MICROCHANNEL FABRICATION BY USE OF PHOTOACID-GENERATOR-TETHERED GEL

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ABSTRACT

We propose a novel method for microchannel fabrication achieved by a combination of a light responsive polymer gel and a micropatterned light irradiation. The gel was constituted of poly(*N*-isopropylacrylamide) (pNIPAAm) modified with blue-light responsive photoacid-generators (PAG). We found that light irradiation to the dry PAG gel resulted in a decrease in degree of swelling of the gel in water. We prepared PAG gel sheet, which covalently bound on a glass substrate, and irradiated it with blue light in a dry state. After swelling in water, we observed that the gel in the irradiated area was thinner than in the irradiated area. On the basis of the results we fabricated microchannels on the PAG gel sheet by means of prior patterned light irradiations and the subsequent swelling.

KEYWORDS
hydrogel, photoresponse, photoacid generator, mirochannel.

INTRODUCTION

Light-irradiation is one of suitable stimulation methods in the field of micro-scale devices, since it affects a target object remotely, locally, and accurately. Therefore, we have considered light-responsive materials as useful materials in the field of micro-devices. We previously showed that microchannels could be formed by use of a light-responsive spiropyran-modified hydrogel [1]. In the method the microchannels could be formed by volume changes of the gel resulted from the light irradiation. However, the spiropyran gels were only operated under acidic conditions, and required continuous irradiation to maintain the microchannel. The problems restrict application fields of the spiropyran gel microchannels. In the present study, we prepared another light responsive polymer gel to solve the above problems. The gel was constituted of pNIPAAm modified with blue-light responsive PAG (Figure 1). We evaluated volume changes of the PAG gel against light irradiation. Furthermore, we developed a novel system in which arbitrary microchannels can be fabricated simply by micropatterned light irradiation using the PAG gel.

EXPERIMENT

PAG monomer was prepared from a reported thioxanthone derivative and *p*-styrene sulfonyl chloride [2,3]. PAG gel was prepared as follows: PAG monomer (2.4 mg, 5.1 µmol), NIPAAm (54.0 mg, 477.2 µmol), MBAAm (3.9 mg, 25.4 µmol), and AIBN (0.83 mg, 5.1 µmol) were dissolved in 1,4-dioxane (603 µL) and nitrogen gas was passed through the solution to exclude oxygen. The solution was filled into in a reaction chamber, which was composed of a glass disk (25 mm in diameter) previously coated with 3-(trimethylsilyl)propyl methacrylate, a polypropylene disk, and a 0.3-mm-thick polypropylene spacer (17 mm in i.d.), and reacted at 70 °C for 3 h. The resulting PAG gel sheet covalently bound on the glass disk was washed by soaking in methanol with several solvent-exchanges and then dried in air.

A dry PAG gel bound on a glass dick was irradiated with blue-light peaked at 436 nm with an intensity of 14 mW/cm^2 by use of a computer-controlled micropattern projection system which was composed of an IX-71 inverted phase-contrast microscope (Olympus, Tokyo, Japan), a DESM-01 computer-controllable maskless micropattern projection unit (Engineering System Co., Matsumoto, Japan), a VB-7000 cooled CCD camera system (Keyence,

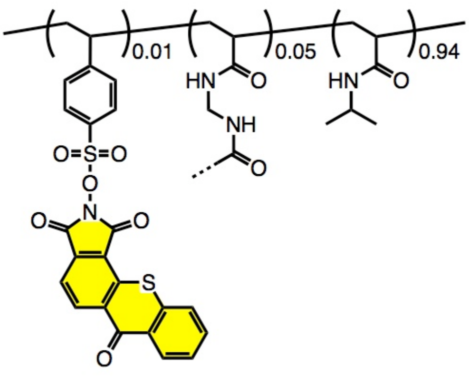


Figure 1: A chemical structure of poly(N-isopropylacrylamide) gel modified with a photoacid-generator (PAG).

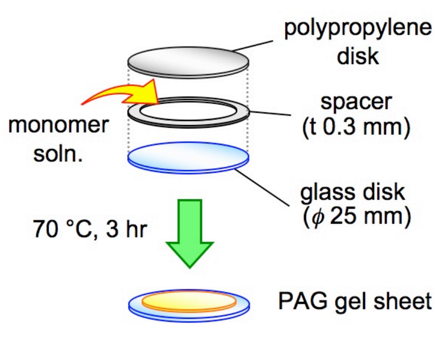


Figure 2: An illustration of procedure for preparation of a PAG gel sheet.

Kyoto, Japan), and a computer [4].

A microfluidic chip was assembled from a glass disk attached with the dry PAG gel, a cap with inlet/outlet ports, and a polypropylene spacer (0.3 mm in thickness) and clamped with a specially designed holder. The gel in the chip was irradiated with blue-light with an intensity of 14 mW/cm^2 in a prescribed pattern by use of the computer-controlled micropattern projection system. Water was filled in the chip and stored for 20 h at rt and then a suspension of red-colored latex beads (0.39 µm in diameter, 0.2 % (w/w), Duke Scientific Corp., Palo Alto, CA) was injected from an inlet port at 4.9 kPa.

RESULTS AND DISCUSSION

A PAG gel sheet was prepared in a mold of 0.3-mm-thickness as shown in Figure 2. One side of the mold was composed of a glass disk which had been functionalized with vinyl groups. Therefore, prepared gel was covalently bound onto the glass disk. Although drying of the gel caused its shrinkage, no remarkable length changes in the in-plane direction was observed because of the bonding. On the other hand, thickness of the gel significantly decreased by the drying. Dry gel pieces that were peeled from the glass disk soaked in water to result in reswelling in thickness direction. However, when the dry gel was irradiated with blue-light prior to soaking, the reswelling was remarkably suppressed (Figure 3). No volume changes were observed when the swollen gel was irradiated with blue light (data not shown).

Scheme 1 showed possible reactions of the PAG in the gel under blue-light irradiation. The PAG was reported to be cleaved at N–O bonding by light irradiation and generates radicals first and then sulfonic acid (Path A) [3]. Path A should cause an increase in degree of swelling of the gel at light-irradiated area because of strong hydration at sulfonate groups. However, the opposite results were obtained in fact as shown in Figure 2. The results suggest another possible Path B was dominant in the irradiation of the gel in the dry state.

Glass disk attached with the dry PAG gel sheet was assembled with a cap separated with a polypropylene spacer of 0.3 mm in thickness to provide a PAG gel chip (Figure 4). A microchannel pattern was irradiated with blue-light on the gel and then water was filled into the chip to swell the gel. Interspace between the glass disk and the cap was filled by swollen gel at unirradiated regions, whereas light-induced suppression of swelling at irradiated regions caused to remain unfilled space to make channel. Twenty hours after the water filling we injected a suspension of red-colored latex beads through an inlet port at 4.9 kPa and confirmed that the suspension flowed in a channel formed along irradiated pattern (Figure 5). No leaking of the suspension to contact face between the swollen gel and the cap was observed in microscope images, suggesting sufficient sealing of the channel under the pressure condition. The results demonstrated that microfluidic channel was easily fabricated by use of the PAG gel chip through processes of light-irradiation and water filling.

CONCLUSIONS

This method to fabricate microchannels in arbitrary pattern was easily carried out by means of blue-light irradiation and the subsequent water filling. The architecture developed in this study will make prototyping process of microfluidic system more easily and less expensive.

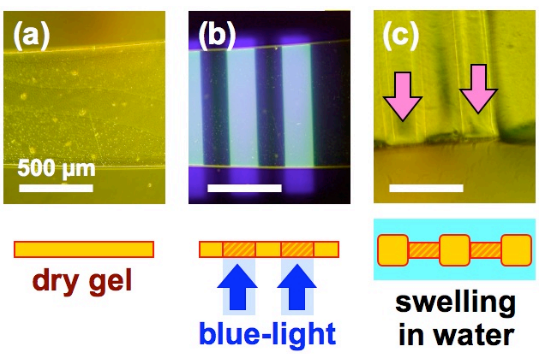
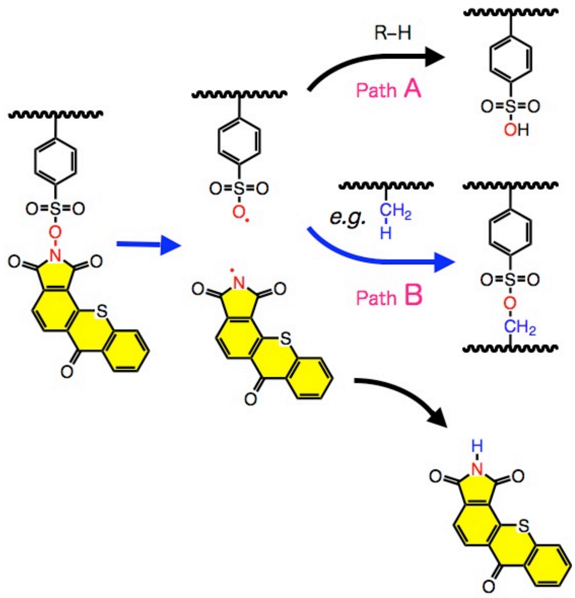


Figure 3. Effects of blue-light irradiation on volume changes in reswelling of a PAG gel. (a and b) Microscopic images of the gel before and during irradiation. (c) Volume changes of the gel in water. Arrows indicate light-irradiated area.



Scheme 1. Possible reaction paths of the PAG in the gel. Path A generates a sulfonic acid group and Path B forms an additional crosslinking in the gel

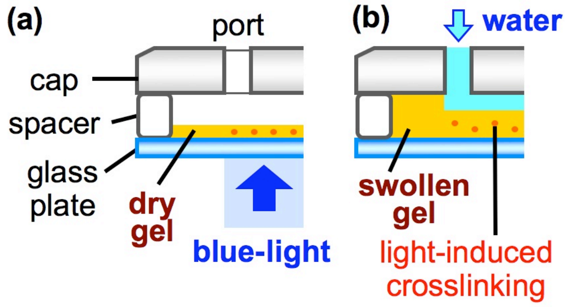


Figure 4: Construction of a chip and mechanism of a microchannel formation. (a) Blue light irradiation to form additional crosslinking in a dry PAG gel. (b) The subsequent water filling to swell the gel. Since a degree of swelling at the light-irradiated regions is suppressed by the additional crosslinking, microchannels are formed as irradiated pattern.

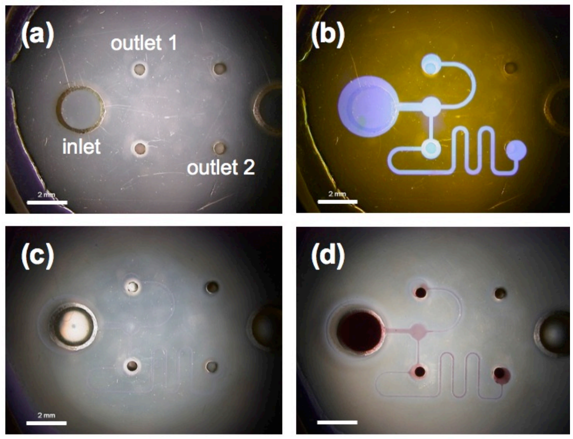


Figure 5: Fabrication of microchannels in a PAG gel chip. (a and b) Microscopic images of the gel before and during irradiation. (c and d) Images after swelling the gel and applying a red-colored latex suspension. Scale bars: 2 mm.

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