S-5200, Hitachi, Tokyo, Japan). The surface chemistry of the films was examined by measuring the attenuated total reflectance (ATR) during FT-IR spectroscopy (FT-IR 610TY, JASCO, Tokyo, Japan), and by ^{1}H-NMR (Bruker, 400 MHz).

Static contact angles were recorded with a drop shape analysis system (Dropmaster 300, KYOWA, Tokyo, Japan) equipped with a video camera. Droplets of water and tetradecane (0.5 μL) were released using a microsyringe on the HC and PC film before and after the ene-thiol click reaction. The static contact angles were measured at a neutral tilting angle (0°).

Measurement of the Liquid Repellency of the Lubricant-Infused PB HC and PC Film: We used a perfluoroalkylether (Krytox 100, Dupont, USA) as the fluorinated lubricant. The fluorinated HC and PC films were infused with the lubricant. Several drops of the fluorinated lubricant were cast onto the fluorinated HC and PC films, and then, the excess lubricant was removed by spinning at its rate 1000 rpm for 1 min. The thickness of the lubricant was around 10 μm from SEM observation. The static and dynamic contact angles were recorded by placing the lubricant-infused HC and PC films on an inclinable arm (Figure S2, Supporting Information). Droplets of water, ethylene glycol, and tetradecane (10 μL) were released on each of the films by using a microsyringe. The static contact angles were measured at a neutral tilting angle (0°). The inclinable arm was then tilted until the liquid began to slide down the sample surface. Subsequently, the advancing (θ_A), receding (θ_R), and sliding (θ_S) angles were determined.

Patterning of PB HC and PC Films: A mask with a 500 μm wide rectangular pattern was placed on the fluorinated PB HC film. The film was then exposed to UV light ($\lambda = 365$ nm) for 90 min under nitrogen to cross-link the polymer.[38,39] After exposure to UV light, the film was ultrasonicated in water for 10 min to remove the upper part of the HC film and obtain a PC structure where it had hardened through cross-linking. The surface structure was observed by optical microscopy. Fluorinated lubricant was then added to the film. The liquid repellency was verified by casting a 30 μL water droplet on the surface.

Controlling the Liquid Repellency: The liquid repellency of the lubricant-infused PC film was controlled by pulling on the film. Each side of the prepared fluorinated PC film was attached with carbon tapes to movable arms and then inclined by 30° (Figure S3, Supporting Information). We were able to stretch or release the PB film by pulling the arms away or by bringing them closer. Fluorinated lubricant was then infused in the PC film to obtain the SLIPS film. The liquid repellency was verified by casting 30 μL water and tetradecane droplets during stretching and releasing the film.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This work was in part supported by Grant-in-Aid for Challenging Exploratory Research (Grant No. 26620170).

Received: March 15, 2015
Revised: April 27, 2015
Published online: May 21, 2015

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[1] T. L. Sun, L. Feng, X. F. L. Gao, Jiang, *Acc. Chem. Res.* **2002**, *38*, 644.
[2] B. X. Leng, Z. Z. Shao, G. de With, W. H. Ming, *Langmuir* **2009**, *25*, 2456.
[3] C. Lee, C.-J. Kim, *Phys. Rev. Lett.* **2011**, *106*, 1.
[4] J. Genzer, K. Efimenko, *Biofouling* **2006**, *22*, 339.
[5] S. J. Pan, A. K. Kota, J. M. Mabry, A. Tuteja, *J. Am. Chem. Soc.* **2013**, *135*, 578.
[6] T.-S. Wong, S. H. Kang, S. K. Y. Tang, E. J. Smythe, B. D. Hatton, A. Grinthal, J. Aizenberg, *Nature* **2001**, *477*, 443.
[7] N. Vogel, R. A. Belisle, B. Hatton, T. S. Wong, J. Aizenberg, *Nat. Commun.* **2013, 4,** 2176.
[8] X. Yao, Y. Hu, A. Grinthal, T. S. Wong, L. Wahadevan, J. Aizenberg, *Nat. Mater* **2013**, *12*, 529.
[9] C. Shillingford, N. MacCallum, T. S. Wong, P. Kim, J. Aizenberg, *Nanotechnology* **2014**, *25*, 014019.
[10] X. Huang, J. D. Chrisman, N. S. Zacharia, *ACS Macro Lett.* **2013**, *2*, 826.
[11] W. Ma, Y. Higaki, H. Otsuka, A. Takahara, *Chem. Commun.* **2013**, *49*, 597.
[12] J. D. Smith, R. Dhiman, S. Anand, E. Eeza-Garduno, R. E. Cohen, G. H. McKinley, K. K. Varanasi, *Soft Matter* **2013**, *9*, 1772.
[13] G. M. Whitesides, *Nature* **2006**, *442*, 368.
[14] L. Mazutis, J. Gilbert, W. L. Ung, D. A. Weitz, A. D. Griffiths, J. A. Heyman, *Nat. Protoc.* **2013**, *8*, 870.
[15] A. R. Parker, C. R. Lawrence, *Nature* **2001**, *414*, 33–34.
[16] R. P. Garrod, L. G. Harris, W. C. Schofield, J. McGettrick, D. O. Teare, J. P. Badyal, *Langmuir* **2007**, *23*, 689.
[17] D. Ishii, H. Yabu, M. Shimomura, *Chem. Mater.* **2009**, *21*, 1799.
[18] D. Ishii, M. Shimomura, *Chem. Mater.* **2013**, *25*, 509.
[19] Y. H. Lai, J. T. Yang, D. B. Shieh, *Lab Chip* **2010**, *10*, 499.
[20] K. Li, J. Ju, Z. Xue, J. Ma, L. Feng, G. Gao, L. Jiang, *Nat. Commun.* **2013**, *4*, 2276.
[21] M. Grunze, *Science* **1999**, *283*, 41.
[22] M. K. Chaudhury, G. M. Whitesides, *Science* **1992**, *256*, 1539.
[23] B. S. Gallardo, V. K. Gupta, F. D. Eagerton, L. I. Jong, V. S. Craig, N. L. Abbott, *Science* **1999**, *283*, 57.
[24] M. G. Pollack, R. B. Fair, A. D. Shenderov, *Appl. Phys. Lett.* **2000**, *77*, 1725.
[25] K. Ichimura, S. K. Oh, M. Nakagawa, *Science* **2000**, *288*, 1624.
[26] I. You, T. G. Lee, Y. S. Nam, H. Lee, *ACS Nano* **2014**, *8*, 9016.
[27] G. Widawski, M. Rawiso, B. Francois, *Nature* **1994**, *369*, 387.
[28] S. A. Jenekhe, X. L. Chen, *Science* **1999**, *283*, 372.
[29] M. H. Stenzel, *J. Mater. Chem.* **2003**, *13*, 2090.
[30] U. H. F. Bunz, *Adv. Mater.* **2006**, *18*, 973.
[31] N. Maruyama, T. Koito, J. Nishida, T. Sawadaishi, X. Cieren, K. Ijiro, O. Karthaus, M. Shimomura, *Thin Solid Films* **1998**, *327*, 854.
[32] O. Karthaus, N. Maruyama, X. Cieren, M. Shimomura, H. Hasegawa, T. Hashimoto, *Langmuir* **2000**, *16*, 6071.
[33] M. Kojima, Y. Hirai, H. Yabu, H. M. Shimomura, *Polym. J.* **2009**, *41*, 667.
[34] H. Yabu, M. Takebayashi, M. Tanaka, M. Shimomura, *Langmuir* **2005**, *21*, 3235.
[35] H. Yamazaki, K. Ito, H. Yabu, M. Shimomura, *Soft Matter* **2014**, *10*, 2741.
[36] L. Li, Y. Zhong, J. Gong, J. Li, C. Chen, B. Zeng, Z. Ma, *Soft Matter* **2011**, *7*, 546.
[37] J. Kamei, Y. Saito, H. Yabu, *Langmuir* **2014**, *30*, 14118.
[38] Y. Nakamichi, Y. Hirai, H. Yabu, M. Shimomura, *J. Mater. Chem.* **2011**, *21*, 3884.
[39] T. Kawano, S. Fujinami, K. Nakajima, H. Yabu, M. Shimomura, *Biomacromolecules* **2013**, *14*, 1208.
[40] C. E. Hoyle, C. N. Bowman, *Angew. Chem. Int. Ed.* **2010**, *49*, 1540.
[41] N. Ten Brummelhuis, C. Diehl, H. Schlaad, *Macromolecules* **2008**, *41*, 9946.
[42] S.-H. Lee, H. W. Kim, J. O. Hwang, W. J. Lee, J. Kwon, C. W. Bielawski, R. S. Ruoff, S. O. Kim , *Angew. Chem. Int. Ed.* **2010**, *49*, 10084.
[43] J.-S. Park, S.-H. Lee, T.-H. Han, S. O. Kim, *Adv. Funct. Mater.* **2007**, *17*, 2315.
[44] S.-H. Lee, J. S. Park, B. K. Lim, C. B. Mo, W. J. Lee, J. M. Lee, S. H. Hong, S. O. Kim, *Soft Matter* **2009**, *5*, 2343.