

Polymers with Dual Light-Triggered Functions of Shape Memory and Healing Using Gold Nanoparticles

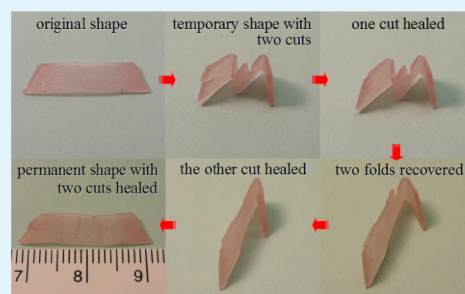
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S Supporting Information

ABSTRACT: Shape-memory and stimuli-healable polymers (SMP and SHP) are two types of emerging smart materials. Among the many stimuli that can be used to control SMP and SHP, light is unique because of its unparalleled remote activation and spatial control. Generally, light-triggered shape memory and optically healable polymers are different polymers and it is challenging to endow the same polymer with the two light-triggered functions because of their structural incompatibility. In this paper, we describe a general polymer design that allows a single material to exhibit both light-controlled shape memory and optical healing capabilities. We show that by chemically cross-linking a crystalline polymer and loading it with a small amount of gold nanoparticles (AuNPs), the polymer displays optically controllable shape memory and fast optical healing based on the same localized heating effect arising from the surface plasmon resonance of AuNPs. The photothermal effect controls, on the one hand, the shape memory process by tuning the temperature with respect to T_m of the crystalline phase and, on the other hand, activates the damage healing through crystal melting and recrystallization. Moreover, we show that these two features can be triggered separately in a sequential manner.

KEYWORDS: shape-memory polymers, stimuli-healable polymers, photoresponsive materials, gold nanoparticles



1. INTRODUCTION

Two types of light-triggered functions of smart polymer materials, namely, shape-memory and healing, have been gaining fast growing interest recently.^{1–25} On the one hand, shape-memory polymers (SMPs) can change their shape in response to an external stimulus by recovering a permanent shape from a programmed temporary shape.^{26,27} They are generally constructed by a chemically cross-linked network that prevents chain relaxation during the temporary shape processing above the polymer's glass transition (T_g) or melting temperature (T_m). SMPs have great potential for many applications such as stimuli-responsive actuators and implant devices for minimally invasive surgery in medicine.²⁸ On the other hand, stimuli-healable polymers (SHPs), developed for the purpose of prolonging the service lifetime and reducing the cost, can repair damage (crack or fracture) with the help of an external stimulus. For SMPs, while directly heating a given polymer to $T > T_g$ or T_m is usually used to activate the permanent shape recovery, stimuli such as light,^{5–14} ultrasound,^{29,30} and electric or magnetic field^{31–35} can also be utilized as effective triggers. In those cases, a stimulus-induced thermal effect is generally at the origin of the shape memory effect.^{4,6–10,12,13,29–36} For SHPs, the various stimuli used to enable the healing process, such as temperature or pH change,^{37–39} exposure to an oscillating magnetic field^{40,41} or light,^{15–25} are generally involved in activating new chemical bond formation and/or providing chain mobility across fracture surfaces. Of the many stimuli known for SMPs and SHPs, light has some unique advantages common for both types of

polymers. It can trigger the shape-memory or healing function remotely without invading the material, locally without compromising the property of the rest of material, and temporarily with an easy switching on-off feature.

To date, light-triggered shape-memory or healing have been developed as different functions for different polymers. It is challenging to endow one single polymer with the two functions; that is, the same polymer not only is capable of undergoing light-controlled shape change but also is optically healable, as schematically illustrated in Figure 1. One reason for this difficulty is the structural incompatibility between the two types of polymers. SMPs require a permanent network structure, typically through chemical crosslinking, which restricts chain motion, and good SMPs usually are stiff polymers with a high modulus. These structural features of SMPs are conflicting with the high chain mobility and interdiffusion required for SHPs. It is of fundamental and applied interest to confer one single polymer material with both light-controlled shape-memory and optical healing capabilities. Although polymers with either light-controlled shape memory^{5–14} or optical healing capability^{15–24} were reported, and a very recent study demonstrated a polymer displaying both light-triggered healing and thermally induced shape memory,²⁵ to date we are unaware of any reports on chemically cross-linked polymers featuring the dual light-enabled functions of

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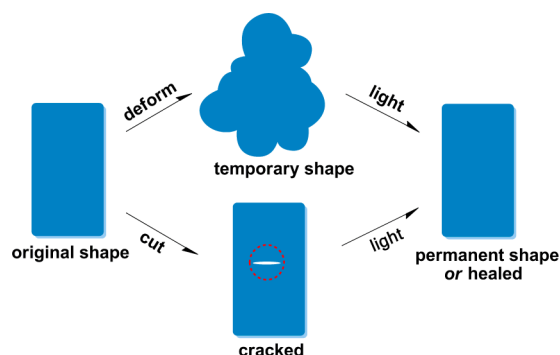


Figure 1. Schematic illustration of light-triggered shape memory and healing exhibited by a same polymer.

shape memory and optical healing. Herein, we make the first demonstration of this kind based on a rational material design.

2. EXPERIMENTAL SECTION

2.1. Materials. Hydrogen tetrachloroaurate tetrahydrate ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$) was purchased from Alfa Aesar. Poly(ethylene oxide) (PEO_{20k} , $M_{20,000}$), poly(ethylene glycol) methyl ether (mPEG_{2k} , $M \sim 2,000$), acryloyl chloride, potassium carbonate (K_2CO_3), ammonium persulfate (APS), N,N,N',N' -tetramethylethylenediamine (TMEDA), N,N' -dicyclohexylcarbodiimide (DCC), 4-(dimethylamino)pyridine (DMAP), 3,3'-dithiodipropionic acid, and other reagents were purchased from Sigma-Aldrich and used as received.

2.2. Synthesis of mPEG_{2k} -SS. 3,3'-Dithiodipropionic acid (5 mmol), DMAP (1 mmol) and mPEG_{2k} (1 mmol) dried under vacuum at 60°C were introduced into dry THF in a 100 mL flask and stirred for 30 min to obtain a homogeneous mixture solution. DCC (1.2 mmol) was then added into the solution and the mixture kept under stirring for 48h at room temperature. The resultant product was first filtered and then precipitated in cold ether. The precipitate was collected and vacuum-dried for 48 h at room temperature to yield 3,3'-dithiodipropionic acid-terminated mPEG_{2k} , referred to as mPEG_{2k} -SS. Its structure was confirmed by ^1H NMR (see Figure S1 in the Supporting Information).

2.3. Preparation of AuNPs Functionalized with mPEG_{2k} -SS. Citrate-stabilized AuNPs were prepared according to a reported method.⁴² The resulting aqueous solution of AuNPs with an average diameter of ~ 10 nm and uniform size distribution observed by TEM (see Figure S2 in the Supporting Information), was concentrated by centrifugation and then added into an aqueous solution of mPEG_{2k} -SS (50 mg/mL) dropwise under vigorous stirring for 48 h. mPEG_{2k} -SS was anchored onto AuNPs via ligand exchange. Afterwards, free mPEG_{2k} -SS was removed by three times of centrifugation at a speed of 22 000 rpm. The obtained AuNPs stabilized by mPEG_{2k} -SS were redispersed in distilled water and ready for further use.

2.4. Preparation of Cross-Linked PEO/AuNP Composite. PEO_{20k} with two chain ends terminated with an acrylate group was first synthesized by reacting HO-PEO-OH (PEO_{20K}) with excessive acryloyl chloride using a literature method.⁴³ ^1H NMR spectrum in Figure S3 in the Supporting Information confirms the structure of

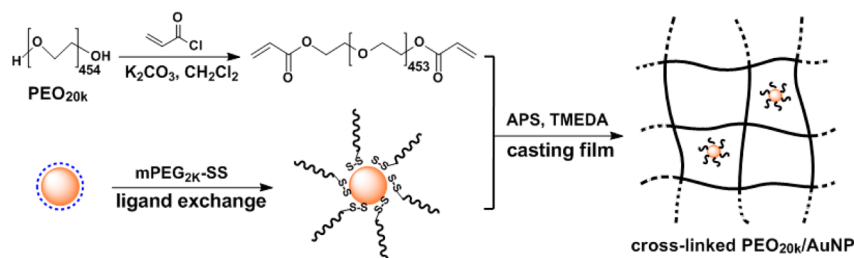
acrylate-capped PEO_{20k} . In order to obtain chemically cross-linked PEO/AuNP composite material, AuNPs functionalized with mPEG_{2k} -SS was mixed together with acrylate-terminated PEO_{20k} and APS (1 wt % relative to the mass of acrylate-terminated PEO_{20k}) in distilled water under sonication to ensure good dispersion, followed by adding the dilute TMEDA to enable the cross-linking reaction at room temperature. After few seconds of further sonication, the mixture was poured into a Teflon mold with an inner diameter of 55 mm, with water first slowly evaporated for 24 h, followed by vacuum-drying for 48 h at room temperature and another 24 h thermal treatment at 60°C . The final sample obtained was cross-linked semi-crystalline PEO_{20k} loaded with AuNPs, referred to as cross-linked PEO/AuNP composite material. Based on the used amounts of acrylate-terminated PEO_{20k} and mPEG_{2k} -SS functionalized AuNPs, the concentration of AuNPs in the composite material was calculated to be 0.003 wt %.

2.5. Characterization Methods. ^1H -NMR spectra were recorded on a Bruker AC 300 spectrometer (300 MHz) using deuterated chloroform as solvent and tetramethylsilane as internal standard. UV-vis absorption spectra were obtained using a Varian 50 Bio spectrophotometer. Thermal phase transition behaviors were investigated by using a TA Q200 differential scanning calorimeter (DSC). Indium was used as the calibration standard; both heating and cooling rate were $10^\circ\text{C}/\text{min}$. Data reported in the paper were collected from the second heating and cooling scans. All the mechanical properties were measured in the tension mode with a Perkin-Elmer DMA 8000 instrument. The shape recovery-induced contraction force was measured by using a specimen of approximately $3.0 \times 1.4 \times 0.2$ mm under a constant strain mode. The tensile stress (stress-strain) experiments for optical healing were performed under a constant loading rate of 0.1 N/min at room temperature. Optical microscopic observations were made on a Leitz DMR-P microscope with hot-stage. Laser exposure experiments were conducted using a PM-532-2000 laser with a wavelength of 532 nm and a tunable power output up to 1 W manufactured by Changchun New Industries Optoelectronics Tech. Co., Ltd.

3. RESULTS AND DISCUSSION

3.1. Preparation of PEO/AuNP Composite. We demonstrate that chemically cross-linked (thermosetting) crystalline polymers containing a very small amount of gold nanoparticles (AuNPs), which are easy to prepare, can exhibit both light-controlled shape memory and optical healing. This material design is based on (1) that photothermally induced melting followed by recrystallization is an effective means to optically heal (weld) thermoplastic crystalline polymers,^{44–48} and (2) the fact that photothermal effect can readily be used for optically controlled shape memory effect.^{6–10} Our working hypothesis is that adding a cross-linked structure, required for shape memory, to crystalline polymers loaded with AuNPs for localized heating upon surface plasmon resonance (SPR) absorption of light, should allow the material to possess the two functions. To investigate this duality, we prepared AuNP-containing cross-linked PEO. As shown in Scheme 1, PEO_{20K} with both chain ends terminated with an acrylate moiety is

Scheme 1. Preparation Procedure of Cross-Linked PEO/AuNP Composite



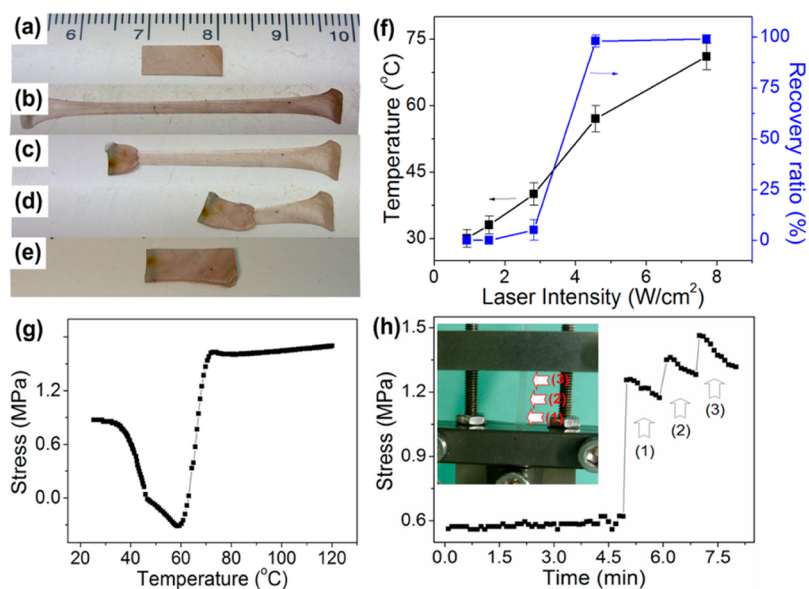


Figure 2. Light-controlled shape-memory of cross-linked PEO/AuNP. (a–e) Pictures of a film at (a) its original shape, (b) in the temporary shape obtained by stretching at 80 °C followed by cooling to room temperature, and (c–e) a three-step recovery to the initial shape by separate laser exposure (7 W/cm²) of the stretched film from left to right. (f) Temperature of a stretched film upon exposure to laser and its shape recovery ratio as a function of applied laser intensity. (g) Change in the tension holding a stretched film under constant strain as a function of temperature. The used film was stretched to 300% strain at 80 °C followed by cooling to room temperature before the mechanical test and the rate of direct sample heating was 5 °C/min. (h) Contraction force generated by exposing the stretched film under constant strain to laser (7 W/cm²) at room temperature. The inset is a picture showing the film under strain and indicating the three separate laser exposures.

mixed with AuNPs functionalized with mPEG_{2K}-SS before cross-linking reaction upon addition of APS and TMDEA; films of cross-linked PEO/AuNP composite were prepared by introducing the reaction mixture into a Teflon mold, followed by curing at room temperature and 60 °C. Unless otherwise stated, films of cross-linked PEO loaded with a trace amount of 0.003 wt % AuNPs, with a thickness of ~0.4 mm, were prepared and utilized for investigation of light-triggered shape memory and optical healing of the polymer. We note that the choice of PEO_{20K} was based on the consideration that the use of a lower molecular weight PEO will increase the network density, which may reduce the PEO crystallinity and chain mobility and, consequently, render the optical healing difficult to achieve. Although UV–vis absorption spectra (see Figure S4 in the Supporting Information) indicated that AuNPs are well dispersed in the cross-linked PEO matrix displaying a SPR absorption band at ~530 nm, DSC measurements (see Figure S5 in the Supporting Information) found that the presence of 0.003 wt % AuNPs could increase the crystallinity of PEO (from 59 to 67%), its melting temperatures on heating (from 60 to 62 °C) and its crystallization temperature on cooling (from 42 to 43 °C). It is to be noted that both melting and crystallization of cross-linked PEO chains in the PEO/AuNP sample take place at above room temperature.

3.2. Light-Controlled Shape Memory. We first investigated separately the two light-triggered functions. The cross-linked PEO/AuNP can indeed undergo light-controlled shape memory process based on the photothermal effect while preserving all the distinct features of using light as the trigger. A set of representative results is shown in Figure 2. Photos a–e were taken to visually demonstrate the spatial and temporal control possibility of using light to activate the shape memory process. A film of initial (and permanent) shape (a) was stretched at 80 °C ($T > T_m$) to 400% deformation followed by cooling to room temperature fixing the temporary, elongated

shape (b). The light-controlled shape recovery was purposely completed by three successive exposures of the film (from left to right, approximately a third length of the film for each exposure) to a laser beam ($\lambda = 532$ nm, 7 W/cm²) (c–e). During each laser exposure, shape recovery (film contraction in this case) occurred only in the illuminated region due to locally photoinduced heating of the polymer to $T > T_m$ of PEO. Thanks to the tunable illumination spot (~3 mm in diameter) and the portable laser device used, the shape recovery can be made to occur on-demand. Given a sufficient laser power, wherever the film is subjected to laser irradiation, shape recovery takes place quickly and only in the selected region, and once the laser is turned off, the process stops almost immediately due to fast cooling of the material to $T < T_m$ of PEO. Control tests found the absence of shape recovery for samples containing no AuNPs under otherwise the same conditions, indicating that without AuNPs, any possible heating effect resulting from laser exposure is by far insufficient to activate the thermal phase transition required for shape recovery. To better understand the dependence of shape recovery on laser exposure, the recovery ratio and the corresponding temperature of the sample at various laser powers (using a digital thermocouple embedded in the film close to the laser spot) were measured and the results are plotted in Figure 2f. Although the temperature increases with increasing the laser power, full shape recovery takes place only at a laser power of about 4 W/cm² at which the sample temperature reaches about 60 °C that is the melting temperature of crystalline PEO.

Another interesting feature associated with light-triggered SMPs is worth demonstration. The spatially and temporally controlled shape recovery process by light means enhanced control in the release of strain energy stored in the stretched film. An easy way to view this consists in fixing a stretched film by the tension clamps of a dynamic mechanical analyzer

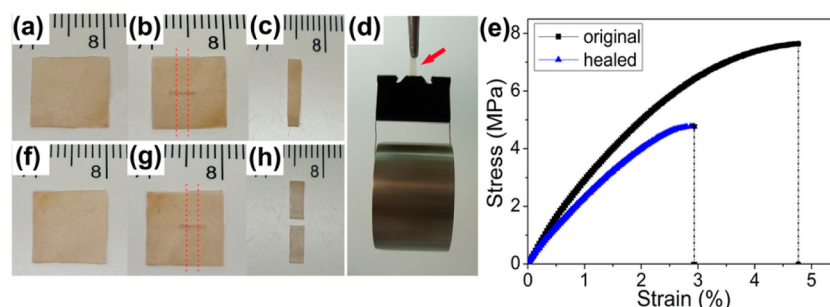


Figure 3. Optical healing of cross-linked PEO/AuNP. (a–e) Pictures and tensile stress test results showing the fast light-triggered healing: (a) original film (~ 0.4 mm in thickness); (b) original film with a cut-through crack made by razor blade; (c) after exposing the crack to laser (13 W/cm^2) for 3 s, a strip was cut out through the initial crack along the red dashed lines indicated in b; (d) the healed strip (indicated by the arrow) could withstand a load $>14\,000$ times its weight; and (e) the stress–strain curve of the healed strip in comparison to its original film. (f, g) Pictures showing the failure of healing by direct heating of the whole sample to $T > T_m$ of PEO: (f) original film; (g) a cut-through crack was imposed by razor blade; and (h) after heating the whole film to 140°C for 3 min followed by cooling to room temperature, a strip was cut out through the initial crack and easily broke onto two pieces, indicating the absence of healing.

(DMA) under the constant strain mode, an initial force being applied to hold the film. A contraction force should be generated when the film tends to contract at $T > T_m$ of PEO to recover the initial shape. To perform the tests, a film stretched to 300% strain at 80°C followed by cooling to room temperature was utilized. For comparison, the conventional thermally induced shape recovery was first realized by heating the sample at a constant rate of 5°C/min . As is seen from the result in Figure 2g, before the sample reaches 60°C , the tension required to hold the stretched film decreased; while from about 60°C where the shape recovery started, a contraction force was generated as revealed by an increase in the tension. The decrease in the tension is a result of the thermal expansion of the film. As will be shown later in the paper, thermal expansion may impact the result of thermally induced healing of the PEO/AuNP material. Because using light allows the shape recovery process to proceed only in the selected region and in a switching on-off manner, it is easy to imagine that light can be used (remotely from a long distance if necessary) to trigger the release of stored strain energy, and thus the corresponding force, in a controllable way as desired. The test result in Figure 2h illustrates the possibility. Using another film stretched to the same strain, laser beam was applied at room temperature first to the low side of the film under strain (indicated by the arrow labeled with “1” in the figure), a contraction force was quickly generated as a result of the photothermally induced shape recovery in the exposed part of the film. In other words, light allows strain energy stored only in that part of the sample to be released. If the film was not held under constant strain, the contraction force could be used to do a mechanical work. The laser spot was then moved to about the middle of the film, a new contraction force was generated upon release of strain energy stored in that region. Finally, the laser was sent to the upper part of the film to generate another force. Due to the constraint of the used DMA sample holder, more sophisticated fashion of light-triggered release of stored strain energy was difficult to achieve, but the simple test in Figure 2h should make the point clear. A couple of additional observations should be mentioned. First, compared to bulk heating of the entire film, laser exposure raises the local temperature quickly so that a contraction force is observed without earlier thermal expansion-induced decrease in the tension holding the film. Secondly, under each laser exposure at a selected area of the film, the rise of the generated

contraction force is followed by an apparent relaxation. At this time, we do not have a clear explanation for this phenomenon. One speculation is that the vicinity of the laser-exposed area may undergo limited heating to $T < T_m$ of PEO, being insufficient for chain relaxation but resulting in thermal expansion, which is possible because of heat propagation and the Gaussian distribution of the laser beam intensities.

3.2. Optical Healing. The same cross-linked PEO/AuNP is also optically healable, confirming that the material design makes it possess both light-triggered functions of shape-memory and healing. An example of results is shown in Figure 3. The optical healing can be observed visually from photos a–d. A cut-through crack was imposed on a film of PEO/AuNP (0.003 wt %) using a razor blade (a), after exposing the crack area to laser (13 W/cm^2) at room temperature for 3 s, a strip was cut out through the initial crack (b). If no optical healing occurred, the strip would break into two halves. The result is that a single-piece strip emerged (c) and could already withstand a load $>14\,000$ times its weight (d), indicating effective healing. To further evaluate the optical healing efficiency, tensile tests were performed on the original and optically healed strip samples. The result in Figure 3e shows that despite the crosslinked chains, the optically healed sample gained about 62% of its original tensile strength after 3 s of laser exposure under the used conditions. According to previous studies,^{42–46} the mechanism for the observed fast optical healing is the melting of crystalline PEO chains on fracture surfaces exposed to laser, followed by recrystallization of interdiffused and interlocked polymer chains on cooling after turning off the laser. Same as the shape memory effect, control test showed that with crosslinked PEO containing no AuNPs, no optical healing occurred under otherwise the same experimental conditions. Moreover, the optical healing could be repeated several times by cutting off the sample at the same place.

An unexpected finding is also shown in Figure 3. The healing mechanism implies that healing could also be achieved by directly heating the whole sample to $T > T_m$ of PEO and subsequently cooling it to room temperature. As shown in photos f–h, quite surprisingly, only optical healing is effective, and the bulk heating cannot lead to healing of the crack. When the whole film containing a cut-through crack was heated to $T > 60^\circ\text{C}$, from 65 to 140°C , for 3 min before cooling to room temperature, the strip cut through the initial crack broke easily,

indicating the absence of any significant healing. The failure of healing by direct bulk heating was also observed in a cross-linked polyethylene.⁴⁹

The difference between exposing only the crack region to a laser beam and directly heating the entire sample containing the crack can be observed on an optical microscope. As shown in Figure 4, after bulk heating at 120 °C and subsequent cooling,

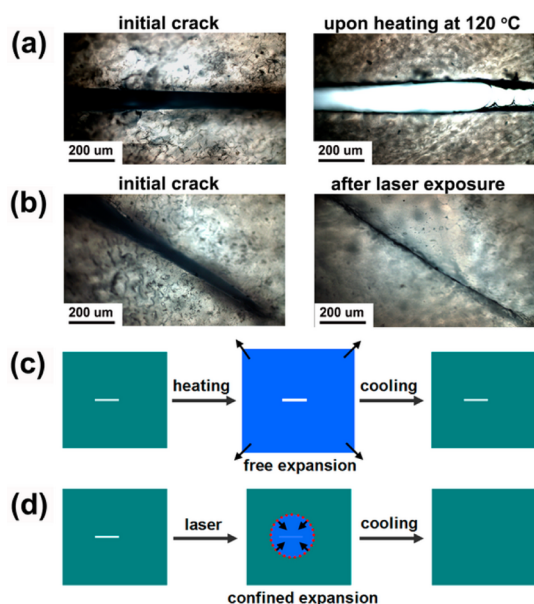


Figure 4. Difference between bulk heating and light-induced local healing. (a, b) Pictures showing the widening of a crack upon direct heating of the whole sample of (a) cross-linked PEO/AuNP, and (b) the effective mending of the crack after exposure to laser. (c, d) Schematic illustration of (c) the free thermal expansion of the sample upon direct heating that prevents crack surfaces from entering into close contact, and (d) the confined thermal expansion upon laser exposure, which helps bringing the crack surfaces together by laser irradiation.

the crack actually widened (a), explaining the difficulty for interdiffusion of polymer chains on fracture surfaces required for effective healing. By contrast, after laser exposure focused on the crack region, the crack was visually mended with merging fracture surfaces (b). The effective and fast optical healing versus the failure of healing upon bulk heating has to originate from the different ways that the cracked sample responds when it is subjected to heating or laser exposure. As schematically depicted in images c and d in Figure 4, when the whole sample is heated, the thermal expansion occurs freely and throughout the sample resulting in an expansion outward that prevents intimate contact of fracture surfaces and chain interdiffusion required for interlocked chain recrystallization. Consequently, no healing occurs. By contrast, when the crack in a sample is selectively exposed to laser, the photothermally induced heating occurs locally within an area essentially determined by the size of the laser beam, resulting in confined thermal expansion that goes mostly inward since the expansion outward cannot develop. Such localized expansion should generate hoop stress to push the fracture surfaces into contact that favors chain interdiffusion so that the recrystallization of polymer chains on cooling after turning off the laser can sew the crack. This finding is important. It shows that the use of light as the trigger based on photothermal effect is not just about having the

appealing features of remote activation, spatial control and switching on-off capability, it may be the only effective stimulus to activate the healing process under certain conditions in a precisely selected region. Whatever the healing mechanism in play, polymer chain interdiffusion across fracture or crack surfaces is necessary. In case where no external force is applied to bring these surfaces into contact, such as manually putting two pieces together practiced in many stimuli-induced healing studies, no effective healing can take place. In such cases, the confined thermal expansion upon exposure to laser pushing crack surfaces into contact become crucial in the stimuli-triggered healing process.

3.4. Sequential Triggering of Both Functions. An important question that can be raised is whether or not the dual optically controlled functionalities can be individually triggered with a same material. We carried out experiments to show that this is doable in many conceivable situations. The example of results in Figure 5 demonstrates that the optical healing and

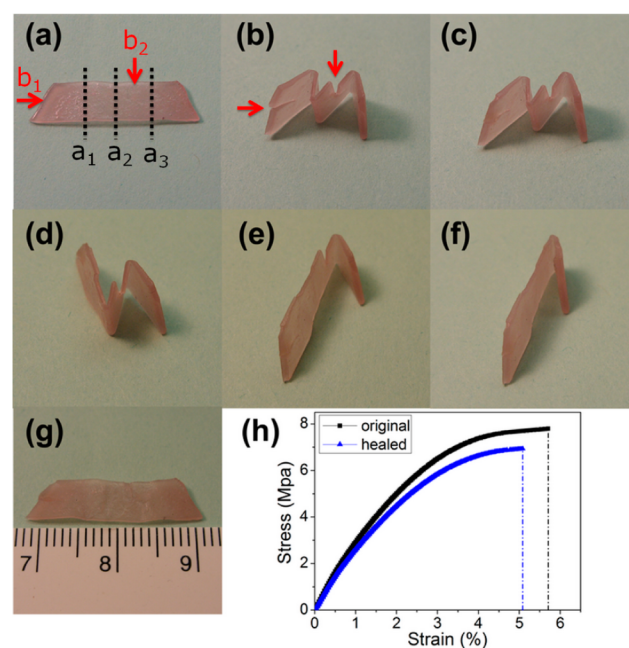


Figure 5. Sequentially triggering the optical healing and the light-controlled shape recovery process for a film of cross-linked PEO/AuNP. (a) Original film (~ 0.4 mm in thickness) with the permanent shape; (b) temporary shape obtained by folding the film along the lines a_1 , a_2 , a_3 at 80 °C followed by cooling to room temperature; then two cuts were made as indicated by red arrows (b_1 and b_2 in photo a); (c) the b_1 cut was healed by exposing the crack to laser (12 W/cm²) for 5 s; (d) the first unbending after 10 seconds laser scanning along the fold a_1 at a power of 6 W/cm², followed by the second unbending under the same condition along the fold a_2 ; (e) the other cut b_2 remained in the film of an intermediate temporary shape; (f) the cut b_2 was optically healed under the same condition as for the cut b_1 ; (g) the third light-triggered unbending along the fold a_3 completed the permanent shape recovery; (h) the stress–strain curves of the original and optically healed film.

light-controlled shape memory effect can be executed in a sequential manner. In this test, a temporary shape was obtained by folding a PEO/AuNP composite film along three lines and two cracks were imposed in two areas (photos a and b). One of the cuts was first optically mended without affecting the temporary shape of the film (photo c). Then, two separate

light-triggered unbending of the film was made to occur, resulting in two intermediate temporary shapes and the second crack remained unrepaired (photos d and e). Finally, the second cut could be optically healed (photo f) and the unbending of the film by exposing the laser along the last fold completed the permanent shape recovery (photo g). Tensile tests on the original and healed films also confirmed the effective optical healing (Figure 5h). This test shows that in many situations, the two light-triggered functions can be individually activated without interfering from each other. Obviously, situations can also be imagined where the two actions cannot be separated. In the present case, if the cut is at the fold, optical healing will inevitably release strain energy in that area, resulting in corresponding shape recovery (unbending).

Before concluding, it should be mentioned that like any optical approaches based on light absorption, the excitation light has to be delivered to the targeted regions in the material in order to achieve an effective shape memory effect or healing. Therefore, the reported method works better for thin and transparent polymer/AuNP nanocomposite materials. For this reason, the demonstrated efficiency of this method requiring a very small amount of AuNPs is important because this low concentration of dispersed nanofillers makes it easier to obtain a homogeneous and transparent nanocomposite and allows the laser light to penetrate deeper inside the material.

4. CONCLUSIONS

We have described a general design for making polymers that are both light-controllable shape-memory and optically healable material. We have demonstrated that by cross-linking a crystalline polymer and loading it with a very small amount of AuNPs, the polymer can be given the two light-triggered functions based on the same photothermal effect arising from the SPR absorption of AuNPs. This photothermal effect controls, on the one hand, the shape memory of the material by tuning its temperature with respect to T_m of the crystalline phase, and, on the other hand, activates the healing of crack via melting of crystallized chains under laser exposure and their recrystallization at the laser-off state. It should be emphasized that although thermal effect is at the origin of the underlying mechanisms for both shape memory and self-healing, using light as the trigger allows all distinguished features associated with optical stimulus to be preserved, including remote activation, spatial and temporal control. Moreover, in many conceivable situations, the two light-triggered functions can be individually activated in a sequential manner with the same material. It was also found that optical healing through chain melting and recrystallization does not work by direct bulk heating of cross-linked freestanding polymer. It works using the photothermal effect because localized heating upon light absorption in confined crack area is what brings crack surfaces into close contact, a key condition for effective healing to occur. The simultaneous displaying of the two appealing and different functions by a single material may widen the possible applications of SMP and SHP.

■ ASSOCIATED CONTENT

Supporting Information

More characterization results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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