

# Light-Controlled Complex Deformation and Motion of Shape-Memory Polymers Using a Temperature Gradient

Hongji Zhang,<sup>†,‡</sup> Hesheng Xia,<sup>\*,§</sup> and Yue Zhao<sup>\*,†</sup>

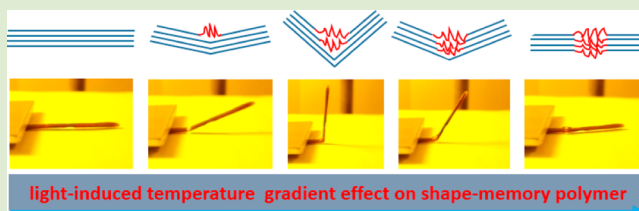
<sup>†</sup>Département de Chimie, Université de Sherbrooke, Sherbrooke, Québec J1K 2R1, Canada

<sup>‡</sup>Key Laboratory of Food Colloids and Biotechnology, Ministry of Education, School of Chemical and Material Engineering, Jiangnan University, Wuxi 214122, China

<sup>§</sup>State Key Laboratory of Polymer Materials Engineering, Polymer Research Institute, Sichuan University, Chengdu 610065, China

**ABSTRACT:** A unique property of photothermal effect-based shape-memory polymers (SMPs) is demonstrated using a chemically cross-linked poly(ethylene oxide) (PEO) loaded with a small amount (0.5 wt %) of gold nanoparticles (AuNPs). We show that controlled surface plasmon resonance absorption of AuNPs allows for the formation of a temperature gradient in the polymer of temporary shape, which results in anisotropic polymer chain relaxation and strain energy release.

This photoinduced temperature gradient effect enables the use of a laser to create a multitude of deformations and to control sophisticated motion executing mechanical work that are otherwise inaccessible with SMPs.

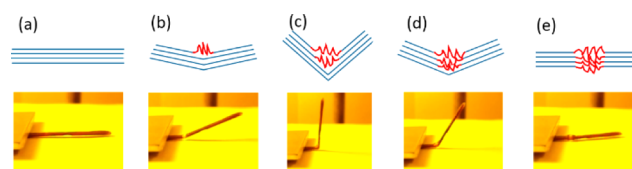


Shape-memory polymers (SMPs) feature the ability to recover a permanent shape from a temporary one.<sup>1–7</sup> A temporary shape is programmed by deforming a SMP above a phase transition temperature  $T_{tr}$  ( $T_g$  or  $T_m$ ) and then cooling it below  $T_{tr}$  to freeze polymer chains. Generally, the return to the permanent shape is activated by heating the polymer above  $T_{tr}$  to trigger polymer chain relaxation and thus release of the strain energy stored during the initial deformation. On the basis of this principle, stimuli other than direct heating, such as light,<sup>8–21</sup> electric or magnetic field,<sup>22–27</sup> and ultrasound,<sup>28,29</sup> have been increasingly exploited for controlling SMPs via stimuli-induced thermal effect. The main interests include the possibility of remote activation and spatial control (owing to localized heating) of the shape recovery process, which opens the door to new applications of SMPs. Examples include spatially programmable recovery of surface features of SMP micro-optical devices using integrated arrays of indium tin oxide (ITO) resistive heaters,<sup>30</sup> infrared (IR) light-induced folding of SMP sheets into 3D objects through patterning of IR-absorbing black ink,<sup>31</sup> and multishape nanocomposites with selective radiofrequency actuations by loading separately the magnetic fillers of iron oxide ( $Fe_3O_4$ ) and carbon nanotubes (CNTs).<sup>32</sup> Another approach for spatially variable shape recovery behavior consists in introducing a  $T_g$  gradient by UV curing of a thermoset on a hot plate with a temperature gradient.<sup>33</sup> Regarding light-controllable SMPs, although there are many ways to make use of photothermal effect for SMPs,<sup>13–20</sup> adding a small amount of gold nanoparticles (AuNPs) or nanorods (AuNRs) for absorbing light at their surface plasmon resonance (SPR) wavelengths and thus generating heat release has proved particularly interesting.<sup>34–36</sup>

For instance, due to the extremely high extinction coefficient of AuNPs,<sup>37</sup> a vanishing amount of 0.003 wt %, which ensures

good transparency and improved light penetration for the SMP sample, can be sufficient.<sup>36</sup> Herein, we unveil yet a new unique property of photothermal effect-based SMPs. By introducing the concept of photoinduced temperature gradient, we demonstrate that unprecedented light-controlled deformations and motions can be achieved with AuNP-loaded SMPs.

Using a chemically cross-linked poly(ethylene oxide) (PEO) containing 0.5 wt % AuNPs (average diameter  $\sim 10$  nm), whose synthesis was previously reported,<sup>36</sup> the concept of photoinduced temperature gradient in SMPs is illustrated in Figure 1. A simple temporary form of the SMP was obtained by stretching a film to about 90% deformation ( $30.5 \times 2.0 \times 1.0$  mm in length, width and thickness) at  $80^\circ C$  ( $>T_m$ ) followed by cooling to room temperature (a). The sketch above the photos depicts the polymer chain orientation along the stretching direction. When a laser of low intensity ( $\lambda = 532$  nm, 0.15 W) was applied vertically from the top to an area of



**Figure 1.** Photos showing a film of AuNP-loaded cross-linked PEO (thickness 1 mm) undergoing bending and unbending upon exposure to laser (532 nm, 0.15 W) due to a temperature gradient effect. The sketch above illustrates the stepwise relaxation of oriented polymer chains giving rise to the deformation and motion.

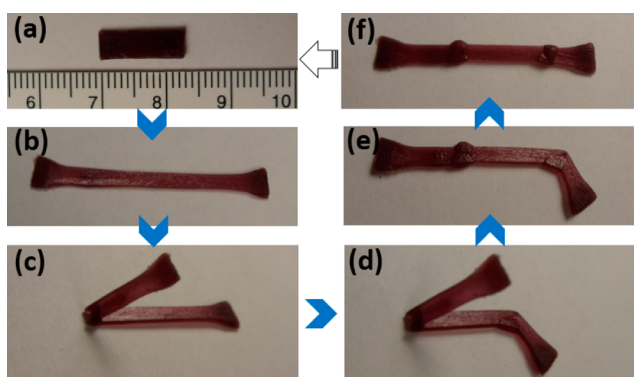
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the film close to the fixed side (laser spot  $\sim 3$  mm in diameter), the film bent toward the laser (b). What happens is that AuNPs located in a thin layer near the surface absorb light first and release heat; consequently, orientated chains in the upper surface undergo relaxation caused by the localized heating, giving rise to bending with a small angle. As laser exposure goes on, heating develops downward along the thickness direction; polymer chain relaxation occurs in deeper and deeper layers. During this process, the bending reaches a maximum angle (near  $90^\circ$  in the example, c) before unbending back to the flat shape (d and e). This demonstration shows that photothermal effect can readily be used to create a temperature gradient that, in turn, results in a gradient in polymer chain relaxation for anisotropic release of the strain energy.

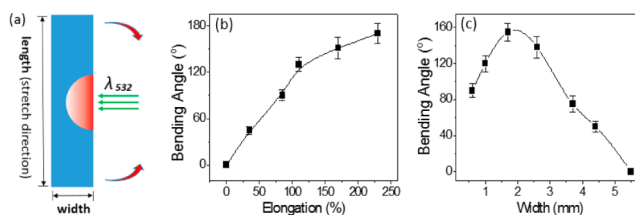
By making use of the light-induced temperature gradient in SMPs, sophisticated shape transformations can be realized in a remotely controllable and finely tunable fashion. The experiment in Figure 2 illustrates this property. An original film (a,



**Figure 2.** Photos showing the possibility of creating sophisticated shape transformations of an AuNP-loaded cross-linked PEO film by using the laser (532 nm, 0.15 W) induced temperature gradient effect.

$13.3 \times 4.4 \times 1.2$  mm) was deformed into a temporary shape (b,  $33.4 \times 2.3 \times 0.6$  mm) by stretching at  $80^\circ\text{C}$ , followed by cooling to room temperature (about 200% strain of the central area). The sample was first treated with the top surface exposed to a laser, resulting in gradient relaxation of oriented polymer chains and, as a result, a large out-of-plane bending (c, bending angle  $> 130^\circ$ ). Once the laser was turned off, since the localized heating was halted with the sample cooled down below  $T_m$ , the temporary shape was fixed. Moreover, where, how, and to what extent making the bending take place can easily be programmed owing to the spatial and temporal control of using a portable laser as a remote trigger. Similarly, when placing the laser beam against one lateral side of the sample, in-plane bending can be achieved for the same reason for gradient chain relaxation (d). Subsequently, on-demand, the out-of-plane and in-plane bending can be made to revert back, in a sequential manner, by applying the laser to the corresponding opposite side of the sample (e and f). The two selected areas exposed to a laser underwent contraction, as expected, with the appearance of the scar-like portions in the film (f). Eventually, the permanent (original) shape was recovered by exposing the whole film to a laser (a).

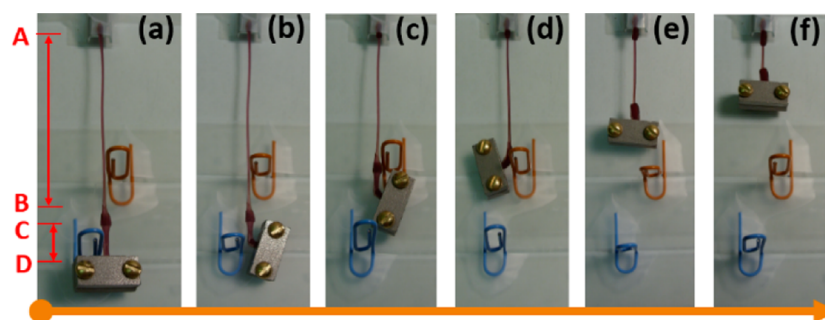
From the above, it is easy to imagine that the temperature gradient, which dictates the SMP deformation and motion behaviors, is dependent upon such parameters as laser intensity, beam size, AuNP content, and sample thickness. Under a laser-induced temperature gradient, the resulting gradient in polymer



**Figure 3.** (a) Schematic showing the laser exposure (532 nm, 0.15 W) on one side of the AuNP-loaded cross-linked PEO film for measurement of the achievable in-plane bending angle. (b) Plot of bending angle vs film elongation at the same width of 1 mm. (c) Plot of bending angle vs film width at the same sample elongation of 150%.

chain relaxation should be related to the amount of strain energy stored in the SMP sample. To make the point, Figure 3 reports the results of two sets of experiments designed to unveil the role of two parameters: stored strain energy and sample width. The experiments were conducted as illustrated in Figure 3a. On the one hand, to investigate the effect of stored strain energy, films with different initial widths were stretched to different elongations at  $80^\circ\text{C}$ , followed by cooling, to reach the same final width of 1 mm. Using the same experimental conditions as in Figure 2, the maximum light-induced in-plane bending angle was measured as a function of film elongation. The result in Figure 3b shows that the achievable bending angle increases with increasing the film elongation. This observation is no surprise because a higher film elongation means a greater degree of polymer chain orientation and thus a larger amount of stored strain energy. Under the light-induced temperature gradient, relaxation of polymer chains from a more extended state to random coil at the molecular level should result in a larger film-bending angle at the macroscopic scale. On the other hand, to observe the effect of the film width on the maximum bending angle, films of different initial widths were stretched to the same elongation of 150% at  $80^\circ\text{C}$  followed by cooling. The data in Figure 3c suggest that at a given laser intensity, AuNP content, and stored strain energy there exists an optimal width for the maximum bending angle. This is also understandable. If the film is too narrow, the photoinduced heating may propagate quickly across the width of the film and the absence of an effective temperature gradient limits the achievable bending. At the opposite, if the film is too wide, a stable temperature gradient can be built, but the contraction force arising from chain relaxation in the region close to the laser exposed lateral side is too weak to bend the rest of the film undergoing no chain relaxation. It is noteworthy that the tests in Figure 3 were designed to isolate the effect of one single parameter. The effect of width on the in-plane bending angle under constant elongation (Figure 3c) is actually indicative of the effect of thickness on the out-of-plane bending angle. The effect of thickness cannot be assessed by stretching one sample to different elongations, because the effect of decreasing thickness is coupled to the effect of increasing stored strain energy.

The multitude of deformations and shape transformations enabled by the photoinduced temperature gradient in SMPs can also be used to execute complex light-guided mechanical work upon the controlled release of strain energy. The experiment in Figure 4 demonstrates the possibility. The purpose of the operation consisted in using only a laser to remotely pull up a load sitting on a slope of  $30^\circ$  leaning angle against the gravitational and frictional force while avoiding



**Figure 4.** Photos showing the light-guided lifting of a piece of metal attached to a stripe of AuNP-loaded cross-linked PEO. Under light-controlled deformation and strain energy release, the mechanical work was completed without collision of the metal with the two obstacles.

obstacles. As shown in *a*, one stripe of the SMP sample (original size:  $18.8 \times 3.1 \times 1.4$  mm) was deformed at  $80^\circ\text{C}$  followed by cooling to afford a temporary shape featuring two sections, labeled “AB” and “CD”, stretched to  $\sim 450\%$  and  $60\%$  elongations, respectively. A piece of metal (5 g) was attached onto the lower end of the film and obstructed by two clips in its path. The following sequence of laser exposures was applied in order to lift the load without colliding with the obstacle. First, the laser beam was aimed at the right side of the film (“CD” section) to make the metal turn right upon light-induced in-plane bending (*b*). This was followed by moving the laser exposure to the upper part of the film (“AB” section) to pull the weight up resulting from light-induced contraction of the film until the piece of metal faced the other clip (*c*). Afterward, the laser exposure was applied against the left side of the lower section of the film to impose in-plane bending that made the load turn left while avoiding the clip (*d*). Finally, after pulling the weight further up using contraction of the upper part of the film, the lower section was unbent (*e*) and the load was lifted up (*f*). The entire work was executed remotely by using a laser.

In summary, we presented the concept of optically inducing a temperature gradient in SMPs and using the resulting anisotropic polymer chain relaxation to create complex shape transformations and execute delicate mechanical work upon light-controlled release of strain energy. In principle, this unique property can be exploited with many kinds of photothermal effect-based SMPs. Nevertheless, the degree of remote activation (long distance), spatial control (location and resolution), and fine-tuning of the temperature gradient by using light is inaccessible or cannot be matched by direct heating or other stimuli.

## AUTHOR INFORMATION

### Corresponding Authors

\*E-mail: yue.zhao@usherbrooke.ca.

\*E-mail: xiahs@scu.edu.cn.

### Notes

The authors declare no competing financial interest.

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## REFERENCES

- (1) Lendlein, A.; Kelch, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 2034–2057.
- (2) Xie, T. *Nature* **2010**, *464*, 267–270.
- (3) Liu, C.; Qin, H.; Mather, P. T. *J. Mater. Chem.* **2007**, *17*, 1543–1558.
- (4) Hu, J.; Zhu, Y.; Huang, H.; Lu, J. *Prog. Polym. Sci.* **2012**, *37*, 1720–1763.
- (5) Habault, D.; Zhang, H.; Zhao, Y. *Chem. Soc. Rev.* **2013**, *42*, 7244–7256.
- (6) Zhao, Q.; Behl, M.; Lendlein, A. *Soft Matter* **2013**, *9*, 1744–1755.
- (7) Meng, H.; Li, G. *Polymer* **2013**, *54*, 2199–2221.
- (8) Lendlein, A.; Jiang, H.; Junger, O.; Langer, R. *Nature* **2005**, *434*, 879–882.
- (9) Kumpfer, J. R.; Rowan, S. J. *J. Am. Chem. Soc.* **2011**, *133*, 12866–12874.
- (10) Zhang, H.; Xia, H.; Zhao, Y. *J. Mater. Chem.* **2012**, *22*, 845–849.
- (11) Hribar, K. C.; Metter, R. B.; Ifkovits, J. L.; Troxler, T.; Burdick, J. A. *Small* **2009**, *5*, 1830–1834.
- (12) Lee, K. M.; Koerner, H.; Vaia, R. A.; Bunning, T. J.; White, T. J. *Soft Matter* **2011**, *7*, 4318–4324.
- (13) Koerner, H.; Price, G.; Pearce, N. A.; Alexander, M.; Vaia, R. A. *Nat. Mater.* **2004**, *3*, 115–120.
- (14) Kohlmeyer, R. R.; Lor, M.; Chen, J. *Nano Lett.* **2012**, *12*, 2757–2762.
- (15) Liu, Y.; Boyles, J. K.; Genzer, J.; Dickey, M. D. *Soft Matter* **2012**, *8*, 1764–1769.
- (16) J. Leng, J.; Wu, X.; Liu, Y. *J. Appl. Polym. Sci.* **2009**, *114*, 2455.
- (17) Liang, J.; Xu, Y.; Huang, Y.; Zhang, L.; Wang, Y.; Ma, Y.; Li, F.; Guo, T.; Chen, Y. *J. Phys. Chem. C* **2009**, *113*, 9921–9927.
- (18) Yang, Y.; Pei, Z.; Zhang, X.; Tao, L.; Wei, Y.; Ji, Y. *Chem. Sci.* **2014**, *5*, 3486–3492.
- (19) Biyani, M. V.; Foster, E. J.; Weder, C. *ACS Macro Lett.* **2013**, *2*, 236–240.
- (20) Meng, H.; Li, G. *J. Mater. Chem. A* **2013**, *1*, 7838–7865.
- (21) Michal, B. T.; Jaye, C. A.; Spencer, E. J.; Rowan, S. J. *ACS Macro Lett.* **2013**, *2*, 694–699.
- (22) Fei, G.; Li, G.; Wu, L.; Xia, H. *Soft Matter* **2012**, *8*, 5123–5126.
- (23) Razaq, M. Y.; Behl, M.; Lendlein, A. *Adv. Funct. Mater.* **2012**, *22*, 184–191.
- (24) Mohr, R.; Kratz, K.; Weigel, T.; Lucka-Gabor, M.; Moneke, M.; Lendlein, A. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 3540–3545.
- (25) Schmidt, A. M. *Macromol. Rapid Commun.* **2006**, *27*, 1168–1172.
- (26) Cho, J. W.; Kim, J. W.; Jung, Y. C.; Goo, N. S. *Macromol. Rapid Commun.* **2005**, *26*, 412–416.
- (27) Leng, J. S.; Lv, H.; Liu, Y.; Du, S. *Appl. Phys. Lett.* **2007**, *91*, 144105–14105–3.

- (28) Li, G.; Fei, G.; Xia, H.; Han, J.; Zhao, Y. *J. Mater. Chem.* **2012**, *22*, 7692–7696.
- (29) Bao, M.; Zhou, Q.; Dong, W.; Lou, X.; Zhang, Y. *Biomacromolecules* **2013**, *14*, 1971–1979.
- (30) Xu, H.; Wang, Y. C.; Wang, S.; Malyarchuk, V.; Xie, T.; Rogers, J. A. *Adv. Funct. Mater.* **2013**, *23*, 3299–3306.
- (31) Liu, Y.; Boyles, J. K.; Genzer, J.; Dickey, M. D. *Soft Matter* **2012**, *8*, 1764–1769.
- (32) He, Z.; Satarkar, N.; Xie, T.; Cheng, Y.-T.; Hilt, J. Z. *Adv. Mater.* **2011**, *23*, 3192–3196.
- (33) DiOrio, A. M.; Luo, X.; Lee, K. M.; Mather, P. T. *Soft Matter* **2011**, *7*, 68–74.
- (34) Maity, S.; Bochinski, J. R.; Clarke, L. I. *Adv. Funct. Mater.* **2012**, *22*, 5259–5270.
- (35) Zhang, H.; Fortin, D.; Xia, H.; Zhao, Y. *Macromol. Rapid Commun.* **2013**, *34*, 1742–1746.
- (36) Zhang, H.; Zhao, Y. *ACS Appl. Mater. Interfaces* **2013**, *5*, 13069–13075.
- (37) Eustis, S.; El-Sayed, M. A. *Chem. Soc. Rev.* **2006**, *35*, 209–217.