

## Novel Photoresponsive Polymer Materials Functionalized with Spirobenzopyran

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### Introduction

Light irradiation is a useful and important control meaning since it can be applied to the object locally and instantaneously in a non-contact manner, and various researches have been carried out to develop the photo-functional polymers composed of photo responsive chromophores. In this study, we synthesized novel copolymers by modifying poly(*N*-isopropylacrylamide) (pNIPAAm), which is a well-known thermo-responsive polymer, with spirobenzopyran, of which the charged state is drastically responsive to the light irradiation. Also we analyzed the photoresponsive characteristics of the aqueous solutions of these copolymers. Further, we prepared various photoresponsive hydrogels composed of the copolymer, and investigated the effect of light irradiation on their properties.

### Experimental

We synthesized pNIPAAm-based copolymers partly modified with a spirobenzopyran (pSPNIPAAm) through radical copolymerization of *N*-isopropylacrylamide and acryl ester of 1',3',3'-trimethyl-6-hydroxyspiro(2*H*-1-benzopyran-2,2'-indoline). The spirobenzopyran monomer was introduced at 1 mol%. The pSPNIPAAm hydrogel was synthesized in a similar procedure using cross-linker. A pSPNIPAAm hydrogel thin layer was prepared through *in situ* polymerization on a flat glass substrate whose surface was modified with vinyl groups.

Absorbance/turbidity spectra of pSPNIPAAm in an aqueous solution were measured at various proton concentrations with a UV-visible spectrometer having a thermoregulated cell holder. The photo-responsive deformation of the pSPNIPAAm hydrogel was observed with a inverted microscope (IX-71, Olympus Co.) equipped with a cooled CCD camera (VB-7000, Keyence Co.). The light irradiation to the solution samples was carried out with a Hg-Xe light source (LC6, Hamamatsu Photonics K.K.) equipped with a set of filters and a liquid-fiber light guide. The wavelength range and total intensity of the irradiating light were 400–440 nm and 30 mW, respectively. The micro-patterned light irradiation onto a pSPNIPAAm hydrogel thin layer was carried out by using a PC-controllable microprojection unit (DESM-01, Engineering System Co.) equipped on a microscope. The wavelength and the intensity of the irradiating light were 436 nm and 112 mW/cm<sup>2</sup>, respectively.

### Results and Discussions

We confirmed that most of the chromophores at side chains of pSPNIPAAm in an aqueous acidic solution were in a protonated opening form in dark exhibiting clear yellowish color. The positively charged chromophores prohibited the global precipitation of the polymer effectively even at relatively high temperatures. When they are irradiated with blue light, however, the chromophores were isomerized to the colorless closed-ring form and dissociated protons effectively. Opposite to protonated open-ring form, the chromophore in this state was basically hydrophobic and destabilized the solution. As a result, it was observed that the drastic and immediate dehydration of polymer was induced aqueous solution containing 0.2–1 mM HCl by light irradiation at around 30 °C. We also confirmed that the chromophore isomerized into the former open-ring protonated form spontaneously in the dark condition and such a photo-responsive change of the aqueous solution was repeatable more than 10 times.

From the experimental results on such photo-responsive properties we obtained for pSPNIPAAm aqueous solutions, it was expected that the volume change is induced by light based on this mechanism of dehydration (Fig.1). As a result of the characterization carried out for the pSPNIPAAm hydrogel, we observed that the small piece of the hydrogel with the size of a few mm shrunk in 0.5 mM HCl aq. in response to the blue light irradiation. The time scale of the

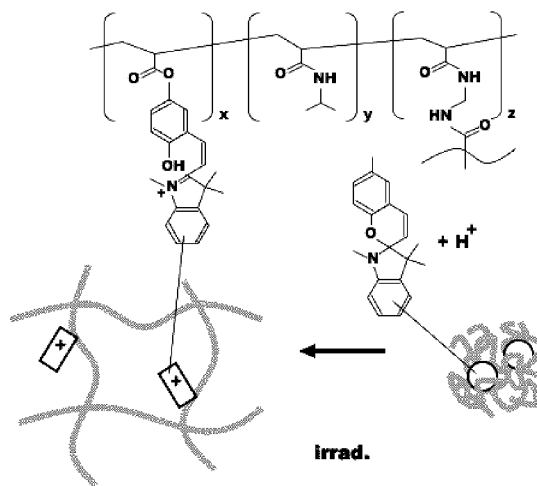


Fig.1 Schematic illustration showing the mechanism of photo-induced shrinkage of pSPNIPAAm hydrogel.

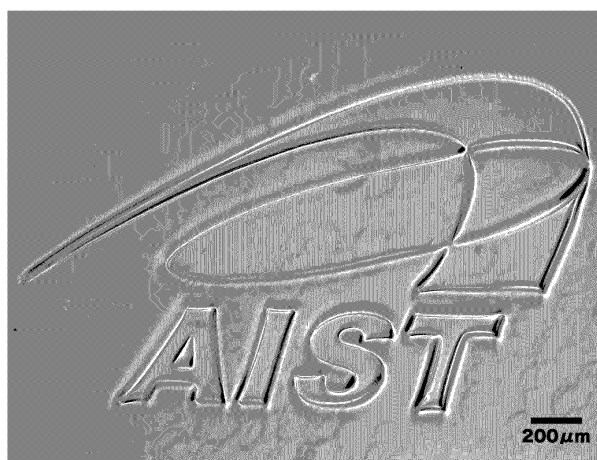


Fig.2 The image of pSPNIPAAm hydrogel layer, which had been stored in 0.5 mM HCl aq. in the dark, after micro-patterned light irradiation.

shrinkage was much dependent on the crosslinking ratio and the mesoscopic structure of the hydrogel.

In the experiment of micro-patterned light irradiation onto a pSPNIPAAm hydrogel thin layer, it was observed that the 5 sec irradiation bleached the color of the hydrogel firstly, and then the shrinkage took place in the following 4 min. From the result, it was suggested for the photo-induced shrinkage of the hydrogel that the ring closure and proton dissociation of the most chromophores were completed in 5 sec of light irradiation and then dehydration of the hydrogel proceeded due to the hydrophobic nature of the resultantly produced isomer. Figure 2 shows the image of the hydrogel layer after micro-patterned light irradiation. The hydrogel in the irradiated region shrank to a half thickness of the former state maintaining sharp outline of the irradiated pattern. In the case shown in Fig.2, the photo-induced thickness change of the hydrogel layer was larger than the width of the letters.

### Conclusions

We developed novel polymer materials composed of thermoresponsive pNIPAAm main chain and photo-responsive side chains of spirobenzopyran. As a result, the copolymer exhibited quite unique response to light irradiation and the change in temperature and pH. Especially the drastic photo-induced dehydration was observed in low pH conditions, and photo-induced micro-relief formation was demonstrated using the hydrogel layer composed of the polymer.

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