Supporting Information

Light-healable hard hydrogels through photothermally induced melting-crystallization phase transition

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1. Synthesis and Characterization of P(DMA-SA)/AuNP Hybrid Hydrogels

1.1 Materials

Azobisisobutyronitrile (AIBN, from Aldrich) and stearyl acrylate (SA, from TCI America) were recrystallized from ethanol solution. N,N-Dimethylacrylamide (DMA), lauryl acrylate (LA), hexyl acrylate (HA) and ethyl acrylate (EA) (all from Sigma-Aldrich) were purified through activated basic alumina column in order to remove inhibitor before use. Gold(III) chloride trihydrate (HAuCl₄·3H₂O), N,N'- methylenebisacrylamide (MBA), sodium borohydride (NaBH₄) and all other reagents used in this study were purchased from Sigma-Aldrich and used as received.

1.2 Synthesis of PA6ACA by RAFT Polymerization.

N-Acryloyl 6-aminocaproic acid (A6ACA)and cyanoisopropyl dithiobenzoate (CIDB) were synthesized using reported methods^[S1, S2]. Poly(N-acryloyl 6-aminocaproic acid) (PA6ACA) was synthesized according to a typical reversible addition-fragmentation chain transfer (RAFT) polymerization procedure. Typically, A6ACA (1.2 g, 6.5 mmol), CIDB (2.8 mg, 0.0127 mmol), AIBN (0.4 mg, 0.00244 mmol) and 3 mL DMSO were introduced into a round-bottom flask with a magnetic stirrer. The mixture was degassed by freeze-pump-thaw cycles, sealed under vacuum, and polymerized at 78 °C for 2.5 h. The resulting polymer was precipitated in an excess amount of cold diethyl ether, purified by repeated precipitations, and dried under vacuum.¹H NMR spectrum of the polymer is shown in Figure S1; from the characteristic peak integrals, the number-average molecular weight was estimated to be ~ 4000 g/mol.



FigureS1. ¹H NMR spectrum of PA6ACA in DMSO-d6.

1.3 TEM Observation of PA6ACA-functionalized Gold Nanoparticles (AuNPs)

TEM was employed to determine the size distribution of PA6ACA-functionalized AuNPs. As shown in Figure S2,their sizes range from ~2.5 nm to ~10 nm,whereas this heterogeneity in size does not affect the present study. We mention that AuNPs surface-functionalized with other polymers such as PDMA were also prepared; but they could not give rise to stable dispersion of AuNPs in the hydrogel during the in-situ free radical copolymerization process.



Figure S2. TEM image of PA6ACA-functionalized AuNPs.

1.4 UV-vis Absorption Spectra of PA6ACA-capped AuNPs in Different Mediums

UV-vis absorption spectra of PA6ACA-functionalized AuNPs dispersed in MeOH, water andthe P(DMA-SA) hydrogel (~ 0.7 mm in thickness) are shown in Figure S3. It is seen that the maximum absorption wavelength of the surface Plasmon resonance of AuNPs ($\lambda_{max} = 532$ nm) and the half-peak width are almost the same, indicating the excellent dispersion of the nanoparticles in theP(DMA-SA) hydrogel.



Figure S3.UV-vis spectra of PA6ACA-functionized AuNPsdispersed in methanol, water and the hydrogel.

1.5 Effect of Chemical or Physical Crosslinking Density on the thermal Phase Transition in Hydrogels

Figure S4 shows the DSC heating and cooling curves (5 °C/min) for hydrogels in Table 1. In *a*, for the samples having the same covalent crosslinker content (1.5 mol% MBA), as the amount of SA decreases, the endothermic peak on heating due to the order-disorder phase transition of the dangling side alkyl chains, becomes less important. The same observation can be made for the exothermic peak (crystallization) on cooling. In *b*, on the other hand, at the same amount of SA (24%), the reversible order-disorder phase transition of the SA side chains is also increasingly restricted by an increasing density of the permanent chemical crosslinking. At the highest 15.0% of MBA, almost no melting or crystallization of the SA chains can be detected. As discussed in the paper, the optical

healing efficiency is directly determined by the extent of the order-disorder phase transition of the dangling side chains in the hydrogel. Therefore, either covalent or physical crosslinking density affects the optical healing.



Figure S4.DSC heating and cooling curves (5 °C/min) of the hydrogels with varying SA content (a) and MBA crosslinker content (b).

2. Instruments and Methods

Thermal phase transition behaviors were investigated by using a differential scanning calorimeter (TA Q200 DSC). Indium was used as the calibration standard and a heating or cooling rate of 5 °C/min was used for all measurements. Data reported in the paper were collected from the second heating or cooling scans. The viscoelastic behavior of he P(DMA-SA)/AuNP hydrogel was measured using a dynamic mechanical analyzer (Perkin-Elmer DMA 8000) in shear mode. The mechanical tensile tests on the hydrogels conducted on a dynamic mechanical thermal analyzer (Rheometric Scientific, DMTA V) using 1 mm/s tensile rate at room temperature. For the light-triggered shape memory effect, the stress required to hold a hydrogel sample at a constant lengthwas measured in stress relaxation mode with the Perkin-Elmer DMA 8000 instrument by keeping a constant strain. UV-vis spectra were recorded on a spectrophotometer (Varian 50 Bio). WAXD measurements were carried out at 20 °C on a Bruker APEX DUO X-ray diffractometer. The hydrogel sample was cut to approximately 0.3x0.3x0.3 mm³, glued

with paratone oil on a sample holder and mounted. Six correlated runs with Phi Scan of 360 degrees and exposure times of 180 seconds were collected with the Cu micro-focus anode (1.54184 Å) and the CCD APEX II detector at 150 mm distance. The diffraction patterns were analyzed using Diffrac.Eva from Bruker. The light exposure experiments were performed using a laser at a wavelength of 532 nm and a tunable power output from 0 W to 1 W (Changchun New Industries Optoelectronics Tech. PM-532-2000). ¹H-NMR spectra were recorded on a Bruker AC 300 spectrometer (300 MHz) usingDMSO-d6 as solvent and tetramethylsilane as internal standard.TEM observation was performed using a Hitachi H-7500 transmission electron microscope (TEM) operating at 60 kV.

References

(S1) A. Phadke, C. Zhang, B. Arman, C.-C. Hsu, R. A. Mashelkar, A. K. Lele, M. J. Tauber, G. Arya and S. Varghese, *PNAS* 2012, **109**, 4383-4388.

(S2) S. H. Thang, Y. K. Chong, R. T. A. Mayadunne, G. Moad and E. Rizzardo, *Tetrahedron Lett*. 1999, 40, 2435-2438.