COMMUNICATION

Three-Dimensional Photomobility of Crosslinked Azobenzene Liquid-Crystalline Polymer Fibers
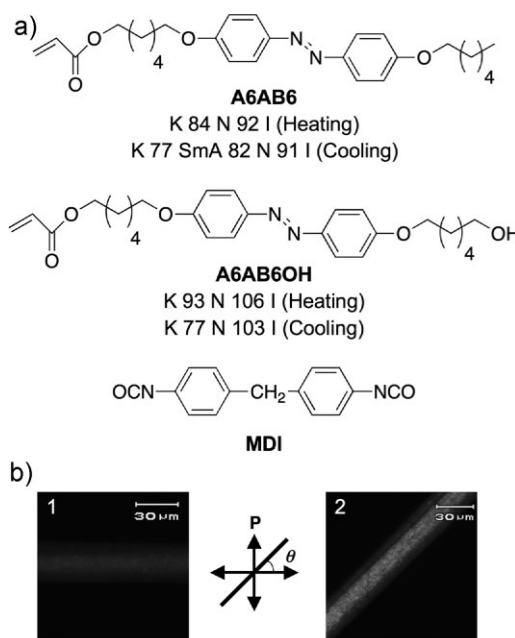
By *Taiki Yoshino, Mizuho Kondo, Jun-ichi Mamiya, Motoi Kinoshita, Yanlei Yu,* and *Tomiki Ikeda**

Human skeletal muscles are composed of many bundles of fibers and their crucial function to convert chemical energy into mechanical work is achieved by generating smooth motion and inducing high stress by external stimuli. Recently, there has been a considerable effort to develop artificial muscles or actuators that can mimic muscle performance, and various materials that resemble human muscles have been reported such as shape-memory alloys,[1,2] polymer gels,[3–5] conducting polymers,[6–8] carbon nanotubes,[9–12] and dielectric elastomers.[13] To achieve smooth motion as in human muscles, it is most desirable to use soft materials with high mechanical flexibility. Crosslinked liquid-crystalline polymers (CLCPs) are unique materials with properties of both of liquid crystals (LCs) and elastomers and especially promising for applications in actuators due to the self-organization nature of LC systems.[14–16] CLCPs responding to external stimuli in the form of fibers were also reported for artificial muscles.[17–19] By incorporating photochromic molecules such as azobenzene moieties into CLCPs, large motions can be induced by photochemical reactions of these azobenzene chromophores.[20–27] Soft actuators driven by light could play an important role for novel applications in a wide range of industrial and medical fields, because light is a clean energy source and can be controlled rapidly and remotely.

In our previous work, we have developed photomobile materials with CLCPs containing azobenzene moieties.[28–33] A bending of the CLCP films composed only of azobenzene mesogens has been observed by irradiation with UV light. The CLCP films can generate surface deformation caused by a change in alignment of LCs upon exposure to UV light, which contributes to the bending. We have also demonstrated new three-dimensional movements of the CLCP and their composite materials driven only by light: a light-driven plastic motor, an inchworm walk, and a flexible robotic arm motion.[34,35] They can convert light energy directly into mechanical work without the aid of batteries, electric wires, or gears. With CLCP fibers containing azobenzene moieties, one may expect the change in alignment of LC mesogens upon exposure to UV light. In this Communication, we report a precise directional control of

photomobility in the CLCP fibers. We were able to induce three-dimensional movement of the CLCP fibers only by light.

The structures of LC monomers (**A6AB6** and **A6AB6OH**) and a crosslinker, 4,4′-methylenebis(phenyl isocyanate) (MDI) used in this study are shown in Figure 1a. **A6AB6** was synthesized according to a procedure similar to that in the literature.[36] The CLCP fibers were prepared by two-step reactions, as previously reported.[15] Firstly, the LC monomers were polymerized by radical polymerization. Then the obtained copolymers were mixed with MDI, and the mixtures were formed into fibers by dipping a tip of a toothpick into the mixture and pulling the mixtures with the toothpick as quickly as possible. Thermal and optical properties of the CLCP fibers were investigated by differential scanning calorimetry (DSC), IR absorption spectroscopy, and polarizing optical microscopy (POM). By DSC measurements, it was found that the CLCP fibers exhibited a glass-transition temperature (T_g) of around $60\,^\circ$C. In IR spectra of the CLCP fibers, the absorption band corresponding to the $N-H$ stretch of the urethane bond was observed at around $3500\,cm^{-1}$.

[*] Prof. T. Ikeda, T. Yoshino, Dr. M. Kondo, Dr. J. Mamiya,
Dr. M. Kinoshita
Chemical Resources Laboratory, Tokyo Institute of Technology
R1-11, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503 (Japan)
E-mail: tikeda@res.titech.ac.jp
Prof. Y. Yu
Department of Materials Science, Fudan University
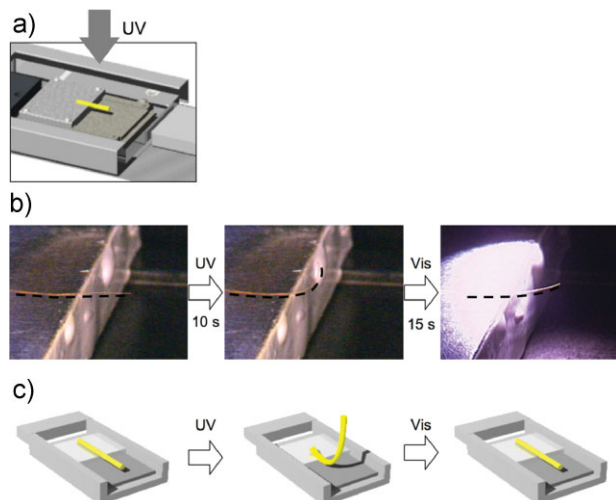220 Handan Road, Shanghai 200433 (P. R. China)

Figure 1. a) Chemical structures of the LC monomers (**A6AB6** and **A6AB6OH**) and the crosslinker (MDI) used in this study. b) Polarizing optical microscopy images of the texture of the CLCP fiber. Sample angle to the analyzer: $\theta = 0^\circ$ (1); $\theta = 45^\circ$ (2). The textures were observed at room temperature. I, isotropic; N, nematic; SmA, smectic A; K, crystal.
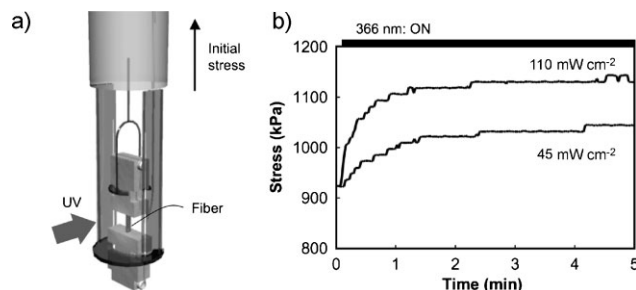
Figure 2. a) Schematic illustration of the experimental setup. b) Photographs of photoinduced bending and unbending in the CLCP fiber upon irradiation with UV light (100 mW cm^{-2}) and visible light (120 mW cm^{-2}). c) Schematic illustration of the states of the fiber after irradiation with UV and visible (Vis) light. The size of the fiber is 20 mm × 20 μm.
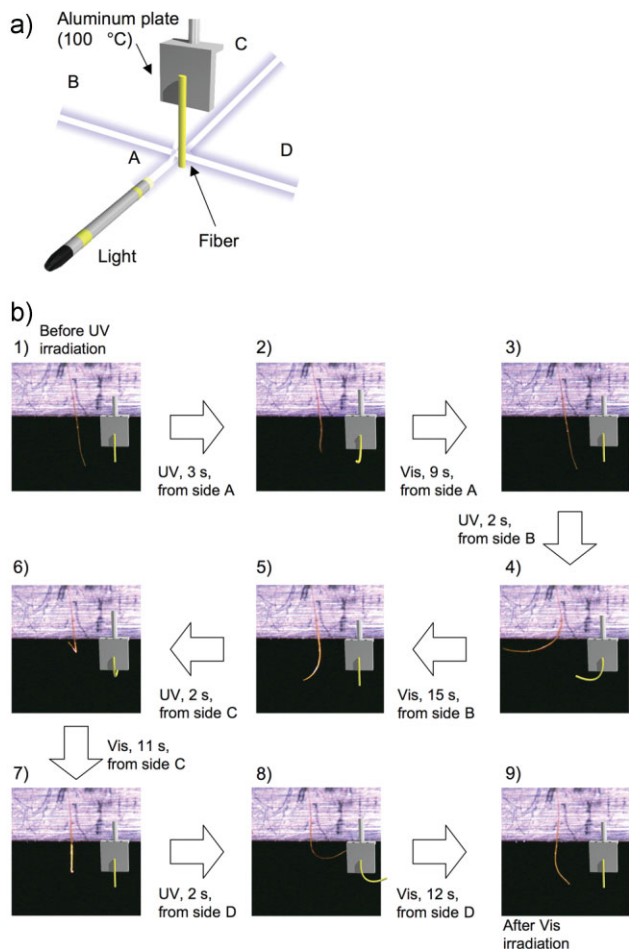

Figure 3. a) Schematic illustration of the experimental setup. b) Change in stress of the CLCP fibers when exposed to UV light at 366 nm with different intensities at 90 °C. An external stress of 930 kPa was loaded initially on the fibers to keep their length unchanged. Average size of the fiber: 6 mm × 80 μm.

POM observations also revealed that the CLCP fiber, which was placed between crossed polarizers, showed a contrast inversion every 45° upon rotating the sample with respect to the analyzer, as shown in Figure 1b. This result indicates that the CLCP fibers show a high order of mesogens along the fiber axis. We investigated the photoresponsive behavior of the CLCP fibers. Part of the CLCP fiber was pasted onto an aluminum block and heated to 90 °C by a hot stage, as shown in Figure 2a. When the CLCP fiber was exposed to UV light at 366 nm, the CLCP fiber bent toward the actinic light source along the fiber axis (Fig. 2b). The bent fibers reverted to the initial flat state upon irradiation with visible light at >540 nm. The photoinduced bending of the CLCP fibers was reversible simply by changing the wavelength of the actinic light, similar to that of the CLCP films.[20,28] As mentioned previously, the CLCP fibers have a high degree of alignment of the mesogens along the fiber axis; therefore, irradiation with UV light leads to a reduction of the alignment order of the azobenzene mesogens along the fiber axis. Moreover, the extinction coefficient of the azobenzene moieties at around 360 nm is large (about 2.0×10^4 L mol^{-1}cm^{-1}) and almost all the incident photons are absorbed at the surface region. This means that the CLCP fibers with a high concentration of azobenzene moieties can generate an alignment change only in the surface region of the fibers upon exposure to UV light. As a result, an uneven distribution of the molecular alignment is produced and the bending motion can be induced in the fiber.

Changing the orientational order in the CLCPs leads to internal stresses and changes of the sample shape.[23,25] We measured the stress generated in the CLCP fibers upon exposure to UV light by thermomechanical analysis (TMA). It was difficult to measure the generated stress in a single fiber due to the measurement limit of TMA. We bundled three pieces of the fiber together side by side and fixed the top and bottom of the CLCP fibers using epoxy glue. As shown in Figure 3a, the bundled CLCP fibers were fixed by clamping both ends of the fibers and

heating to 90 °C, which is higher than the T_g value of the CLCP fiber. Initial stress was loaded onto the bundled fibers to keep their length constant. The stretching direction was parallel to the fiber axis. Upon irradiation with UV light, the generated stress increased and reached 120 and 210 kPa when the light intensity was 45 and 110 mW cm^{-2}, respectively. It was found that a higher intensity of UV light could generate larger stress, as shown in Figure 3b. Additionally, the bending time of the fibers decreased significantly with an increase in light intensity because actinic light with a higher intensity produces a higher concentration of cis-azobenzene moieties and, thus, a larger surface contraction.

A three-dimensional control of a bending direction in the CLCP fibers was carried out with the experimental setup shown in Figure 4a. Since the shape of the CLCP fiber was approximately cylindrical, the CLCP fiber could be irradiated with light under the same conditions from every side. The freestanding CLCP fiber was placed on an aluminum block, heated with a thermocouple to 100 °C, and irradiated with UV and visible light. Figure 4b(1) shows the CLCP fiber before photoirradiation. Upon irradiation at 366 nm (100 mW cm^{-2}) for 3 s from the side A, the CLCP fiber bent toward an actinic light source (Fig. 4b(2)). Then, the bent fiber reverted to its initial state upon irradiation with visible light for 9 s (Fig. 4b(3)). The direction of the bending upon photoirradiation could be controlled by changing the irradiation direction of the actinic light. As shown in Figure 4b(4–9), upon continuous irradiation with UV and visible light from the sides B, C, and D, the CLCP fiber bent toward the actinic light source and reverted to its initial state, respectively (for a video demonstration, see the Supporting Information). The three-dimensional control of the bending of the fibers was achieved by manipulating the irradiation conditions.

In conclusion, we prepared CLCP fibers containing an azobenzene moiety, and irradiation with 366-nm light caused the fibers to bend along the alignment direction of mesogens toward the actinic light source. The bent fibers recovered their initial state after exposure to visible light. The direction of the bending could be controlled by changing an irradiation spot of the fibers. The generated stress upon contraction of the natural surface length reached 210 kPa, a value that is similar to the stress in human muscles (around 300 kPa). The directional control in photomobility of the CLCP fibers may lead to potential applications in artificial muscles and light-driven actuators.

Materials
Views

www.MaterialsViews.com

ADVANCED
MATERIALS

www.advmat.de

COMMUNICATION

a)

b)

Figure 4. a) Schematic illustration of the experimental setup. b) Photographs of the CLCP fiber that exhibits photoinduced bending and unbending behavior upon irradiation with UV light (100 mW cm^{-2}) and visible light (120 mW cm^{-2}). The inset of each photograph is a schematic illustration of the state of the fiber. The size of the fiber is 30 mm × 20 μm.

Detailed synthetic procedures for the materials in this Communication can be found in the Supporting Information.

Acknowledgements

[1] M. V. Gandhi, B. S. Thompson, *Smart Materials and Structures*, Chapman & Hall, London, UK **1992**.
[2] J. D. Madden, *Science* **2006**, *311*, 1559.
[3] Y. Osada, H. Okuzaki, H. Hori, *Nature* **1992**, *355*, 242.
[4] *Polymer Sensors and Actuators*, (Eds: Y. Osada, D. E. De Rossi), Springer, Heidelberg, Germany **2000**.
[5] *Polymer Gels and Networks*, (Eds: Y. Osada, A. R. Khokhlov), Marcel Dekker, Inc, New York, USA **2002**.
[6] R. H. Baughman, *Synth. Met.* **1996**, *78*, 339.
[7] W. Lu, A. G. Fadeev, B. Qi, E. Smela, B. R. Mattes, J. Ding, G. M. Spinks, J. Mazurkiewicz, D. Zhou, G. G. Wallace, D. R. MacFarlane, S. A. Forsyth, M. Forsyth, *Science* **2002**, *297*, 983.
[8] E. Smela, *Adv. Mater.* **2003**, *15*, 481.
[9] R. H. Baughman, C. Cui, A. A. Zakhidov, Z. Iqbal, J. N. Barisci, G. M. Spinks, G. G. Wallace, A. Mazzoldi, D. De Rossi, A. G. Rinzler, O. Jaschinski, S. Roth, M. Kertesz, *Science* **1999**, *284*, 1340.
[10] P. Kim, C. M. Lieber, *Science* **1999**, *286*, 2148.
[11] Y. Zhang, S. Iijima, *Phys. Rev. Lett.* **1999**, *82*, 3472.
[12] G. M. Spinks, G. G. Wallace, L. S. Fifield, L. R. Dalton, A. Mazzoldi, D. De Rossi, I. I. Khayrullin, R. H. Baughman, *Adv. Mater.* **2002**, *14*, 1728.
[13] R. Pelrine, R. Kornbluh, Q. Pei, J. Joseph, *Science* **2000**, *287*, 836.
[14] P.-G. de Gennes, M. Hébert, R. Kant, *Macromol. Symp.* **1997**, *113*, 39.
[15] J. Küpfer, H. Finkelmann, *Macromol. Chem. Phys.* **1994**, *195*, 1353.
[16] D. L. Thomsen, P. Keller, J. Naciri, R. Pink, H. Jeon, D. Shenoy, B. R. Ratna, *Macromolecules* **2001**, *34*, 5868.
[17] J. Naciri, A. Srinivasan, H. Jeon, N. Nikolov, P. Keller, B. R. Ratna, *Macromolecules* **2003**, *36*, 8499.
[18] T. Kaneko, K. Yamaoka, Y. Osada, J. P. Gong, *Macromolecules* **2004**, *37*, 5385.
[19] S. V. Ahir, A. R. Tajbakhsh, E. M. Terentjev, *Adv. Funct. Mater.* **2006**, *16*, 556.
[20] T. Ikeda, J. Mamiya, Y. Yu, *Angew. Chem. Int. Ed.* **2007**, *46*, 506.
[21] C. J. Barrett, J. Mamiya, K. G. Yager, T. Ikeda, *Soft Matter* **2007**, *3*, 1249.
[22] H. Finkelmann, E. Nishikawa, G. G. Pereira, M. Warner, *Phys. Rev. Lett.* **2001**, *87*, 015501.
[23] P. M. Hogan, A. R. Tajbakhsh, E. M. Terentjev, *Phys. Rev. E* **2002**, *65*, 041720.
[24] M.-H. Li, P. Keller, B. Li, X. Wang, M. Brunet, *Adv. Mater.* **2003**, *15*, 569.
[25] C. L. M. Harvey, E. M. Terentjev, *Eur. Phys. J. E* **2007**, *23*, 185.
[26] C. L. van Oosten, D. Corbett, D. Davies, M. Warner, C. W. M. Bastiaansen, D. J. Broer, *Macromolecules* **2008**, *41*, 8592.
[27] T. J. White, S. V. Serak, N. V. Tabiryan, R. A. Vaia, T. J. Bunning, *J. Mater. Chem.* **2009**, *19*, 1080.
[28] T. Ikeda, M. Nakano, Y. Yu, O. Tsutsumi, A. Kanazawa, *Adv. Mater.* **2003**, *15*, 201.
[29] Y. Yu, M. Nakano, T. Ikeda, *Nature* **2003**, *425*, 145.
[30] Y. Yu, M. Nakano, A. Shishido, T. Shiono, T. Ikeda, *Chem. Mater.* **2004**, *16*, 1637.
[31] M. Kondo, Y. Yu, T. Ikeda, *Angew. Chem. Int. Ed.* **2006**, *45*, 1378.
[32] Y. Yu, T. Maeda, J. Mamiya, T. Ikeda, *Angew. Chem. Int. Ed.* **2007**, *46*, 881.
[33] J. Mamiya, A. Yoshitake, M. Kondo, Y. Yu, T. Ikeda, *J. Mater. Chem.* **2008**, *18*, 63.
[34] M. Yamada, M. Kondo, J. Mamiya, Y. Yu, M. Kinoshita, C. J. Barrett, T. Ikeda, *Angew. Chem. Int. Ed.* **2008**, *47*, 4986.
[35] M. Yamada, M. Kondo, R. Miyasato, Y. Naka, J. Mamiya, M. Kinoshita, A. Shishido, Y. Yu, C. J. Barrett, T. Ikeda, *J. Mater. Chem.* **2009**, *19*, 60.
[36] A. Angeloni, D. Caretti, C. Carlini, E. Chiellini, G. Galli, A. Altomare, R. Solaro, M. Laus, *Liq. Cryst.* **1989**, *4*, 513.

Adv. Mater. **2010**, *22*, 1361–1363

© 2010 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

WILEY
InterScience®
DISCOVER SOMETHING GREAT

1363