Thermo-responsive Manipulation of a Water Plug in a Poly(*N*-isopropylamide)-modified Glass Capillary

Tohru Saitoh,* Ayahito Sekino, and Masataka Hiraide
Department of Molecular Design and Engineering, Nagoya University, Chikusa, Nagoya 464-8603

(Received April 12, 2004; CL-040391)

A thermo-responsive polymer, poly(*N*-isopropylacrylamide), was used for the modification of the inner surface of a glass capillary. The modification was performed by the coupling Bind-Silane™ (3-acryloxypropyltrimethoxysilane) on glass surfaces and a subsequent radical polymerization of *N*-isopropylacrylamide and methylenebis(acrylamide) with ammonium persulfate—*N*,*N*,*N*′,*N*′-tetramethylethylenediamine. A water plug placed in the capillary was successfully manipulated by warming the portion of the capillary. The movement was attributed to the wettability gradient of the inner surfaces of the polymer-modified capillary.

Fluid control or manipulation has been a topic of research increasing interest in the analyses using micro fluidic systems. Fluids are typically transported inside microchannels using a syringe pump or a pressure head for physically driven flows[1–5] or an electric field for electrokinetic flows.[6,7] Such systems require the external instruments and delicate operations for the fluid control. In order to achieve further development of microfluidic system, the driving force to move the fluid must come from within the channels.

Some stimuli-responsive hydrogels have been employed for fabricating self-regulating systems in microchannels.[8,9] They reversibly swell and shrink and, hence, act as valves or regulators that can be responsive to temperature, pH, and certain chemical species. However, accurate and precise synthesis procedures are necessary for fabricating these regulators. Poor reproducibility of the shape or the physical performance seems to be another problem in such hydrogel-based components.

Previously, we designed a novel liquid control system using temperature-induced wettability change on the channel walls that had been modified with a thermo-responsive polymer, poly(*N*-isopropylacrylamide) [PNIPAAm].[10] The capillary action of water inside a polymer-modified glass capillary was significantly degraded above the lower critical solution temperature (LCST, ca. 32 °C)[11–13] of PNIPAAm. In a branched channel, the liquid stream was successfully switched and entirely flowed toward opposite side of the polymer-modified capillary being heated.

Recently, the wettability gradient over channel walls in a microanalytical device was successfully utilized for the migration of a water plug.[14,15] Hydrophobic and hydrophilic regions were patterned inside channel networks using self-assembled monolayer chemistry. In the present study, we attempt temperature-induced manipulation of a water plug in microchannels. A glass capillary modified by PNIPAAm in the inner surface was used.

The glass capillary (EM minicaps™, i.d. 900 mm) was obtained from EM capillary (Germany). The inside was rinsed with 1 M NaOH and then washed with water. After drying the capillary, it was filled with a toluene solution of 10% (v/v) Bind-Silane™ (3-acryloxypropyltrimethoxysilane, Amarsham Biosciences, Piscataway, USA) for 16 h. The tube was washed with ethanol and subsequently with water. Next, an aqueous mixture of *N*-isopropylacrylamide (NIPAAm) and methylenebis(acrylamide) (Bis), ammonium persulfate (APS), and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TEMED) were introduced into the capillary under nitrogen atmosphere. The amounts of chemicals were 1.70 g of NIPAAm, 0.11 mg of Bis, 0.05 g of APS, and 25 μL of TEMED for 25 mL of water. After the polymerization, the tube was well washed with water.

The thermo-responsive wettabilities of the PNIPAAm-modified glass surfaces prepared in different conditions were evaluated by measuring water contact angles (Figure 1). The wettability was dramatically changed around the LCST of PNIPAAm. The results suggest that warming or cooling the surfaces can modulate the water permeation. With less amounts of monomers for the polymerization, the wettability change was exiguous. In contrast, the use of greater amounts of monomer choked up the capillary.

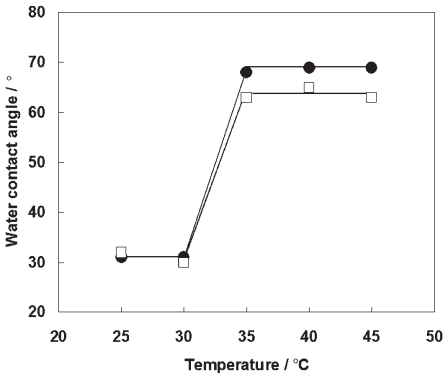

Figure 1. Temperature dependence of water contact angle on PNIPAAm-modified glass surfaces. Amounts in 25 mL of reaction solution: (●) NIPAAm: 1.70 g, Bis: 0.11 mg, (□) NIPAAm: 0.42 g, Bis: 5.7 mg.

Approximately 1 μL of water plug was placed into the PNIPAAm-modified capillary tube using a microsyringe. Then, the outer sides of the capillary near the water plug were warmed with a pair of solder irons. The temperature of the solder irons was set to 45 °C by regulating electric power with transformers. The movement of the water plug was monitored with a TelescoMicro microscope system composing of a Nikon COOLPIX 4500 digital camera and a TelescoMicro ED4x18D. The temperature at the respective portion of the capillary was measured with a Horiba infrared thermometer IT-540.

Successful result of the temperature-induced manipulation

of a water plug was exhibited in Figure 1. Figure 1A shows a glass capillary in which a water plug was placed. When a point near the water plug was warmed with a pair of solder irons, the plug was moved toward the opposite direction of the warmed position (Figure 1B). The movement occurred immediately and almost finished within 5 s. The expanded view including the results of temperature measurement was also shown in Figure 1C. The water plug arrived at the position where the temperature is almost the same as LCST. The plug was further moved when it was followed by the solder irons. Therefore, the water plug could be freely located at the optional position of PNIPAAm-modified capillary. On the other hand, the water plug in unmodified glass capillary was negligibly moved, even if the capillary was heated at 50 °C. Hydrophobic–hydrophilic gradient based on the temperature-induced phase transition of thermo-responsive polymer on surfaces of wall was effective for the liquid manipulation of such a narrow flow channel.

Recently, the fabrication of microfluidic devices including more complicate channels or 3-D structure have begun to be attempted.[16,17] In such analytical devices, the fabrication of fluid control system will require cumbersome and highly delicate procedures. In contrast, the modification of polymer was easy. Different kind of stimuli-responsive polymer will be modified at the objective point of the channels by using a pattern masking and a photoinduced radical polymerization. Further studies about the polymer modification and the manner to carry stimuli at the position to be responded will be fruitful for developing a novel self-regulated liquid manipulation system for microchannels.

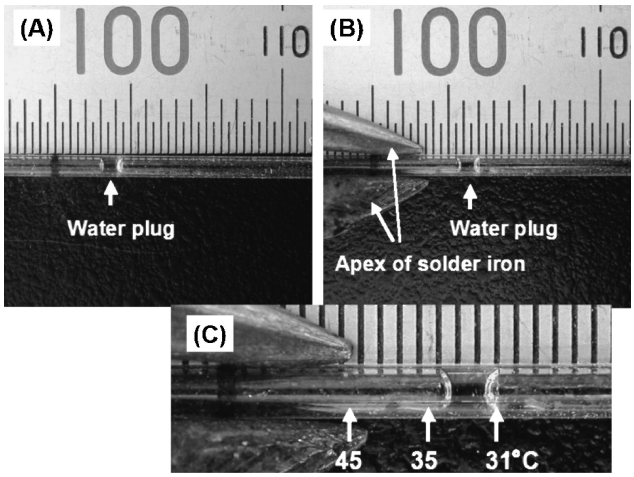

Figure 2. Temperature-induced movement of a water plug in a PNIPAAm-modified glass capillary.

This study was supported by a Grant-in-Aid for Scientific Research Japan (C) (14550781).

References

1 S. I. Miyazaki, T. Kawai, and M. Araragi, *IEEE*, **9**, 283 (1991).
2 D. C. Duffy, H. L. Gills, J. Lin, N. F. Sheppard, and G. J. Kollog, *Anal. Chem.*, **71**, 4669 (1999).
3 K. Hosokawa, T. Fujii, and I. Endo, *Anal. Chem.*, **71**, 4781 (1999).
4 M. A. Unger, H. P. Chou, T. Thorsen, A. Scherer, and S. R. Quake, *Science*, **288**, 113 (2003).
5 M. Tokeshi, T. Minagawa, and T. Kitamori, *Anal. Chem.*, **71**, 4781 (1999).
6 S. C. Jacobson, T. E. Mcknight, and J. M. Ramsey, *Anal. Chem.*, **71**, 4455 (1999).
7 L. Bousse, C. Cohen, T. Nikiforov, A. Chow, A. R. Kopf-Sill, R. Dubrow, and J. W. Parce, *Annu. Rev. Biophys. Biomol. Struct.*, **29**, 155 (2000).
8 D. J. Beebe, J. S. Moore, J. M. Bauer, Q. Yu, R. H. Liu, C. Devadoss, and B. H. Jo, *Nature*, **404**, 588 (2000).
9 D. T. Eddington and D. J. Beebe, *Adv. Drug Delivery Rev.*, **56**, 199 (2004).
10 T. Saitoh, Y. Suzuki, and M. Hiraide, *Anal. Sci.*, **18**, 203 (2002).
11 M. Heskins and J. E. Guillet, *J. Macromol. Sci.*, **A2**, 1141 (1968).
12 R. F. S. Freitas and E. L. Cussler, *Chem. Eng. Sci.*, **42**, 97 (1987).
13 H. G. Shild and D. A. Tirrell, *J. Phys. Chem.*, **94**, 4352 (1990).
14 H. Handique, D. T. Burke, C. H. Mastrangelo, and M. A. Burns, *Anal. Chem.*, **72**, 4100 (2000).
15 B. Zhao, J. S. Moore, and D. J. Beebe, *Science*, **291**, 1023 (2001).
16 N. A. Polson and M. A. Hayes, *Anal. Chem.*, **73**, 312A (2001).
17 Y. J. Chuang, F. G. Tseng, J. H. Cheng, and W. K. Lin, *Sens. Actuators, A*, **103**, 64 (2003).

Published on the web (Advance View) July 5, 2004; DOI 10.1246/cl.2004.912