# OPTICAL MICROFLUID CONTROL BASED ON PHOTORESPONSIVE POLYMER GEL MICROVALVES

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### Introduction

Microfluidics is a key technology for integrated analytical systems on microchip. One of the main microfluidic components for realizing integrated microfluidic devices is a microvalve. The microvalve controlled by light irradiation is one of the most attractive microvalves for integrated flow control because flow control by light irradiation enables non-contact fluid control and flow control by local light irradiation enables independent control of multiple fluids.

Several research groups have reported light-induced fluid control based on change of surface wettability (1, 2). Fluids on microchips were addressed by the external ultraviolet (UV) light or 785 nm laser light irradiation. The method is simple method to control fluids on microchips. However, once the channel has been wetted with the fluid, it is difficult to stop the fluid. Sershern et al. proposed optically controlled microvalve based on the volume change of nanocomposit hydrogel composed of thermoresponsive polymer poly(*N*-isopropylacrylamide) (pNIPAAm) gel containing nanoparticles that have strong optical-adsorption (3). The optical energy as strong as 1600 to 2700 mW/cm<sup>2</sup> was transformed into heat by nanoparticles, and the heat induced shrinkage of thermoresponsive pNIPAAm gel and resulted in the opening of microvalves. In their system, the two microvalves were controlled independently by irradiating light with different wavelength. However, heat transfer between adjacent valves may well be a problem for integrated microvalve operation.

Recently, our research group developed a photoresponsive polymer, pNIPAAm functionalized with spirobenzopyran chromophore (pSPNIPAAm), which shows solubility change in aqueous solution triggered by light irradiation (4). The pSPNIPAAm gel has also been introduced to the surface of the porous membrane and applied to photoresponsive gate membrane (5). As shown in Figure 1, blue light isomerization irradiation induces the of SP chromophore from protonated open-ring structure to closed-ring structure. It causes the polymer chain to be hydrophobic, resulting in shrinkage of the gel in aqueous solution. The driving force for physical property change of pSPNIPAAm is based on the photoisomerization of chromophore, which is induced



by the light intensity as small as  $30 \text{ mW/cm}^2$  (4). Therefore, expensive laser apparatus is unnecessary to trigger photoresponsive physical property change.

In this study, pSPNIPAAm gels were applied to the photoresponsive microvalve. The pSPNIPAAm gels were fabricated in a polydimethylsiloxane (PDMS) microchannel by in situ photopolymerization. By means of local light irradiation, independent control of multiple pSPNIPAAm gel microvalves were demonstrated.

#### **Experimental Part**

Silicon wafers were obtained from Asahi Metal (Tokyo, Japan). Negative photoresist, SU-8 50 was obtained from MicroChem (Newton, USA). Ethyl lactate was obtained from Wako Pure Chemical Industries (Osaka, Japan). PDMS prepolymer and curing agent (Sylgard 184) were obtained from Dow Corning (Midland, USA).

*N*-isopropylacrylamide (NIPAAm, Wako) was purified by recrystallization in a mixed solution of hexane and toluene and dried under a vacuum. 1',3',3'-trimethyl-6-hydroxyspiro(2*H*-1-benzopyran-2,2'-indoline) (Acros Organics, Geel, Belgium), acryloyl chloride (Wako), *N*,*N*methylene-bis(acrylamide) (MBAAm, Wako), 2,2dimethoxy-2-phenyl acetophenone (DMPA, Sigma-Aldrich, St. Louis, USA), and 1-buthanol (Wako) were used without further purification.

Polydimethylsiloxane (PDMS) microchip for modeling multiple sample distribution was fabricated (Figure 2). The PDMS microchip was fabricated using the standard soft lithographic techniques (6-8).

Three photoresponsive polymer, pSPNIPAAm, gel microvalves were fabricated by in situ photopolymerization on a single PDMS microchip. A reaction mixture solution was prepared by dissolving the NIPAAm monomer (452 mg, 4.0 mmol), the acrylated spirobenzopyran monomer (14.0 mg, 0.04 mmol), MBAAm (10.8 mg, 0.07 mmol), and DMPA (10.2 mg, 0.04 mmol) into 1-buthanol (1.0 mL). Fluid microchannel made from PDMS was filled with the reaction mixture solution containing NIPAAm monomer, the acrylated



Photoresponsive polymer gels

Figure 2. Microchip for modeling fluid photoresponsive manipulation and polymer gel microvalves formed by in situ photo-polymerization. (a) A PDMS microchip with microfluidic channels. A main channel was connected to three branch microchannels with micropillars to support the gels. Colored circles designate the UV light irradiated areas during in situ photopolymerization. (b) Three pSPNIPAAm gels after swelling. Three gels were fabricated in three branch microchannels.

spirobenzopyran monomer, MBAAm, and DMPA. Focused UV light was irradiated to 450  $\mu$ m circular areas at the desired positions in microchannel for 10 seconds. The gels were swelled to larger size than the width of microchannels after washing and swelling.

#### Results

Microvalve control by local light irradiation was demonstrated. A solution containing blue die was introduced into main microchannel at 3.4 kPa. Blue light with a wavelength range from 420 to 440 nm was irradiated to each gel at 29 °C. Each valve was opened by blue light irradiation from 18 to 30 seconds (Figure 3). Local light irradiation enabled the independent control of multiple microvalves. Blue light irradiation induced the color fade out of the pSPNIPAAm gels, which indicates isomerization of

spirobenzopyran chromophore, and resulted in the shrinkage of the gels. It caused the opening of microvalve.

The typical intensity of the irradiated blue light was 20 mW/cm<sup>2</sup> in our system. Since the gel shrinkage is induced by photoisomerization of spirobenzopyran chromophore, the intensity to control pSPNIPAAm gel is very weak compared to previously reported optically controlled the microvalve using nanocomposit hydrogel (more than 1600 mW/cm<sup>2</sup>) (3). Therefore, our system does not require expensive laser equipment. Low light intensity leads the small increase in temperature. Therefore, in the present study, the heat transfer between adjacent valves does not affect the microvalve control. Therefore, pSPNIPAAm gel microvalve is suitable for integrated fluid control system compared to the previously reported microvalves composed of thermoresponsive hydrogel.

## Discussion

The flow control by light irradiation provides a non-contact and independent flow control on microchip. Micro-patterned light irradiation with optical projection devices enables the parallel control of multiple microvalves. Therefore, optical fluid manipulation will create a novel prospect for highly integrated microfluidic devices. We think photoresponsive polymer gel microvalve will be an advantageous technique for integrated multifunctional microfluidic devices.

## References

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Figure 3. Independent control of multiple pSPNIPAAm gel microvalves by means of local light irradiation. Blue light was locally irradiated to each pSPNIPAAm gel microvalve to open microvalve. Each valve was opened by 18 to 30 s irradiation.

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