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Supporting Information

Optically Triggered and Spatially Controllable Shape-Memory Polymer-Gold Nanoparticle Composite Materials

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Table S1. DSC data of XbOCL films with different amounts of AuNPs. The crystallinity of XbOCL in the films was calculated from the melting enthalpies.[1]

Sample	T_m (°C)	T_c (°C)	$\triangle H_m$ (J/g)	X_c (%)
XbOCL	46.50	24.60	40.16	28.28
XbOCL/AuNPs (0.1 wt%)	40.32	9.30	25.34	17.85
XbOCL/AuNPs (0.4 wt%)	35.19	1.13	21.13	14.88
XbOCL/AuNPs (1.0 wt%)	36.10	2.24	19.18	13.51

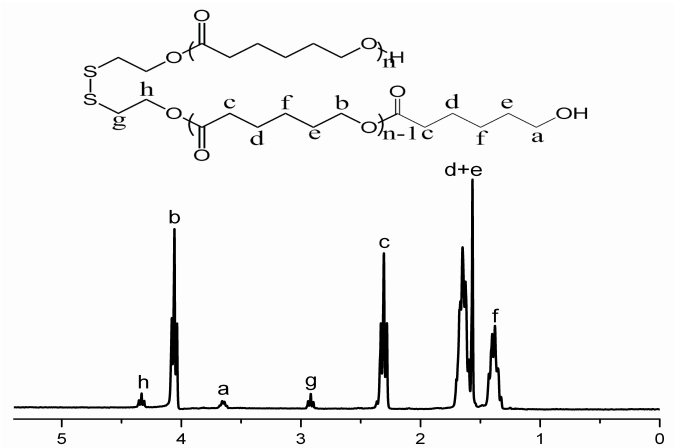

Figure S1. ^{1}H NMR spectrum of PCL-SS-PCL in $CDCl_3$

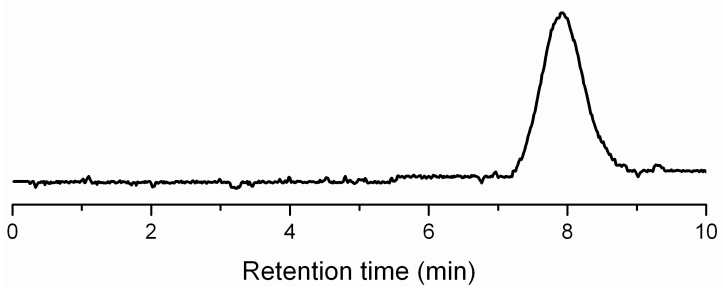

Figure S2. GPC trace of PCL-SS-PCL

Experimental Details

Materials

Oligoglycerin (polyglycerine No. 500, hydroxyl value 977) was supplied by Sakamoto Yakuhin Kogyo Co. Ltd. (Osaka). Hydrogen tetrachloroaurate tetrahydrate ($HAuCl_4 \cdot 4H_2O$) was purchased from Alfa Aesar. All other reagents were purchased from Aldrich and used as received.

Synthesis of Poly(ε-caprolactone) disulfide (PCL-SS-PCL)

Poly(ε-caprolactone) disulfide (PCL-SS-PCL) was synthesized by using ring opening polymerization (ROP) initiated by ′2,2 -dithiodiethanol and catalyzed by tin(II) 2-ethylhexanoate. Typically, ε-caprolactone (34.2 g, 0.3 mol) and 2,2′-dithiodiethanol (1.54 g, 0.01mol) were added into a flask under vacuum for 24h at 50 ^{o}C to remove water. Afterwards, the tin(II) 2-ethylhexanoate (122 mg, 0.3 mmol) was introduced and the mixture was stirred under vacuum at 120 ^{o}C for 12h. The resulting product was then dissolved in chloroform and precipitated in excess of cold methanol. The precipitate was collected and dried in a vacuum oven at room temperature for 3 days to yield the PCL-SS-PCL. The molecular structure and molecular weight were characterized were characterized by using ^{1}H NMR and GPC (see Figure S1 and Figure S2). The sample has a M_n of about 3000 g/mol (from ^{1}H NMR) and a polydispersity index (PDI) of 1.31 (from GPC).

Preparation of AuNPs functionalized by PCL-SS-PCL

The citrate-stabilized AuNPs was prepared according to a reported method.[2] The resulting aqueous solution containing AuNPs stabilized by citrate was concentrated by centrifugation and then added into the THF solution of PCL-SS-PCL (20 mg/mL) dropwise under a vigorous stirring for 24h. The PCL-SS-PCL was anchored onto the citrate-stabilized AuNPs via ligand exchange.[3] Afterwards, free PCL-SS-PCL was removed by three times of centrifuge. The obtained AuNPs stabilized by PCL-SS-PCL could readily be redispersed in chloroform. The AuNPs were confirmed by UV-vis absorption spectra and TEM.

Preparation of AuNPs/XbOCL composites

XbOCL is the branched oligo(ε-caprolactone) (bOCL, M_n ≈14,000, PDI=1.14) cross-linked by hexamethylene diisocyanate (HMDI). To prepare the composite material of XbOCL loaded with AuNPs, bOCL (100 mg, 0.007 mmol) was first dissolved in 1 mL of chloroform under stirring; HMDI (4.7 mg, 0.028 mmol) and AuNPs functionalized by PCL-SS-PCL were then introduced into the stirred solution. The mixture was poured into a Teflon dish (diameter 40 mm), with the solvent slowly evaporated for 12h. The mixture was then incubated at 80 ^{o}C for 24h under nitrogen. The crude film was washed thoroughly with chloroform and DMF, followed by drying under vacuum at 60 ^{o}C for 2 days. The final sample obtained was a cross-linked, semi-crystalline, AuNPs-loaded XbOCL film.

Characterizations

^{1}H-NMR spectra were recorded on a Bruker AC 300 spectrometer (300 MHz) using deuterated chloroform as solvent and tetramethylsilane as internal standard. The degree of polymerization of ε-CL segments was calculated from the integral ratio of the repeating methylene peak (δ 3.65 ppm) and terminal methylene peak (δ 4.07 ppm) of the caprolactone units and the molecular weight distribution (M_w/M_n) of bOCL and PCL-SS-PCL were determined by a Waters gel permeation chromatograph (GPC) instrument equipped with a Waters 410 differential refractometer detector and a Waters 996 photodiode array detector. The measurements were performed at 35 °C using one column (Waters Styragel HR4E, 7.8 mm×300 mm, 5 μm beads). Polystyrene (PS) standards were used for the calibration and tetrahydrofuran (THF) as the eluent (flow rate: 1.0 ml/min). UV-vis spectra were recorded with a Varian 50 Bio spectrophotometer, while the distribution of AuNPs functionalized by PCL-SS-PCL in XbOCL networks was examined using a Hitachi H-7500 transmission electron microscope (TEM) operating at 60 kV. The phase transition behaviors were investigated by using a TA Q200 differential scanning calorimeter (DSC), using indium as the calibration standard and a heating or cooling rate of 10 °C/min over a range from -40 °C to 100 °C purged with nitrogen. The mechanical properties were measured in the tension mode with a Perkin-Elmer DMA 8000 instrument. All the stress relaxation experiments were carried out under a constant elongation of 20% by using a specimen with dimensions of approximately 2.08×2.02×0.15 mm and a heating or cooling rate of 1 °C/min. The light exposure experiments were conducted using a PM-532-2000 laser with a wavelength of 532 nm and a tunable power output from 0 W to 1 W (manufactured by Changchun New Industries Optoelectronics Tech. Co., Ltd).

References

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