Supporting Information

Photoinduced Triple Shape Memory Polyurethane Enabled by Doping with Azobenzene and GO

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Materials

4-Aminoethoxybenzene, sodium nitrite ($NaNO_2$), sodium carbonate (Na_2CO_3), phenol, hydrochloric acid (HCl), sodium hydroxide (NaOH), dimethylformamide (DMF), potassium carbonate (K_2CO_3), potassium iodide (KI) were purchased from Beijing Chemical Works. 11-Bromo-1-undecanol was purchased from J&K Scientific, Ltd.

Characterizations

^{1}H-NMR spectra were recorded on a Bruker 500MHz spectrometer to confirm the molecular structure of the synthesized EHAB. The thermal properties of EHAB was studied by differential scanning calorimetry (Perkin-Elmer DSC8000). The heating and cooling rates were 10 °C/min. The textures of EHAB was investigated and the birefringent properties of the composite films were performed using polarizing optical microscopy (POM) (ZEISS Axio Scope A1). The mechanical properties of the composite films were exhibited by

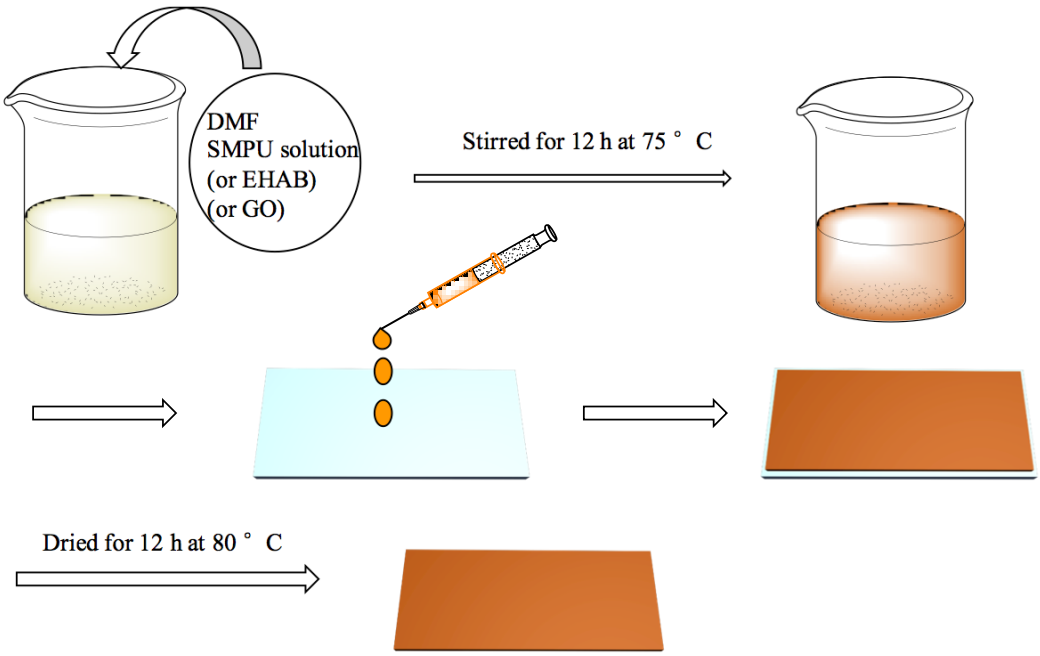
microcomputer-controlled electronic universal testing machine (CMT-10, Jinan Liangong Testing Technology Co., Led). Scanning electron microscopy (SEM) images were obtained on a Hitach S-4800. Two driving light sources are implemented by different instruments (UV-light: HTLD-4 Ⅱ Shenzhen Height-LED Opto-electronic Tech Co., Ltd. NIR-light: MDL-H Changchun New Industries Optoelectronics Technology Co., Ltd).

Table S1. The components of four sample films.

Films	Component	PU/g	GO/mg	EHAB/mg
1	Neat PU	1.8		
2	PU-GO	1.8	10.3	
3	PU-EHAB	1.8		12.3
4	PU-GO-EHAB	1.8	10.3	12.3

Table S2. Summary of mechanical properties of the four sample films.

Films	Component	Length (mm)	Width (mm)	Thickness (mm)	Elongation at break (%)	Breaking stress (MPa)
1	Neat PU	21	2	0.315	514	21.4
2	PU-GO	20	2	0.261	560	22.7
3	PU-EHAB	22	2	0.289	505	13.6
4	PU-GO-EHAB	20	2	0.271	480	18.4



Scheme S1. Schematic illustration of fabrication process of the polymer composite films.

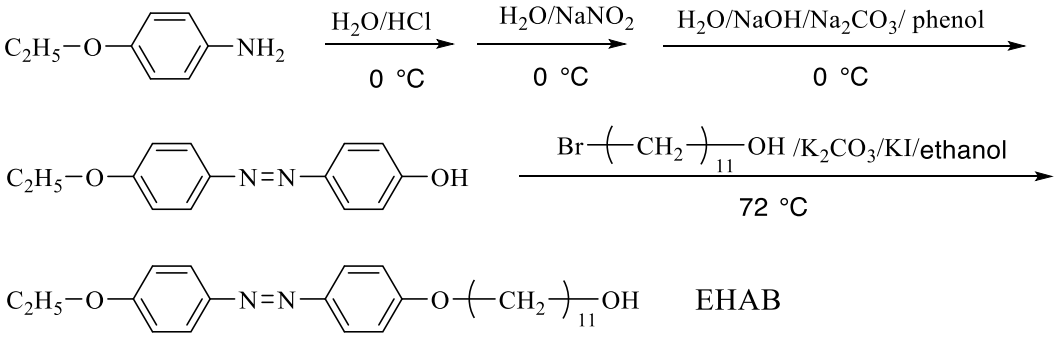


Fig. S1: Synthesis of 4'-ethyoxy-4-(11-hydroxyundecyloxy)azobenzene (EHAB)

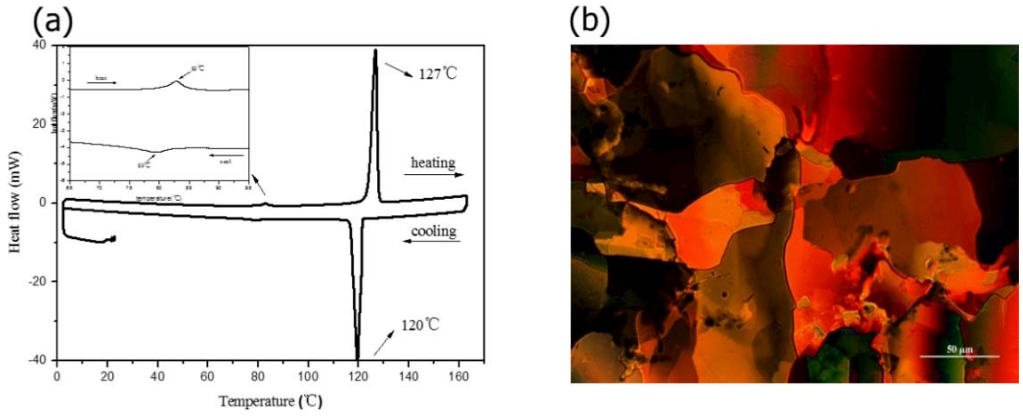
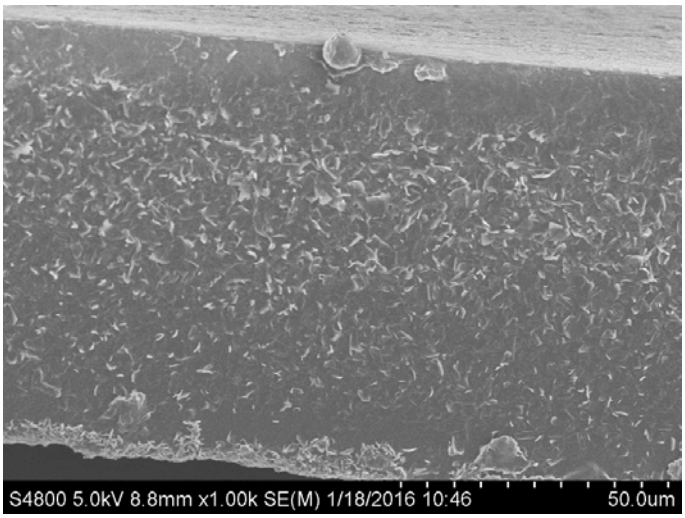
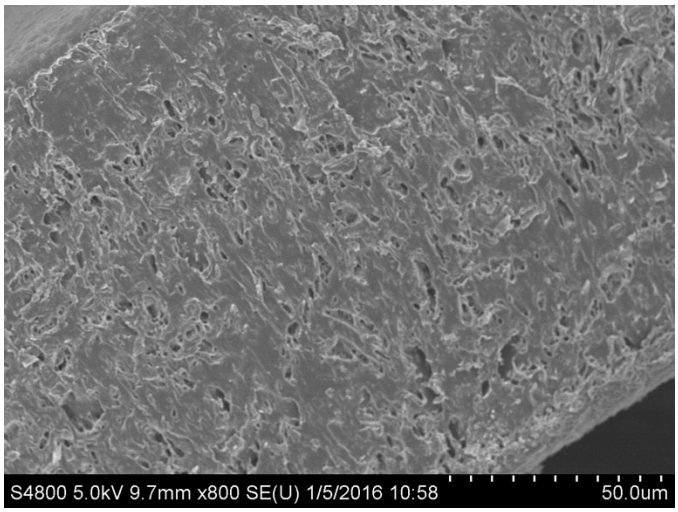


Fig. S2. Thermal properties of EHAB. (a) DSC curve and (b) POM image (500 ×) of EHAB at 125 °C. EHAB shows its melting point at 83 °C and clearing point at 127 °C on heating. Typical smectic liquid crystal texture was observed with POM.



(a)



(b)

Fig. S3. SEM images of the cross-section of PU-GO-EHAB film (a) before and (b) after washing with ethanol to get rid of EHAB.

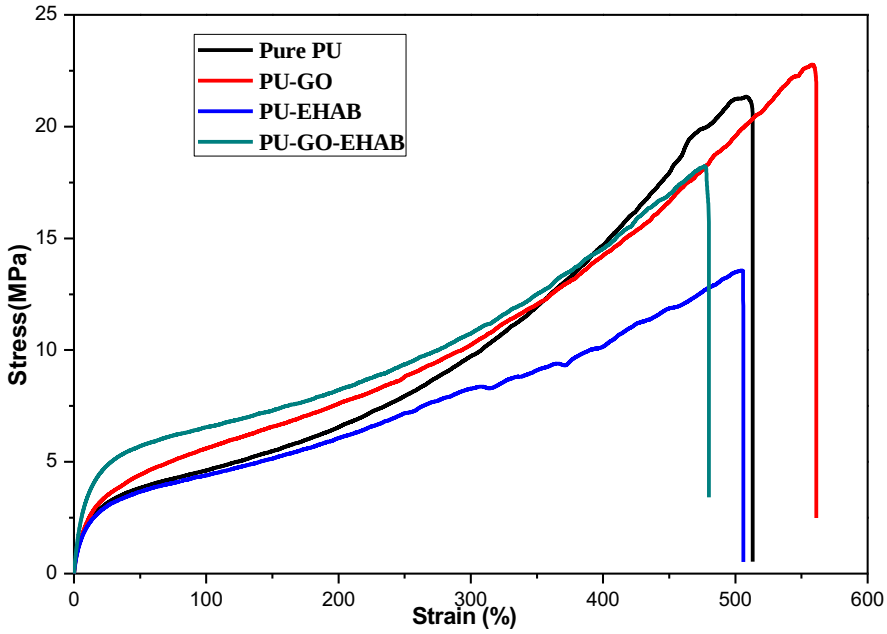
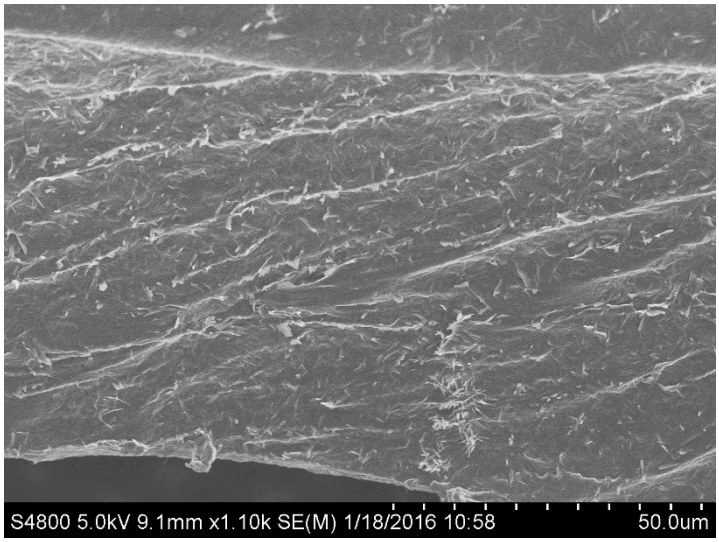
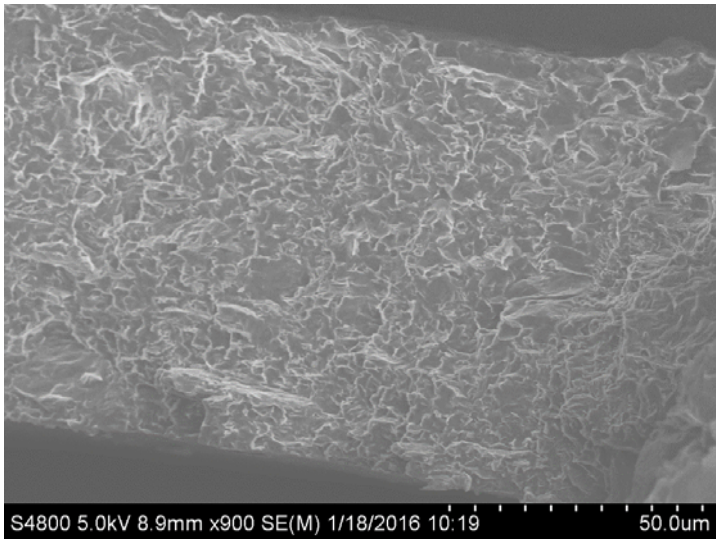


Fig. S4. The stress-strain curves of the four films measured at room temperature**.**



(a)



(b)

Fig. S5. SEM images of cross-section of stretched PU-GO-EHAB films (a) before and (b) after washing with ethanol.

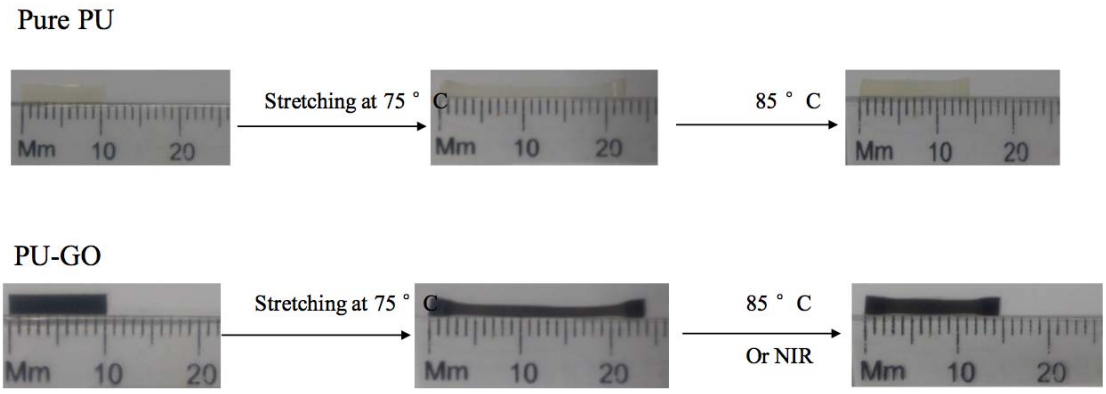


Fig. S6. Thermal and NIR -responsive behaviors of pure PU and PU-GO.

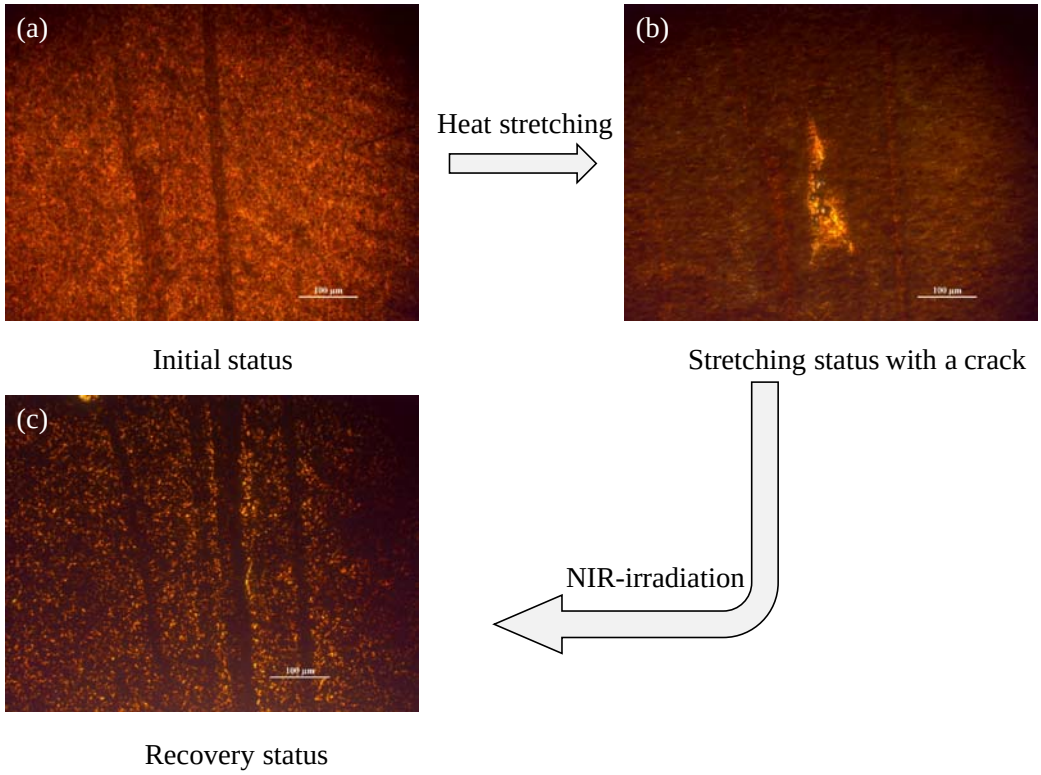


Fig. S7. POM images (50×) of self-healing property of PU-GO-EHAB film. (a) Initial status. (b) After mechanical stretching. (c) Recovery status upon exposure to NIR-light for 30 minutes.