Electronic Supplementary Material (ESI) for Soft Matter.

Supporting Information

Well-defined and Biocompatible Hydrogels with High Strength and Reversible Photoresponsive Properties

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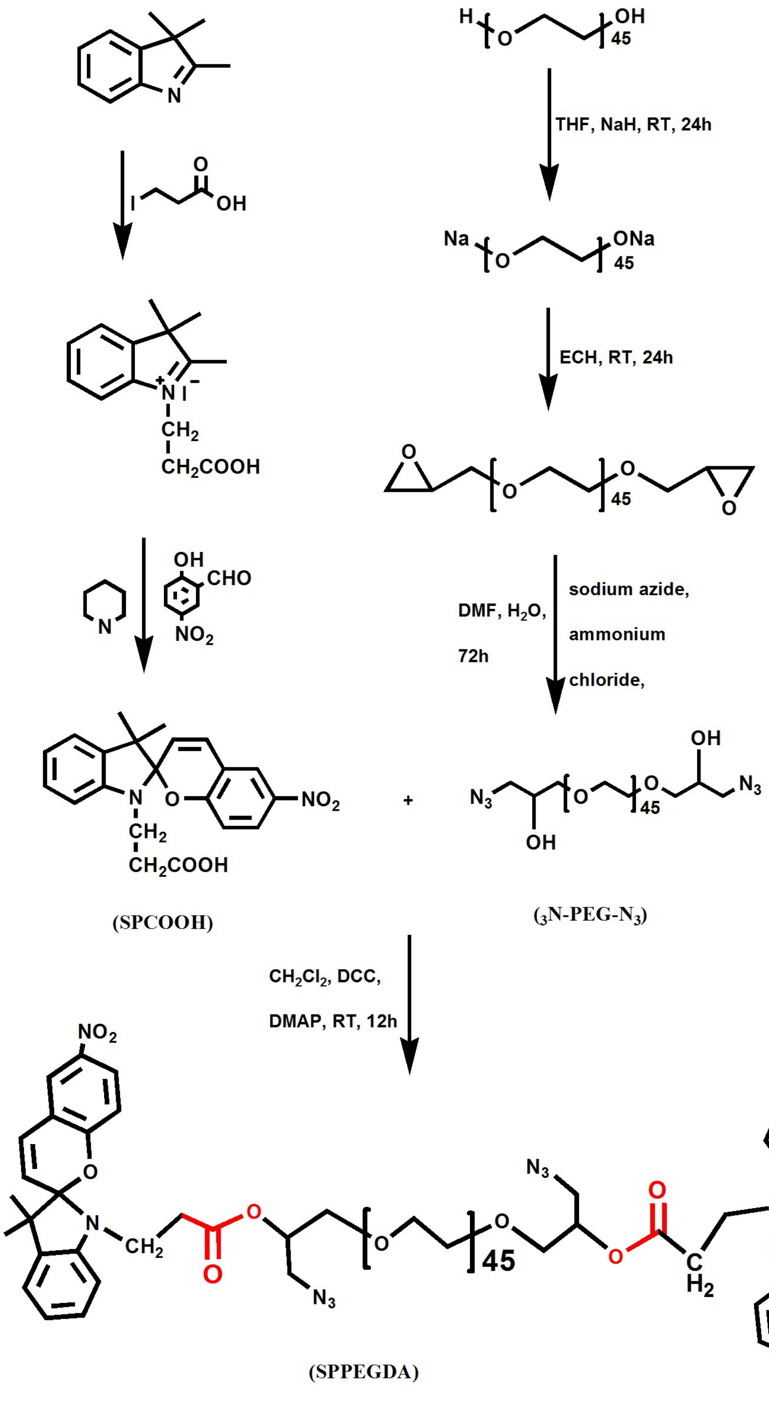
Synthesis of Poly(ethylene glycol)-diazide (N_3-PEG-N_3)

Poly(ethylene glycol)-diazide was prepared from PEG according to the method reported previously.[1] Ten gram (5 mmol) of PEG_{45} (Mn=2000 g/mol) and 100 mL of dry THF were added to a warm 250 mL three-neck flask under the nitrogen. The mixture was heated to 40^{o}C until the complete dissolution of PEG. Then, the solution was cooled to room temperature and 0.265 g (11 mmol) of NaH was added. After stirring at room temperature under nitrogen atmosphere for 24 h, 4.625 g (50 mmol) of epichlorohydrin (ECH) was added to the mixture and the reaction was allowed to proceed for another 24 h. Then, the reaction mixture was passed through a glass wool/Celite column to remove salt and byproducts. After that, the solution was concentrated by rotary evaporation and precipitated in an excess amount of diethyl ether. After filtration and drying under vacuum overnight, about 9.8 g of white solid was obtained. After that, about 5 g (2.5 mmol) of above product, 3.25 g (50 mmol) of sodium azide and 0.27 g (5 mmol) of ammonium chloride were dissolved in 40 mL of DMF/water (1/1 in volume ratio). The mixture was kept at 50^{o}C under stirring for 72 h and then cooled down to room temperature. After extracting with methylene dichloride there times (20 mL each), the organic phase was passed through an alumina column to remove residue reactants and dried over anhydrous magnesium sulfate overnight. Then the solution was concentrated and precipitated in an excess amount of diethyl ether. The resulting product was filtered and dried under vacuum overnight. About 4.5 g of white color solid was obtained (90% yield).



Scheme S1. Synthesis of SPPEGDA (ECH, epichlorohydrin; DMF, Dimethyl Formamide; DCC, N,N'-dicyclohexylcarboiimide; DMAP, 4-dimethylamino-pyridine)

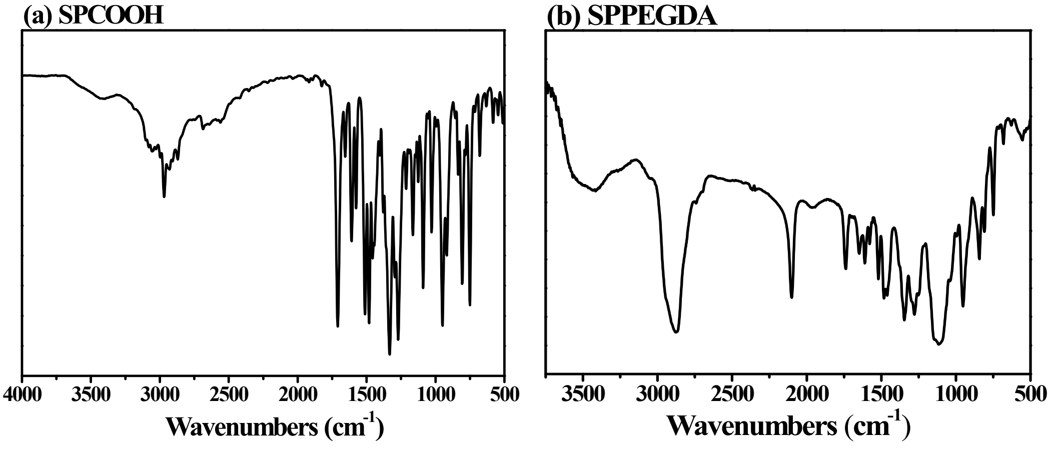


Fig. S1 FTIR spectra of (a) SPCOOH and (b) SPPEGDA.

(a) 3430 cm^{-1} (ν_{OH}), 3015 cm-1 ($\nu_{=CH}$), 3040-3090 cm^{-1} (aromatic, ν_{C-H}), 2977 cm^{-1} and 2900 cm^{-1}(aliphatic, ν_{C-H}), 1712 cm^{-1} ($\nu_{C=O}$), 1646 cm^{-1} (aromatic, ν_{C-C}), 1624 cm^{-1} and 1370 cm^{-1} (ν_{NO2}), 1520 cm^{-1} ($\nu_{C=C}$), 1470 cm^{-1} (aliphatic, δ_{C-H}), 1290 cm^{-1}, 1210 cm^{-1}, 1168 cm^{-1}, 1020 cm^{-1} (ν_{C-O-C}), 930 cm^{-1}-625 cm^{-1} (aromatic, δ_{C-H}). (b) 3430 cm^{-1} (ν_{OH}), 3050 cm^{-1} (aromatic, ν_{C-H}), 2980 cm^{-1} (aliphatic, ν_{C-H}), 2098 cm-1 (ν_{-N3}), 1710 cm^{-1} ($\nu_{C=O}$), 1650 cm^{-1} (aromatic, ν_{C-C}), 1620 cm^{-1} and 1370 cm^{-1} (ν_{NO2}), 1520 cm^{-1} ($\nu_{C=C}$), 1470 cm^{-1} (aliphatic, δ_{C-H}), 1330 cm^{-1} (ν_{C-N}), 1260 cm^{-1}, 1160 cm^{-1} and 1020 cm^{-1} (ν_{C-O-C}), 930 cm^{-1}-650 cm^{-1} (aromatic, δ_{C-H}).

In order to verify the reversibility in CA swelling ratio change, two Vis-UV irradiation cycles by alternating illumination were performed. The results were shown in Fig. S2. After being exposed to UV light for 2h, the swelling ratio of PEG-SP hydrogel remained higher swelling ratio. In contrast, the swelling ratio of PEG-SP hydrogel under Vis irradiation experienced a decrease, indicating that the present of SP was responsible for the change in hydrophilicity on the hydrogel surface.

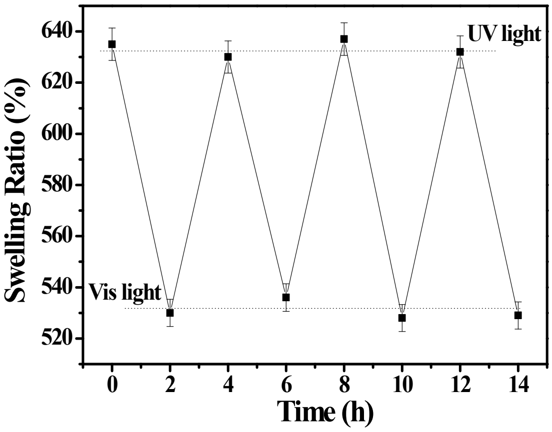


Fig. S2 The reversible swelling ratio changes of the PEG-SP hydrogel.

References

1. L. Q. Xu, F. Yao, G. D. Fu and E. T. Kang, *Biomacromolecules*, 2010, **11**, 1810–1817.