

Supplementary Information

Integrating shape-memory technology and photo-imaging on a polymer platform for a high-security information storage medium

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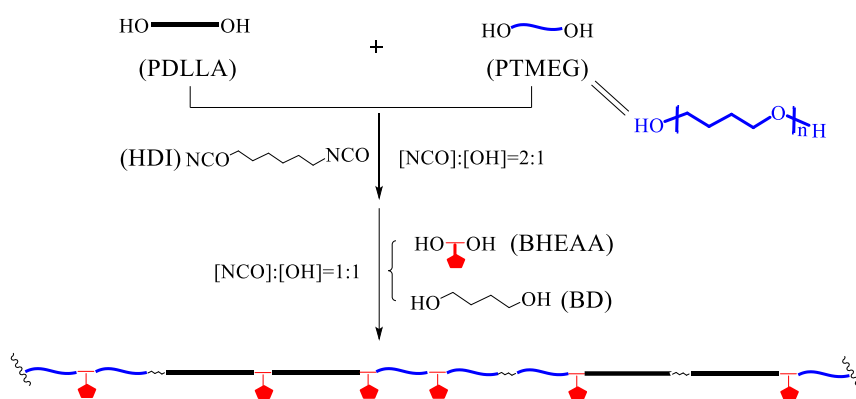
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1. Experimental details

1.1 Synthesis of anthracene-containing copolymer

The preparation of target copolymer involves three steps: 1) synthesis of *N,N*-Bis(2-hydroxyethyl)-9-anthracenemethanamine (BHEAA), 2) synthesis of poly(D,L-lactide) diol (PDLLA), and 3) synthesis of copolymer AN-PDLLA-PTMEG, and the details are available in our previous works (ref. 10 and 11). Here, the brief procedures in step 3) are illustrated in Scheme S1 and described in the followings. Firstly, a mixture of PDLLA and PTMEG ($m_{\text{PDLLA}}:m_{\text{PTMEG}}=42:58$) was put into a reaction flask and dehydrated at 50 °C under vacuum for 3 hours, during which an exhausting-refilling process was repeated three times, followed by injecting $\text{C}_2\text{H}_4\text{Cl}_2$ into the reaction vessel as solvent and raising the temperature to 75 °C. Then, after PDLLA and PTMEG completely dissolved, 1,6-Hexamethylene diisocyanate (HDI) and five drops of dibutyltin dilaurate (DBTL) were added, and the reaction was kept for 3 h with stirring. Then, BHEAA and a predetermined amount of 1,4-Butanediol (BD) were added to start the chain-extending reaction for another 4 h. Finally, the resulting solution was cooled and then poured into a large amount of cold ether and hexane ($v_{\text{ether}}:v_{\text{hexane}}=1:4$) to give AN-PDLLA₄₂-PTMEG which was a yellow flocculent solid and dried in a vacuum oven.



Scheme S1 The routes for preparing anthracene-containing copolymer from PDLLA, PTMEG, and BHEAA.

1.2 Preparation of polymer films

All the films in this work were obtained by solution casting. The procedures were dissolving a predetermined amount of AN-PDLLA₄₂-PTMEG (depends on target thickness of film) in chloroform (CHCl₃), pouring into a smooth Teflon dish, volatilizing solvent in fume hood, drying in an oven, and finally drying under vacuum.

1.3 Photo-imaging and verification

The photo-imaging process with the irradiation of 365 nm UV light was conducted in a customized glove box filled with flowing argon. During irradiating, a specific 3D printed photomask was placed on the surface of the anthracene-containing film. The light intensity (to the film) was 5.1 mW·cm⁻² and the irradiation time was 1 h.

To verify the printed photo-image, the irradiated film was exposed to 254 nm UV light quickly.

2. Characterization methods

Nuclear magnetic resonance (NMR). ¹H-NMR spectra of the synthesized products were recorded by a Bruker AV400 spectrometers (400 Hz, Germany) at room temperature with deuterated chloroform (CDCl₃) as solvent and tetramethyl silane (TMS) as an internal reference.

Gel permeation chromatography (GPC). The test was carried out with a HLC-8320 system (Tosoh Corporation, Japan) equipped with a refractive index detector and two columns, a TSK gel super HZM-M and a TSK gel SuperHZ3000. Tetrahydrofuran (THF) acted as elution solvent with a flow rate of 0.6 mL·min⁻¹ at 40 °C and a polystyrene standard was used for calibration.

Ultraviolet-visible (UV-vis). UV spectra of a thin AN-PDLLA₄₂-PTMEG film (thickness: 30 μm) before and after 365 nm UV irradiation were recorded by a UV-vis spectrophotometer (VARIAN, USA) in the wavelength range of 200-600 nm, and the test was performed at room temperature. As a comparison, pristine PDLLA₄₂-PTMEG film was also tested.

Differential Scanning Calorimetry (DSC). The tests were performed on a DSC Q200 instrument (TA, USA). Heating and cooling scan were conducted between -60 and 190 $^{\circ}\text{C}$ using a heating/cooling rate of 10 $^{\circ}\text{C}/\text{min}$ under a steady flow of ultrahigh purity nitrogen.

Dynamic mechanical analysis (DMA). The measurements were performed on a DMA Q800 instrument (TA, USA). The tests run from -80 to 100 $^{\circ}\text{C}$ at a heating rate of 3 $^{\circ}\text{C}/\text{min}$, and the frequency was 1 Hz.

Shape memory test. The details are available in our previous works (Ref. 10-13).

3. Additional photos regarding the visibility of photo-image

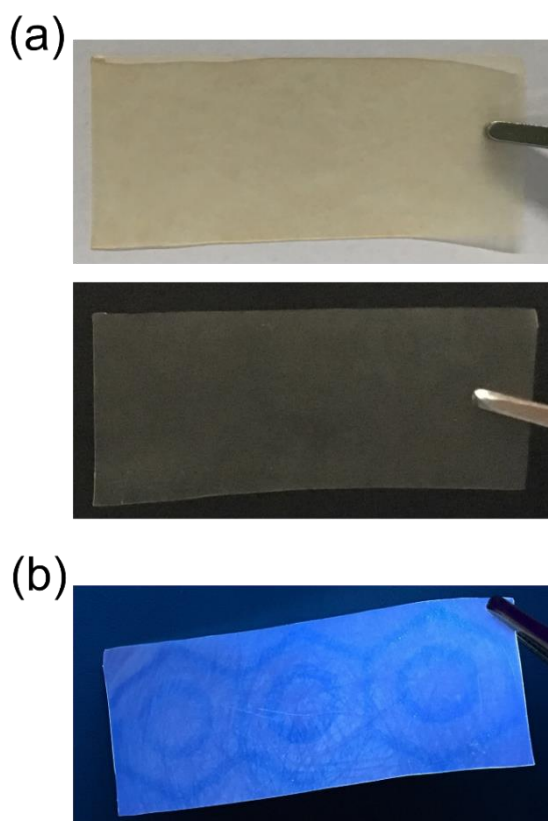


Fig. S1. Pictures revealing the fact that photo-image is only visible under 254 nm UV. (a) Film after photo-imaging with “anthracene” photomask, and its digital photographs taken under natural light with white (top) and black background (bottom); (b) The unique feature of photo-image that only visible when exposing to 254 nm UV light.