Photo Mechanical Effect of a Gel by Sensitized Photochromic Reaction

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1 Introduction
Recently functional gels have been attracting much attentions from the view point of intelligent materials such as photo-mechanical gels [1,2]. Those intelligent gel systems are expected to be various applications, such as DDS, micro-machine and so on. We have developed photomechanical material based on the photochromic reaction of azo-derivatives [3]. Artificial switching of light is required, however, for switching their shape repeatedly. Therefore those photomechanical materials whose shape spontaneously change upon photo-irradiation without external switching are desirable. The purpose of this study is constructing photomechanical gels that exhibit spontaneous expansion-construction behavior upon on photo stimulus via sensitization reaction.

2 Experimental
Chemical structures of gels used in this study are shown (Figure1). Azobenzene acrylamide (Azo-AAm), p-nitroazobenzene acrylamide (NAzo-AAm) and benzophenone acrylamide (bp-AAm) are synthesized by acrylation of the corresponding materials, aminoazobenzene, 4-((4-nitrophenyl)diazenyl)aniline and p-hydroxybenzophenone, respectively. a-Cyclodextrin (CD)-AAm are synthesized by acrylation of amino-CD using acryloyl chloride in the same way. aCD-Azo gel is synthesized by radical copolymerization of mixed solution of aCD-AAm, Azo-AAm, acryl-
methlenebisacrylamide (MBAAm) in water/DMF (water:DMF = 1:1). NAzo-S gel is synthesized by radical copolyization of mixture of NAzo-AAm, bp-AAm, acrylamide(AAm) and methlenebisacrylamide (MBAAm) in dimethyl-sulphoxide (DMSO) using azobisisobutyronitrile as an initiator. Photoinirradiation was performed with a low-pressure mercury lamp and ultrahigh-pressure mercury lamp combined with band-pass filters to monochromate.

3 Results and Discussion

Figure 2 shows volume swelling ratio of αCD-Azo gels, αCD-Azo-S gels, and NAzo-S gels immersed in water/DMF solution for about 12 hours. αCD-Azo gels and αCD-Azo-S gels become swollen state in hydrophilic solvent composition, however, NAzo-S gels become swollen state in hydrophobic solvent.

Figure 2 Volume swelling ratio of gels immersed in water/DMF for about 12 hours. αCD-Azo gels (red), αCD-Azo-S gels (blue), and NAzo-S (green).

Figure 3 shows the change in absorption spectra of αCD-Azo-S gels under photoirradiation of ultraviolet light (λ = 254, 365 nm). Photoirradiation of 365 nm light induced isomerization of azo group from trans- to cis-form, while reverse photo- isomerization occurs by the photoirradiation of 254 nm light. Sensitizer has absorption in this wavelength region, but azobenzene does not have so large absorption in this region, meaning that the reaction was induced by the sensitization via benzophenone moiety.

Figure 3 Change in absorption spectra of αCD-Azo-S gels under photoirradiation of ultraviolet light. Before photoirradiation (black), after photoirradiation of 365 nm light, and after photoirradiation of 254 nm light, respectively.

Volume change of NAzo-gels and αCD-Azo gels was induced by the photoirradiation, namely their gel volumes decreased by the photoirradiation based on the trans-cis photoisomerization. This volume change can be attributed to the inclusion of trans-azobenzene into CD, while cis-azobenzene cannot be included in CD. The volume change stopped when the gels were placed in dark. The volume change of αCD-Azo-S gels continued even keeping the gels in dark after photoirradiation, meaning that the structural change during the photoirradiation was memorized in the gel network, which induced the volume change of the gels even in dark after the photoirradiation.

Figure 4. Change of volume swelling ratio when αCD-Azo-S gel is irradiated ultraviolet light (λ = 254, 365 nm) for each 30 min

Figure 4. shows change in volume swelling ratio of αCD-Azo-S gels under photoirradiation immersed in 10% or 80% DMF solution. 365 nm light was irradiated until 30 min, then 254 nm light was irradiated. Volume of αCD-Azo-S gels in 80%DMFaq become larger under photoirradiation of 365 nm light, and then the volume rapidly becomes shrink by the photoirradiation at 254 nm. In other hand,
αCD-Azo-S gels immersed in 10%DMFaq become swollen both by the photoirradiation at 365, and 254 nm. This phenomenon is explained that small change in the trans/cis composition drastically induced volume change of the gel in steady-state of photochromic reaction.

**Conclusion**

Photo-mechanical gels containing sensiteizes were prepared and their volume change by photoirradiation was investigated. The volume change of the gels was induced by the photoirradiation via photosensitization. The induced photochemical change was memorized in αCD-Azo gels which continue to volume change even after photoirradiation in dark.

**References**

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