Lab on a Chip

PAPER

View Article Online
View Journal

Cite this: DOI: 10.1039/c4lc01486c

Inkjet print microchannels based on a liquid template†

Yuzhen Guo,[ab] Lihong Li,[a] Fengyu Li,*[a] Haihua Zhou[a] and Yanlin Song*[a]

Received 19th December 2014,
Accepted 3rd February 2015

DOI: 10.1039/c4lc01486c

www.rsc.org/loc

A simple method to fabricate microchannels is demonstrated based on an inkjet printing liquid template. The morphology of the liquid template can be well controlled by using ink with viscosity sensitive to temperature. The as-prepared Y-shape microchannel is used as a microfluidic reactor for an acylation fluorigenic reaction in a matrix of polydimethylsiloxane (PDMS). Arbitrary modification of the microchannels could be easily realized synchronously with the formation of the microchannels. By grafting polyethylene glycol (PEG) onto the internal surface, an anti-biosorption microchannel is obtained. The facile method will be significant for the fabrication of a microfluidic chip with functional modifications.

Introduction

A microchannel system is an important tool for the realization of fluidics at the micro level, which provides a powerful platform for the fields of biochemistry,[1–4] nanoscale manipulation,[5–8] digital fluidic devices[9] and bionics.[10–12] So far, the fabrication of microchannel systems mainly relies on photolithography-based techniques,[13] such as imprint lithography,[14–16] soft lithography[17] and electron beam lithography.[18] However, the photolithography-based technique strongly depends on photo-mask and photosensitive materials, which limits the flexibility of fabrication.[19] As an efficient technique, printing technology has shown great prospects in pattern-based fabrication[20–22] and functional material fabrication[23] for electronic devices,[24,25] plate-making and microchannels.[26,27] To fabricate microchannels using a printing technique, a few strategies have been proposed. For example, do Lago and Wheeler *et al.* have developed an inkjet printing method to construct a groove structure for a microfluidic device.[28–31] However, a post bonding or laminating step was needed to achieve an enclosed microchannel. Furthermore, a sacrifice template strategy was exploited by Lewis *et al.*, in which enclosed microchannels were fabricated in one step.[32] Generally, polymer-based inks, such as wax,[33] shellac[34] and sucrose,[35] were used as prototypes for a solid template. However, polymer-based inks strongly depend on extrusion direct write printing due to their high viscosity,[36] and removal of the template is complicated. In contrast, a liquid template could be easily achieved by inkjet printing and removed by evaporation. However, the control of Rayleigh instability[37] is a great challenge for building a liquid template with controllable morphology. That is, under the effect of surface tension, the liquid pattern in plastic in an environment of air or liquid tends to break up and relaxes into discontinuous spherical droplets,[38–40] which will break the integrity of the template. Therefore, to obtain a stable liquid template, the Rayleigh instability must be inhibited. In this paper, the Rayleigh instability is successfully inhibited by adopting materials with viscosity sensitive to temperature. The liquid template with stable morphology is prototyped by inkjet printing and used to fabricate microchannels. A typical microfluidic reactor is demonstrated by an acylation fluorigenic reaction in a matrix of PDMS. Furthermore, arbitrary modification of the microchannels could be realized synchronously with the formation of microchannels through an interfacial reaction. By grafting PEG onto the internal surface, an anti-biosorption microchannel is obtained. The as-prepared microfluidic reactor and anti-biosorption microchannel will be of significance for biochemical microfluidic device fabrication.

Fig. 1 is the scheme for the fabrication process of a typical microfluidic reactor by inkjet printing. The first step is pouring the PDMS prepolymer mixture into a container (a). Then the Y-shape pattern is printed onto the surface of the prepolymer mixture (b). The Y-shape pattern is wrapped into the prepolymer mixture spontaneously and acts as a template (c). Next, the prepolymer mixture thermally cures. Meanwhile, the liquid template evaporates, leaving the Y-shape

[a] *Beijing National Laboratory for Molecular Sciences (BNLMS), Key Lab of Green Printing, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China. E-mail: ylsong@iccas.ac.cn, forrest@iccas.ac.cn*

[b] *Graduate University of the Chinese Academy of Sciences, Beijing 100049, PR China*

† Electronic supplementary information (ESI) available: S1. preparation of printable ink; S2. curvature analysis of the branched microchannel; S3. curvature analysis of the junction between two channels with different diameters; S4. fabrication resolution of microchannels; S5. difference in capillary rise between unmodified microchannel and PEG modified microchannel. See DOI: 10.1039/c4lc01486c

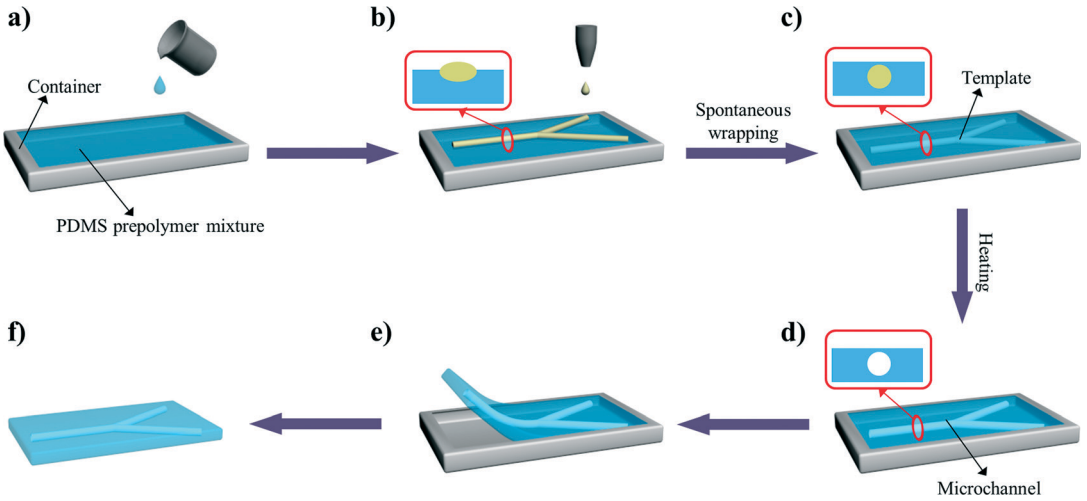

Fig. 1 Scheme for the fabrication process of a typical microfluidic reactor by inkjet printing: (a) pouring the PDMS prepolymer mixture into a container; (b) printing a Y-shape pattern on the surface of the prepolymer mixture. Inset: relative position sketch of the pattern and prepolymer mixture surface; (c) standing for a few seconds to allow the pattern to be wrapped spontaneously. Inset: relative position sketch of the pattern and prepolymer mixture surface; (d) after heating the prepolymer mixture with the liquid template, the prepolymer mixture thermally cures and the liquid template evaporates, leaving the microchannel in the PDMS matrix. Inset: section sketch of the microchannel in the matrix; (e) peeling off the fabricated PDMS matrix with microchannel; (f) the typical microfluidic reactor in the PDMS matrix.

microchannel in the PDMS matrix (d). The matrix is peeled off from the container (e), and a typical microfluidic reactor is obtained (f).

Experimental

Prepolymer mixture for printing substrate

The prepolymer mixture for the printing substrate was prepared by mixing PDMS prepolymer and crosslinker (Slygard 184, Dow Corning) at the mass ratio of 10 : 1 and degassed by centrifuging at 200 rpm (ZONKIA HC-3018). Then the mixture was poured into a container with a depth of about 1 mm and kept there for a period of time to allow it to flow level.

Ink

The ink was prepared by mixing undecanol (Alfa Aesar Inc., Chinese) and ethyl lactate (Alfa Aesar Inc., Chinese) at the mass ratio of 3 : 1 (see ESI† S1). For functional modification of the internal surface of the microchannel, vinyl-terminated poly(ethylene glycol) methacrylate (OEGMA) was added into the ink at 5 wt%.

Wetting behaviour of the ink on the surface of the prepolymer mixture

The PDMS prepolymer mixture was poured into a rectangular glass tank and a droplet of the ink (about 3 μL) was injected onto the surface of the prepolymer mixture. An OCA20 machine (dataphysics, Germany) was used to observe the wetting behaviour of the droplet on the surface of the PDMS prepolymer mixture from the side.

Printing

The prepared ink was injected into a cartridge and printed by a Dimatix Materials Printer (FUJIFILMDMP-2800 series, Japan) with a 10 pL drop orifice (DMC-11610). The glass container with prepolymer mixture was placed on the platform of the printer. The temperature of the glass container was controlled by a water bath. A Y-shape pattern was inkjet printed onto the surface of the prepolymer mixture at a drop space of 5 μm. The morphology stability of the pattern was observed by a built-in camera on the printer. After printing, the PDMS prepolymer mixture was heated at 90 °C for 3 h in an oven.

Wetting and anti-biosorption properties of microchannels

To examine the wetting property, about 1 μL of deionized water was injected into the microchannels using a syringe. An optical microscope with a CCD camera was used to observe the meniscus morphologies of water in the microchannels and to evaluate the contact angle of water on the internal surface of the microchannel.

FITC-labelled BSA protein (10 mg ml^{-1}, Bellancom Chemistry) was dissolved in a borate buffer solution (pH = 7.4) at the volume ratio of 1 : 10. To examine the anti-biosorption, the prepared FITC-labelled BSA protein solution was injected into the microchannels and then incubated in the dark at 37 °C for 1 h, followed with rinsing with borate buffer solution. Fluorescence images were recorded on an Olympus fluorescence microscope (BX51, Olympus Co., Ltd) (excitation, 495 nm; emission, 525 nm). The average fluorescence intensity is directly proportional to the amount of adsorbed protein.

Characterizations

The rheology property of the ink at different temperatures was characterized by an AR2000EX Rheometer (TA instrument) with parallel flat plates (D = 40 mm). A gap of 1000 μm was used, and the temperature ranged from 40 °C to 0 °C with a cooling rate of 2 °C min^{-1}. All measurements were conducted at a constant shear rate of 10 rad S^{-1}. The densities of the ink and prepolymer mixture were determined by the weight–volume method. SEM images were obtained using a field-emission scanning electron microscope (S-7500, Japan Hitachi). X-ray photoelectron spectroscopy (XPS) was performed to analyse the content of elements on the Thermo Scientific ESCA Lab 250Xi using 200 W monochromated Al Kα radiation. The 500 μm X-ray spot was used for XPS analysis. The full image of the microchannel reactor was captured by a digital camera 60D (Canon Co., Ltd).

Results and discussion

When the ink droplets are printed onto the surface of the prepolymer mixture, it is required that the prepolymer mixture wraps the ink droplets to form a liquid template. In the case of an ink droplet wetting on the surface of the liquid substrate, four possible equilibrium regimes have been proposed:[41] (1) total wetting where the ink droplet spreads until it reaches an equilibrium thickness on the order of molecular size; (2) partial wetting where the ink droplet forms a lens on the surface of the liquid substrate; (3) pseudopartial wetting where the ink droplet forms a lens with a thin film covering the liquid substrate surface; (4) pseudototal wetting where the ink droplet forms a lens covered by a thin film of the liquid substrate.

To obtain an embedded template, the pseudototal wetting regime is needed. Fig. 2(a) presents the wetting behaviour of an ink droplet on the surface of the PDMS prepolymer mixture, in which the serial patterns indicate the evolution process of wetting with time. As viewed from the side, the ink droplet forms a lens after being injected onto the surface of the PDMS prepolymer mixture. The lens is slowly wrapped by the prepolymer mixture in the following few seconds, which indicates the pseudototal wetting regime of the ink droplet on the surface of the PDMS prepolymer mixture. Finally, the ink droplet is totally wrapped in the PDMS prepolymer mixture. The densities of the ink and the PDMS prepolymer mixture are measured to be 0.86 g ml^{-1} and 1.04 g ml^{-1}, respectively (Table S1†). Due to the lower relative density, the ink droplet will not sink down into the prepolymer mixture continually, which will guarantee the stable position of the template in the prepolymer mixture (see Fig. S2†).

Similar to the behaviour of an ink droplet discussed above, the pattern printed onto the surface of the PDMS prepolymer mixture could also be wrapped into the prepolymer mixture. During the thermal curing of the PDMS prepolymer mixture at 90 °C, the pattern wrapped in the substrate plays the role of the template. With the holding time increasing, the liquid template evaporates, leaving the

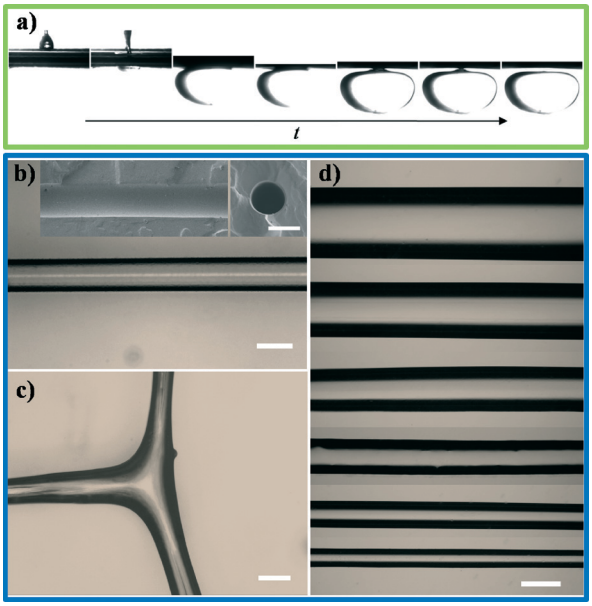

Fig. 2 a) Wetting behaviour of an ink droplet on the surface of the PDMS prepolymer mixture; b) optical image of a microchannel with a diameter of about 100 μm (scale bar = 100 μm). Inset: SEM images of a cross section (right) and a longitudinal section (left) of a 100 μm microchannel (scale bar = 100 μm); c) optical image of a branch-shape microchannel (scale bar = 50 μm); d) optical images of microchannels with different diameters (200–900 μm) (scale bar = 500 μm).

microchannel in the PDMS matrix. Fig. 2(b) shows the microchannel with a diameter of about 100 μm. The insets present the cross section morphology, showing the smooth and cylindrical profile of the microchannel. The diameter of the microchannels could be easily controlled by designing the scale of the template printed. As shown in Fig. 2(d), the microchannels with diameters of about 200 μm, 300 μm, 400 μm, 500 μm, 600 μm, 700 μm and 900 μm were successfully fabricated.

In addition to the linear microchannels, branch-shape microchannels are also achieved. Due to the effect of curvature difference, the sharp angle between adjacent branches is unstable. The mass transfer driven by the curvature difference[42] in the template would turn the unstable sharp angle into the stable fillet angle (details in ESI† S2), which sequentially leads to the formation of the microchannels with a fillet angle, as shown in Fig. 2(c).

For the formation of microchannels, the morphology of the liquid template should be well controlled. Generally, a liquid thread in another liquid tends to break up and relaxes into discontinuous spherical droplets under the effect of surface tension,[43] which will break the continuous morphology of the liquid template. Rayleigh *et al.* have revealed that a higher viscosity could contribute to reducing the break up of the liquid thread, which can be represented by the relaxation time τ, which is equal to $\eta^3/(\rho\gamma^2)$,[37,44] where η is the viscosity of the liquid thread, γ is the interfacial tension and ρ is the density difference between the two phases. According to the above discussion, manipulation of the viscosity of the liquid

template (η) could be used to control the Rayleigh instability (τ). That is, Rayleigh instability would be inhibited by simply increasing the viscosity of the liquid template. To achieve this, ink with viscosity sensitive to temperature is adopted as a prototype for the liquid template, while the PDMS prepolymer mixture with high viscosity is adopted as the liquid substrate. Fig. 3 presents the relationship between the rheology property of the ink and temperature in the range of about 25 °C to 3 °C. At 22 °C, the viscosity of the ink is about 9.8 mPa S, while at around 4 °C, the viscosity increases to above 40 mPa S rapidly.

The insets in Fig. 3 show the continuity of the pattern at different temperatures. When the temperature of the PDMS prepolymer mixture is controlled at 22 °C, the pattern lines printed on the surface of the prepolymer mixture are unstable and break up as shown in Fig. 3 inset (a). Due to the high viscosity of the substrate, the individual parts relax into spherical droplets slowly compared with the normal liquid thread in air.[45] When the temperature of the PDMS prepolymer mixture is decreased to about 3–4 °C, the viscosity of the ink increases to above 40 mPa S at the moment of contact with the cold prepolymer mixture surface. It is shown that the pattern lines printed on the surface of the prepolymer mixture are quite stable and have no sign of any breakage in Fig. 3 inset (b).

Functional modification has been an important research topic in the application of microfluidic devices,[46] in which post-treatment is usually needed to graft functional groups onto the inner surface of the preformed microchannel.[47] Here, the unique formation mechanism of the microchannels using a liquid template implied that we might be able to simplify the two-step procedure to one step *via* an interfacial reaction during the formation of the microchannels. According to eqn (1) S1,† the hydrosilylation is the basic reaction of PDMS curing, and the vinyl group is the key reactive chemical group that reacts with the silane.[48] Adding vinyl-terminated functional molecules to the template is a convenient way of chemically modifying the PDMS.[49] Fig. 4 shows the scheme of the synchronous modification of PEG based on the hydrosilylation reaction. The vinyl-terminated poly(ethylene glycol)methacrylate (OEGMA) molecules are added into the ink. After being printed, the ink droplets are wrapped into the PDMS prepolymer mixture subsequently. During the thermal curing of the PDMS prepolymer mixture, the vinyl-terminated OEGMA molecules participated in the hydrosilylation reaction at the interface of the ink and PDMS prepolymer mixture (see eqn (2) S1†). Following formation of the microchannels, the PEG groups are grafted onto the internal surface of the PDMS microchannel ultimately. The existence of PEG groups on the internal surface of the microchannels has been confirmed by the high resolution X-ray photoelectron spectra (XPS) of C 1s peaks, as shown in the ESI† S5. Based on this strategy, arbitrary modification could be realized by adding vinyl-terminated functional molecules into the ink.

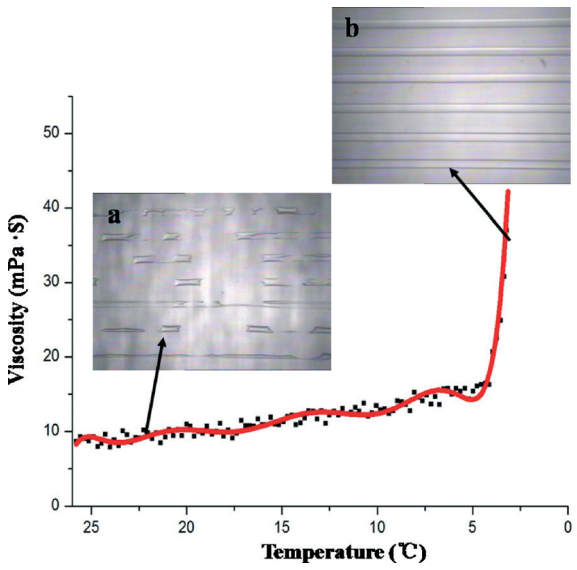

Fig. 3 Rheology property of the ink at different temperatures. Inset: digital photograph of the pattern printed on the surface of the PDMS prepolymer mixture at about 22 °C (a) and at about 3–4 °C (b).

To visualize the wetting effect of modifying the PDMS microchannel with PEG groups, the meniscus morphologies of water in the PEG modified microchannel and unmodified microchannel are shown in Fig. 5(a). In the unmodified microchannel, the meniscus morphology shows a contact angle of about 90°, which reflects the hydrophobic property of PDMS. While in the PEG modified microchannel, the contact angle of water is only about 60°. When one end of the microchannel was immersed in water, a capillary rise was observed in the PEG modified microchannel but no rise in the unmodified microchannel was observed (see ESI† S6 and Fig. S10). The favourable wettability of the PEG modified microchannel makes it promising for anti-biosorption applications.[50]

The anti-biosorption property of PDMS grafted with PEG groups plays a crucial role in the application of microfluidic chips for biochemistry.[49] In this work, FITC-labelled BSA protein was used to test the anti-biosorption property of the microchannels. Fig. 5(b) shows the fluorescence intensities of the internal surfaces for the unmodified and PEG modified microchannel after FITC-labelled BSA protein incubation for 1 h at 37 °C. The nonspecific adsorption of BSA protein on the internal surface of the PEG modified microchannels is significantly decreased compared with the unmodified PDMS microchannels. Therefore, the anti-biosorption property of the PDMS microchannels is improved greatly after being modified with PEG groups.

An organic phase chemical reaction was performed to demonstrate the application of the as-prepared microfluidic reactor. A typical Y-shape microfluidic reactor was fabricated and the acylation fluorigenic reaction was carried out. Non-fluorescent dansyl chloride and tetraethylenepentamine solution in ethanol were injected into the two branches of the Y-shape microreactor, respectively (Fig. 5(c)). When the two reagents met at the intersection, fluorescent dansyl-amide

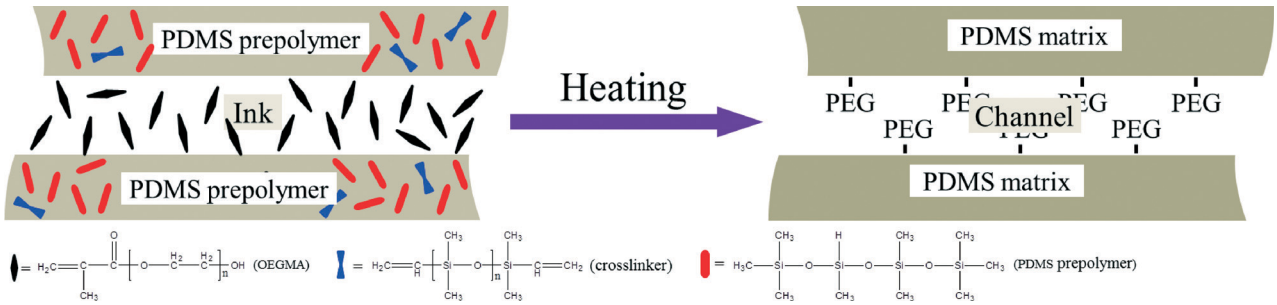

Fig. 4 Scheme of synchronous modification based on the hydrosilylation reaction. The vinyl-terminated OEGMA in the ink takes part in the hydrosilylation reaction at the interface of the ink and prepolymer mixture.

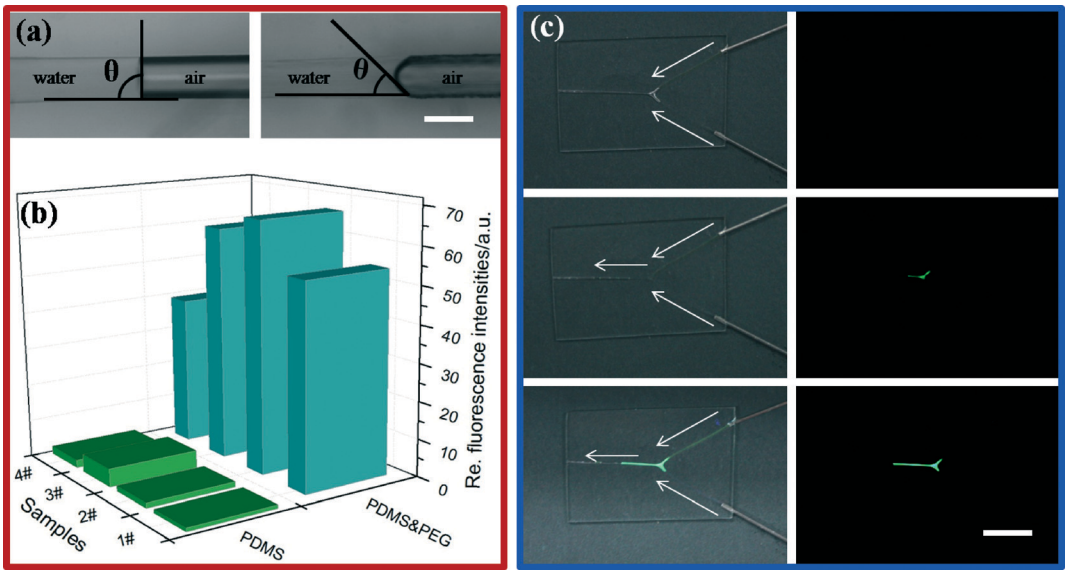

Fig. 5 (a) The images of the meniscus morphology of water in a PDMS microchannel (left) and a PEG modified microchannel (right) (scale bar = 1000 μm); (b) fluorescence intensity of the surface of unmodified PDMS and PEG modified microchannels after FITC-labelled protein incubation followed by borate buffer rinsing; (c) digital photographs of the bioluminescence reaction in a typical microfluidic reactor (scale bar = 1 cm).

was produced and gave a clear fluorescence emission under 365 nm ultraviolet light exposure. The organic phase reaction reveals the wide applicability of microchannel fabrication using an inkjet printing liquid template.

Conclusion

In summary, we have demonstrated the fabrication of microchannels based on a liquid template by inkjet printing. The morphology of the liquid template was well controlled by adopting ink with viscosity sensitive to temperature. How to inhibit the Rayleigh instability and achieve a liquid template with stable morphology in the PDMS prepolymer mixture was explored. Through an interfacial reaction, PEG is grafted onto the inner surface of the PDMS microchannel. This approach can allow for arbitrary modification of the internal surface of the PDMS microchannels synchronously with the formation of the microchannels by adding vinyl-terminated functional molecules into the template. This strategy for the fabrication and synchronous modification of microchannels has great prospects for applications in the complex vascular network with biological functions, such as self-healing and bioabsorption.

Acknowledgements

F. Y. Li and Y. L. Song thank the financial support of 973 Program (no. 2013CB933004), the National Nature Science Foundation (grant no. 51473173, 51203166, 51473172, 21301180 and 21303218), and the "Strategic Priority Research Program" of the Chinese Academy of Sciences (grant no. XDA09020000).

Notes and references

1 T. Rodrigues, P. Schneider and G. Schneider, *Angew. Chem., Int. Ed.*, 2014, 53, 5750.
2 K. S. Elvira, X. C. Solvas, R. C. Wootton and A. J. Demello, *Nat. Chem.*, 2013, 5, 905.

3 R. Jimenez-Martinez, D. J. Kennedy, M. Rosenbluh, E. A. Donley, S. Knappe, S. J. Seltzer, H. L. Ring, V. S. Bajaj and J. Kitching, *Nat. Commun.*, 2014, **5**, 3908.
4 B. Gorey, M. R. Smyth, B. White and A. Morrin, *J. Mater. Chem. C*, 2014, **2**, 6004.
5 J. O. Tegenfeldt, C. Prinz, H. Cao, S. Chou, W. W. Reisner, R. Riehn, Y. M. Wang, E. C. Cox, J. C. Sturm, P. Silberzan and R. H. Austin, *Proc. Natl. Acad. Sci. U. S. A.*, 2004, **101**, 10979.
6 D. Huh, K. L. Mills, X. Zhu, M. A. Burns, M. D. Thouless and S. Takayama, *Nat. Mater.*, 2007, **6**, 424.
7 X. Mu, W. Zheng, J. Sun, W. Zhang and X. Jiang, *Small*, 2013, **9**, 9.
8 K. Mawatari, Y. Kazoe, H. Shimizu, Y. Pihosh and T. Kitamori, *Anal. Chem.*, 2014, **86**, 4068.
9 K. Choi, A. H. Ng, R. Fobel and A. R. Wheeler, *Annu. Rev. Anal. Chem.*, 2012, **5**, 413.
10 K. S. Toohey, N. R. Sottos, J. A. Lewis, J. S. Moore and S. R. White, *Nat. Mater.*, 2007, **6**, 581.
11 J. F. Patrick, K. R. Hart, B. P. Krull, C. E. Diesendruck, J. S. Moore, S. R. White and N. R. Sottos, *Adv. Mater.*, 2014, **26**, 4302.
12 H.-J. Koo and O. D. Velev, *J. Mater. Chem. A*, 2013, **1**, 11106.
13 S. K. Y. Tang and G. M. Whitesides, Basic Microfluidic and Soft Lithographic Techniques, in *Optofluidics: Fundamentals, Devices and Applications*, ed. Y. Fainman, L. P. Lee, D. Psaltis and C. Yang, McGraw-Hill Professional, 2010, p. 7.
14 J. Wu, R. Chantiwas, A. Amirsadeghi, S. A. Soper and S. Park, *Lab Chip*, 2011, **11**, 2984.
15 M. B. Mikkelsen, A. A. Letailleur, E. Sondergard, E. Barthel, J. Teisseire, R. Marie and A. Kristensen, *Lab Chip*, 2012, **12**, 262.
16 L. J. Guo, X. Cheng and C. F. Chou, *Nano Lett.*, 2004, **4**, 69.
17 G. S. Fiorini and D. T. Chiu, *BioTechniques*, 2005, **38**, 429.
18 R. E. Fontana, J. Katine, M. Rooks, R. Viswanathan, J. Lille, S. MacDonald, E. Kratschmer, C. Tsang, S. Nguyen, N. Robertson and P. Kasiraj, *IEEE Trans. Magn.*, 2002, **38**, 95.
19 S. M. Park, Y. S. Huh, H. G. Craighead and D. Erickson, *Proc. Natl. Acad. Sci. U. S. A.*, 2009, **106**, 15549.
20 T. Janoschka, A. Teichler, B. Häupler, T. Jähnert, M. D. Hager and U. S. Schubert, *Adv. Energy Mater.*, 2013, **3**, 1025.
21 A. Teichler, J. Perelaer and U. S. Schubert, *J. Mater. Chem. C*, 2013, **1**, 1910.
22 S. Wunscher, B. Seise, D. Pretzel, S. Pollok, J. Perelaer, K. Weber, J. Popp and U. S. Schubert, *Lab Chip*, 2014, **14**, 392.
23 X. Lin, T. Ling, H. Subbaraman, L. J. Guo and R. T. Chen, *Opt. Express*, 2013, **21**, 2110.
24 L. Li, Y. Guo, X. Zhang and Y. Song, *J. Mater. Chem. A*, 2014, **2**, 19095.
25 J. Lessing, A. C. Glavan, S. B. Walker, C. Keplinger, J. A. Lewis and G. M. Whitesides, *Adv. Mater.*, 2014, **26**, 4677.
26 W. Wu, C. J. Hansen, A. M. Aragón, P. H. Geubelle, S. R. White and J. A. Lewis, *Soft Matter*, 2010, **6**, 739.
27 W. K. Coltro, D. P. de Jesus, J. A. da Silva, C. L. do Lago and E. Carrilho, *Electrophoresis*, 2010, **31**, 2487.
28 R. Fobel, A. E. Kirby, A. H. Ng, R. R. Farnood and A. R. Wheeler, *Adv. Mater.*, 2014, **26**, 2838.
29 W. K. Coltro, J. A. da Silva, H. D. da Silva, E. M. Richter, R. Furlan, L. Angnes, C. L. do Lago, L. H. Mazo and E. Carrilho, *Electrophoresis*, 2004, **25**, 3832.
30 M. Abdelgawad, M. W. Watson, E. W. Young, J. M. Mudrik, M. D. Ungrin and A. R. Wheeler, *Lab Chip*, 2008, **8**, 1379.
31 W. K. Coltro, E. Piccin, J. A. da Silva, C. L. do Lago and E. Carrilho, *Lab Chip*, 2007, **7**, 931.
32 J. A. Lewis and G. M. Gratson, *Mater. Today*, 2004, **7**, 32.
33 D. Therriault, R. F. Shepherd, S. R. White and J. A. Lewis, *Adv. Mater.*, 2005, **17**, 395.
34 L. M. Bellan, M. Pearsall, D. M. Cropek and R. Langer, *Adv. Mater.*, 2012, **24**, 5187.
35 J. Lee, J. Paek and J. Kim, *Lab Chip*, 2012, **12**, 2638.
36 W. Wu, A. De Coninck and J. A. Lewis, *Adv. Mater.*, 2011, **23**, H178.
37 J. Eggers, *Rev. Mod. Phys.*, 1997, **69**, 865.
38 A. Utada, A. Fernandez-Nieves, J. Gordillo and D. Weitz, *Phys. Rev. Lett.*, 2008, **100**, 014502.
39 J. Eggers, *Phys. Rev. Lett.*, 2002, **89**, 084502.
40 J. Fowlkes, S. Horton, C. M. Fuentes and P. D. Rack, *Angew. Chem., Int. Ed.*, 2012, **51**, 8768.
41 J. Sebilleau, *Langmuir*, 2013, **29**, 12118.
42 W. W. Mullins, *Metall. Mater. Trans. A*, 1995, **26**, 1917.
43 S. Kakac, B. Kosoy, D. Li and A. Pramuanjaroenkij, Microfluidics Based Microsystems, *Proceedings of the NATO Advanced Study Institute on Microfluidics Based Microsystems: Fundamentals and Applications*, Springer, New York, 2010.
44 M. Moseler, *Science*, 2000, **289**, 1165.
45 P. G. de Gennes, F. Brochard-Wyart and D. Quéré, *Capillarity and Wetting Phenomena*, Springer, New York, NY, 2003.
46 Z. Zhang, X. Feng, F. Xu, X. Liu and B. F. Liu, *Electrophoresis*, 2010, **31**, 3129.
47 T. B. Stachowiak, D. A. Mair, T. G. Holden, L. J. Lee, F. Svec and M. J. Jean, *J. Sep. Sci.*, 2007, **30**, 1088.
48 M. L. van Poll, S. Khodabakhsh, P. J. Brewer, A. G. Shard, M. Ramstedt and W. T. S. Huck, *Soft Matter*, 2009, **5**, 2286.
49 M. L. van Poll, F. Zhou, M. Ramstedt, L. Hu and W. T. S. Huck, *Angew. Chem.*, 2007, **119**, 6754.
50 J. Zhou, H. Yan, K. Ren, W. Dai and H. Wu, *Anal. Chem.*, 2009, **81**, 6627.

