Polymer Journal (2014) 46, 827–830

www.nature.com/pj

RAPID COMMUNICATION

High-strength gel actuator driven by a photothermal effect

Polymer Journal (2014) **46,** 827–830; doi:10.1038/pj.2014.78; published online 17 September 2014

An actuator is a transducer that can convert external energy into mechanical motion. The most familiar example of an actuator is a muscle, which can convert chemical energy into mechanical motion. The materials of useful actuators should possess softness and strength in response to external stimuli. Among the various materials used for developing soft actuators, polymers are promising materials owing to their high processability and softness. Therefore, the potential of various types of polymer materials, such as polymer gels[1] and conducting polymers,[2] have been investigated.

Liquid-crystalline elastomers (LCEs) have been determined to be suitable for making soft actuators because of their molecular order and elasticity.[3,4] An LCE can convert external energy into mechanical motion via a cooperative change in molecular alignment. In previous studies of LCE actuators, an azobenzene LCE, which incorporates an azobenzene moiety into an LCE as a crosslinker, has attracted attention as a photoresponsive actuator.[5–8] Although it is important to use materials with high mechanical flexibility and durability to fabricate practical photoresponsive actuators, no effective material architecture that addresses these aspects has yet been reported. It is expected that developing high-strength photomechanical materials will have a broad range of applications. Moreover, considering radiation sources, most of the photomechanical LCEs have been manipulated by irradiation with ultraviolet or visible light. In contrast to short-wavelength radiation, infrared (IR) irradiation as the stimulus light is useful for developing practical actuators because IR light is a lower-energy light source for biological molecules.[9–11] Herein, we report a photomechanical material composed of a double-network hydrogel (DNG)[12,13] that exhibits high mechanical strength, and we focus on the photothermal effect, a change in molecular alignment in the gel induced by IR irradiation.

The sample gels were synthesized by multistep radical polymerization. In the first gel preparation, we poured the cationic monomer *N*-[3-(*N*,*N*-dimethylamino)propyl]acrylamide methyl chloride quaternary (DMAPAA-Q; 2.0 M), the crosslinking agent *N*,*N*′-methylenebis(acrylamide) (MBAA; 10 mM) and the radical initiator 2,2′-azobis(2-methylpropionamidine)dihydrochloride (10 mM) into a glass mold measuring $25 \times 25 \times 1.5\,mm^3$. The glass cells containing the mixture were heated to 60 °C for 24 h and then immersed in acrylamide (2.0 M), MBAA and KPS (1.0 mM) aqueous solution at 5 °C for 1 week. After swelling, the gel was heated to 60 °C for 24 h, and the gel was then peeled from the mold. The gel was glued to two glass clamps for mechanical tests, and its size was $30 \times 20 \times 0.5$

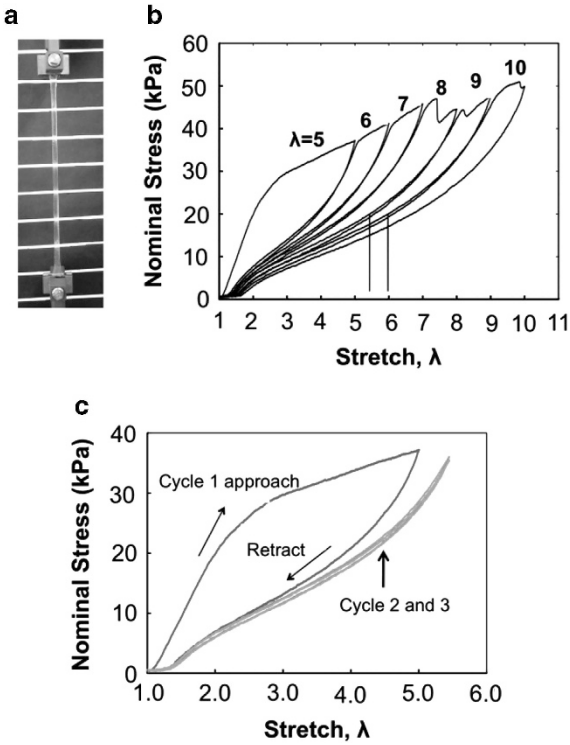

Figure 1 (**a**) Photograph demonstrating the tensile capability of the double-network hydrogel (DNG), which can elongate to more than 11 times its original length. (**b**) Samples of the DNG were subjected to a cycle of loading and unloading of varying maximum stretch. (**c**) Successive loading and unloading cycles, stretching a DNG sample three times. A full color version of this figure is available at *Polymer Journal* online.

mm^3. First, we investigated the effect of the crosslinker concentration, MBAA, on the mechanical properties because this element affects the strength and elasticity of the gel (Supplementary Figure S1).[14] The critical stretch length of the gel increases with decreasing crosslinker concentration in the second gel preparation (Supplementary Figure S2). However, the gel containing low crosslinker concentration (<0.2 mM) showed little elasticity even while exhibiting high stretchability of beyond 20 times the original length. Based on the results, a crosslinker concentration of 0.2 mM was chosen for the second gel preparation. In the preparation condition, the gel showed elastic elongation to >11 times its original length without rupture (Figure 1a). Systematic loading and unloading experiments at uniaxial tension showed a significant hysteresis during the first loading cycles, and the hysteresis increased strongly with the applied maximum deformation (Figure 1b). However, this hysteresis was not observed after the second loading cycle (Figure 1c). Similar hysteresis has also been reported to occur in tough DNGs.[9] This phenomenon is explained by the effect of the first ionic network on the mechanical property. That is, the first fragile network formed by an ionic interaction is broken into small clusters by elongation, and the clusters act as crosslinkers of long polyacrylamide chains. The crosslinkers of the first network clusters slide on the stretching chains of the second networks, resulting in high stretchablility.[15] In this case, the sliding network clusters are also formed by ionic polyDMAPAA-Q (Supplementary Figure S2), and they give rise to high stretchability in the gel.

A photomechanical LCE should possess molecular anisotropy for effective mechanical actuation along the preferential direction of deformation.[16] Generally, LCE properties are used to add molecular order to a material. In this study, we give molecular order to the DNG by stretching along a specified direction. Figure 2 shows a polarizing image of the stretched sample. As viewed through crossed polarizers, the transmittance of the backlight through the DNG was the brightest when the angle between the analyzer and the stretching direction was at 45 and 135°. This result indicates that the polymer networks were aligned along the stretching direction. Next, to investigate the IR response of the DNG system, we used an IR light with an intensity of 130 mW cm^{-2} at 1000 nm. In this study, we used low-intensity IR light to limit water evaporation. The DNG samples were fixed at both ends using mechanical clips, and the IR light source was focused on the central region of the sample. Figure 3a shows the photomechanical behavior of DNG upon irradiation with IR light. When IR light was used, the nominal stress increased, indicating photoinduced contraction of the gel. The photoinduced mechanical change reverted after the irradiation stopped. Furthermore, this actuation behavior occurred repeatedly. The results indicate that the high-strength photomechanical material made using DNG without additives, such as CNTs to enhance absorption, can mechanically respond to IR irradiation. Next, we investigated the photothermal effect on the actuation by monitoring the temperature profile of the irradiated area (Figure 3b).

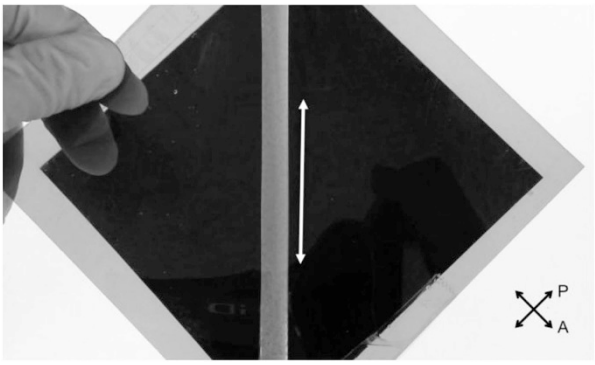

Figure 2 Photograph demonstrating the molecular alignment in the stretched double-network hydrogel (DNG) in the polarizing optical state. The white arrow shows the stretching direction. P and A represent the polarizer and analyzer, respectively. A full color version of this figure is available at *Polymer Journal* online.

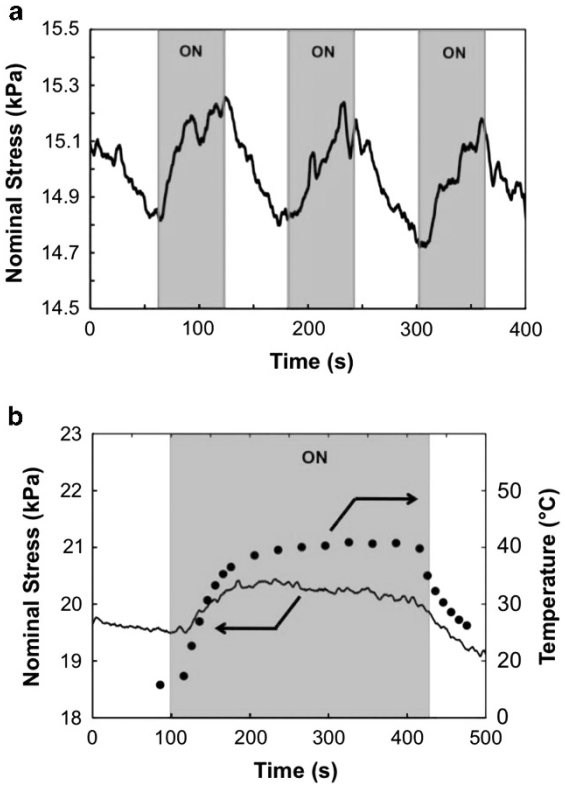

Figure 3 Change in strain of the double-network hydrogel (DNG) sample under infrared (IR) irradiation. (**a**) Stress responses to IR stimulus of the DNG with elongation to five times the original length. (**b**) The relationship between change in stress and temperature upon irradiation with IR light. Highlighted regions indicate periods of IR irradiation. A full color version of this figure is available at *Polymer Journal* online.

Upon IR irradiation, the temperatures of the irradiated area increased to approximately 60 °C due to absorption of IR light by the water component in the DNG. The change in nominal stress was induced by IR irradiation and yields good agreement with the increase in temperature. The change in nominal stress increased gradually after irradiation for 180 s, even when a maximum temperature of 60 °C was maintained. If the actuation behavior arose solely from the volume change caused by water vaporization, the change in nominal stress would continue to increase. Therefore, the decrease in the nominal stress indicates minimal response of the actuation by volume change with vaporization of the water component. To clarify the mechanism of the photoinduced actuation, we then investigated the effect of molecular order on the photomechanical motion. Figure 4 shows the photoinduced mechanical effect at various degrees of stretching ($\lambda = 2, 3, 4, 5$) under IR irradiation. All of the stretched DNGs contracted upon IR irradiation and exhibited relaxation after irradiation stopped. Apparently, samples that stretched more experienced an increased change in the nominal stress (Figure 5), indicating the importance of molecular alignments in the DNG for the actuation behavior. That is, the actuation behavior is induced by a change in the molecular alignment as a result of the photothermal effect of IR absorption.

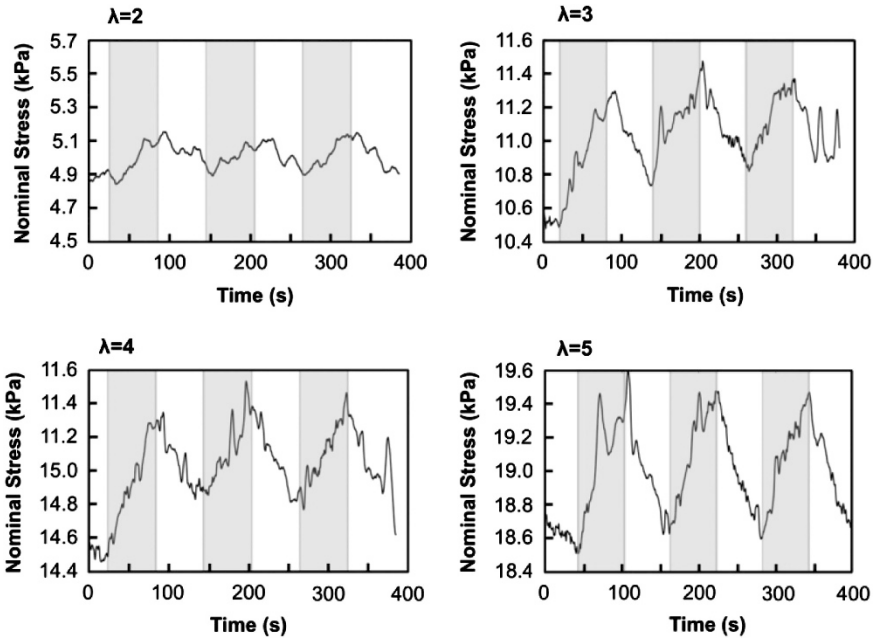

Figure 4 Change in stress of double-network hydrogel (DNG) samples subjected to various degrees of stretching ($\lambda = 2, 3, 4, 5$) under infrared (IR) light stimulus. Highlighted regions indicate periods of IR irradiation. A full color version of this figure is available at *Polymer Journal* online.

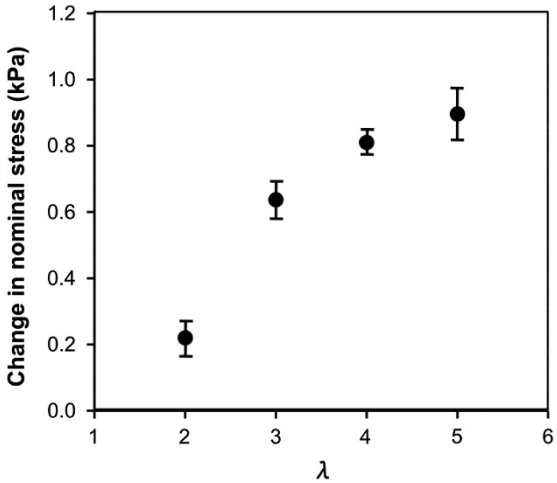

Figure 5 Change in stress with various elongation degrees ($\lambda = 2, 3, 4, 5$), averaged over three times. Error bars show standard deviation.

In this study, we showed actuation behavior in high-strength DNGs induced by the photothermal effect. In the photomechanical DNG system, the water component acts as an absorber of IR light and converts light energy into heat energy to facilitate mechanical actuation. The heat energy induces a cooperative change in the aligned molecular structure with stretching. The gel is not only a high-strength material but is also prepared using commercial reagents with simple reaction steps, consists largely of water (approximately 90 wt%) and responds to IR light. Therefore, we believe that this material system has the potential to provide practical photomechanical actuators for a broad range of applications.

ACKNOWLEDGEMENTS

This work was supported by CLUSTER (the second stage) of the Ministry of Education, Culture, Sports, Science and Technology, Japan.

Kunihiko Okano, Aya Nogami and Kouichi Asakura

Department of Applied Chemistry, Keio University, Yokohama, Kanagawa, Japan
E-mail: okano@applc.keio.ac.jp

1 Osada, Y., Okuzaki, H. & Hori, H. A polymer gel with electrically driven mobility. *Nature* **355,** 242–244 (1992).
2 Baughman, R. H. Conducting polymer artificial muscles. *Synth. Met.* **78,** 339–353 (1996).
3 De, Jeu & Wim, H. (ed.) *Liquid Crystal Elastomers: Materials and Applications* (Springer, 2012).
4 Zentel, R. Liquid crystalline elastomers. *Adv. Mater.* **1,** 321–329 (1989).
5 Finkelmann, H., Nishikawa, E., Pereira, G. G. & Warner, M. A new opto-mechanical effect in solids. *Phys. Rev. Lett.* **87,** 015501 (2001).
6 Hogan, P. M., Tajbakhsh, A. R. & Terentjev, E. M. UV manipulation of order and macroscopic shape in nematic elastomers. *Phys. Rev. E.* **65,** 041720 (2002).
7 Natansohn, A & Rochon, P. Photoinduced motions in azo-containing polymers. *Chem. Rev.* **102,** 4109 (2002).
8 Ikeda, T. Photomodulation of liquid crystal orientations for photonic applications. *J. Mater. Chem.* **13,** 2037 (2003).
9 Koerner, H., Price, G., Pearce, N. A., Alexander, M. & Vaia, R. A. Remotely actuated polymer nanocomposites stress-recovery of carbonnanotube-filled thermoplastic elastomers. *Nat. Mater.* **3,** 115–120 (2004).

10 Ahir, S. V. & Terentjev, E. M. Photomechanical actuation in polymer-nanotube compsites. *Nat. Mater.* **14,** 491–495 (2005).
11 Ji, Y., Huang, Y., Rungsawang, R. & Terentjev, E. M. Photomechanical actuation in polymer-nanotuve composites. *Adv. Mater.* **22,** 3436–3440 (2010).
12 Gong, J. P. Why are double network hydrogels so tough? *Soft Matter* **6,** 2583–2590 (2010).
13 Gong, J. P., Katsuyama, Y., Kurokawa, T. & Osada, Y. Double network hydrogels with extremely high mechanical strength. *Adv. Mater.* **15,** 1155–1158 (2003).
14 Sun, J. Y., Zhao, X., Illeperuma, W. R. K., Chaudhuri, O., Oh, K. H. & Mooney, D. J. Highly stretchable and tough hydrogels. *Nature* **489,** 133–136 (2012).
15 Na, Y.H., Tanaka, Y., Kawaguchi, Y., Furukawa, H., Sumiyoshi, T., Gong, J. P. & Osada, Y. Necking phenomenon of double-network gel. *Macromolecules* **39,** 4641–4645 (2006).
16 Ikeda, T., Mamiya, J. & Yu, Y. Photomechanics of liquid-crystalline elastomers and other polymers. *Angew. Chem. Int. Ed.* **46,** 506–528 (2006).

Supplementary Information accompanies the paper on Polymer Journal website (http://www.nature.com/pj)