Anisotropic Photomechanical Motion of Semicircular-shaped Microfibers That Contain Dyes

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We prepared polyacrylamide-based fibers containing the dyes Methylene Blue or Acid Red 52 and observed their photomechanical motion upon light illumination. The fibers bend upon the application of photoillumination. The fibers recover their original shapes when photoillumination ends. The fibers bend anisotropically in a specific direction. The absorption properties and photobending behavior of the fibers are related.

Photoresponsive materials that change shape in response to light have attaracted much attention because they can be applied as photodriven motors,¹ actuators,^{2–12} and new types of solar energy-conversion systems.^{8,11,13–19} Materials exhibiting a volume change in response to light are of interest.^{20–23} For example, hydrogels that show a volume change upon the application of light have been reported previously.^{24,25} The basic mechanism for the volume change is a solvent absorption or desorption process. However, this has a drawback for practical application because the absorption or desorption process can only be achieved in the presence of a solvent and not in air. Another drawback is that the volume change is slow. Thus, materials showing a rapid volume change in air are desired. In this work, we prepared polyacrylamide (PAA)-based fibers containing the dyes Methylene Blue (MB) or Acid Red 52 (AR), and we observed photomechanical motion upon light illumination.

The fibers were prepared as follows: A viscous water solution (10 mL) containing PAA (1 g, MW: 5000000–6000000, Polysciences, Inc.) was added with either MB (32 mg, 0.1 mmol) and/or AR (58 mg, 0.1 mmol) followed by stirring for 1 h. A part of the resulting viscous liquid was anchored using a stick and then pulled up to readily form fibers of 100 to 1000 mm in diameter. The fibers were placed on a polystyrene substrate to dry for 24 h at room temperature at a humidity of 50%.

Figure 1 shows SEM images of the obtained fibers. The fibers prepared by the pulling method followed by placing on a plastic substrate have a structure with half their surface being flat (Figure 1a). This structure forms because when the fiber was placed onto the plastic substrate the bottom of the fiber became semicircular in shape. After drying the fiber retains this shape. The diameter of the fiber is several hundred nm. On the other hand, the fibers prepared without having been placed on the plastic substrate are circular, and their diameters are several hundred nm (Figure 1b).

We observed photobending of the fibers upon light illumination when using a Xe lamp. Figure 2 shows optical photos of the fibers before and after the photoillumination of







Figure 2. Optical photos of the bending behavior of a PAA/MB fiber (a) after illumination from the right side, (b) before illumination and (c) after illumination from the left side.

the PAA/MB fiber. The fiber shows bending behavior upon the application of photoillumination. The shape of the fiber recovered its initial position after photoillumination stopped. The reversibility of the bending behavior that was triggered by photoillumination was repeated more than 80 times. This bending behavior was also observed in the PAA fibers containing AR. In contrast, the PAA/MB fiber with a circular shape did not show bending behavior.

Interestingly, the fiber shows anisotropic bending in a specific direction. In Figure 2, the fiber was illuminated from the right side, and the fiber bent to the right side. On the other hand, when the fiber was illuminated from the left side, it again bent toward the right side. The important point of this specific bending should originate from the shape of the fiber with the fiber always bending toward the flat surface.

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Figure 3. Optical photos of a (a) PAA/MB fiber (a) after illumination at 550 nm, (b) before illumination, and (c) after illumination at 650 nm and a PAA/MB,AR fiber (d) after illumination at 550 nm, (e) before illumination, and (f) after illumination at 650 nm.



Figure 4. Absorption spectra for MB and AR.

The photobending behavior and wavelength of light illumination is related. The PAA/MB fibers bend upon illumination at 650 nm but show no response at 550 nm (Figures 3a–3c). The bending behavior is related to the absorption properties of the MB. As shown in Figure 4, the MB has a strong absorption at around 650 nm and only a small abosorption around 550 nm. These results indicate that the absorption of MB is related to the photobending of these fibers. In contrast, for the PAA/AR fibers, illumination at 550 nm causes bending and illumination at 650 nm does not cause bending. This is also related to the absorption of AR. AR absorbs at 550 nm and not at 650 nm.

The PAA fibers containing both MB and AR show bending behavior upon illumination at 550 and at 650 nm (Figures 3d– 3f). This means that we can widen the absorption wavelength for photobending behavior using different dyes.

The mechanism for the bending behavior of the fibers is being investigated and will be reported in the future. It may be related to a photothermal effect, thermal expansion or shrinkage and/or absorption or desorption of water molecule upon the illumination of the fiber.^{24,25} The fibers may have a large surface area, which may contribute the rapid desorption and absorption of water molecules.

In conclusion, we prepared photoresponsive fibers based on PAA containing dyes. The fibers show photobending behavior upon illumination with light. The fibers show anisotropic bending. The absorption properties and the photobending behavior are related.

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References

- M. Yamada, M. Kondo, J.-i. Mamiya, Y. Yu, M. Kinoshita, C. J. Barrett, T. Ikeda, *Angew. Chem., Int. Ed.* 2008, 47, 4986.
- 2 K. D. Harris, R. Cuypers, P. Scheibe, C. L. van Oosten, C. W. M. Bastiaansen, J. Lub, D. J. Broer, J. Mater. Chem. 2005, 15, 5043.
- 3 S. V. Ahir, E. M. Terentjev, *Nat. Mater.* 2005, *4*, 491.
- 4 Y. Yu, T. Ikeda, Angew. Chem., Int. Ed. 2006, 45, 5416.
- 5 T. Ikeda, J.-i. Mamiya, Y. Yu, Angew. Chem., Int. Ed. 2007, 46, 506.
- 6 C. J. Barrett, J.-i. Mamiya, K. G. Yager, T. Ikeda, *Soft Matter* 2007, *3*, 1249.
- 7 C. L. van Oosten, C. W. M. Bastiaansen, D. J. Broer, *Nat. Mater.* 2009, 8, 677.
- 8 T. Ikeda, M. Nakano, Y. Yu, O. Tsutsumi, A. Kanazawa, *Adv. Mater.* 2003, *15*, 201.
- 9 T. Yoshino, M. Kondo, J.-i. Mamiya, M. Kinoshita, Y. Yu, T. Ikeda, *Adv. Mater.* 2010, *22*, 1361.
- 10 H. J. Choi, K.-U. Jeong, L.-C. Chien, M.-H. Lee, J. Mater. Chem. 2009, 19, 7124.
- 11 S. Kobatake, S. Takami, H. Muto, T. Ishikawa, M. Irie, *Nature* 2007, 446, 778.
- 12 H. Koshima, N. Ojima, H. Uchimoto, J. Am. Chem. Soc. 2009, 131, 6890.
- 13 Y. Yu, M. Nakano, T. Ikeda, Nature 2003, 425, 145.
- 14 M. Kondo, Y. Yu, T. Ikeda, Angew. Chem., Int. Ed. 2006, 45, 1378.
- 15 G. van der Veen, W. Prins, *Nature* **1971**, *230*, 70.
- 16 C. D. Eisenbach, Polymer 1980, 21, 1175.
- 17 O. M. Tanchak, C. J. Barrett, *Macromolecules* 2005, 38, 10566.
- 18 Y. Yu, T. Maeda, J.-i. Mamiya, T. Ikeda, *Angew. Chem.* 2007, *119*, 899.
- 19 Y. Yu, M. Nakano, A. Shishido, T. Shiono, T. Ikeda, *Chem. Mater.* 2004, 16, 1637.
- 20 L. Kuroki, S. Takami, K. Yoza, M. Morimoto, M. Irie, *Photochem. Photobiol. Sci.* 2010, 9, 221.
- 21 H.-K. Kim, X.-S. Wang, Y. Fujita, A. Sudo, H. Nishida, M. Fujii, T. Endo, *Macromol. Chem. Phys.* **2005**, *206*, 2106.
- 22 T. Seki, R.-i. Fukuda, M. Yokoi, T. Tamaki, K. Ichimura, *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2375.
- 23 S. Lu, S. Ahir, V. Velasco, B. King, P. Xu, E. M. Terentjev, B. Panchapakesan, J. Micro-Nano Mechatronics 2009, 5, 29.
- 24 A. Suzuki, T. Tanaka, Nature 1990, 346, 345.
- 25 T. Tatsuma, K. Takada, T. Miyazaki, Adv. Mater. 2007, 19, 1249.

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