SUPPORTING INFORMATION for

Strain Hardening and Highly Resilient Hydrogels Crosslinked by Chain-Extended Reactive Pseudo-Polyrotaxane

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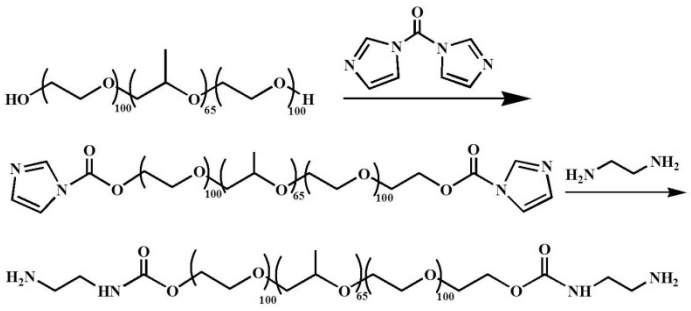
Synthesis procedure.

Synthesis of H_2N-PEG-PPG-PEG-NH_2

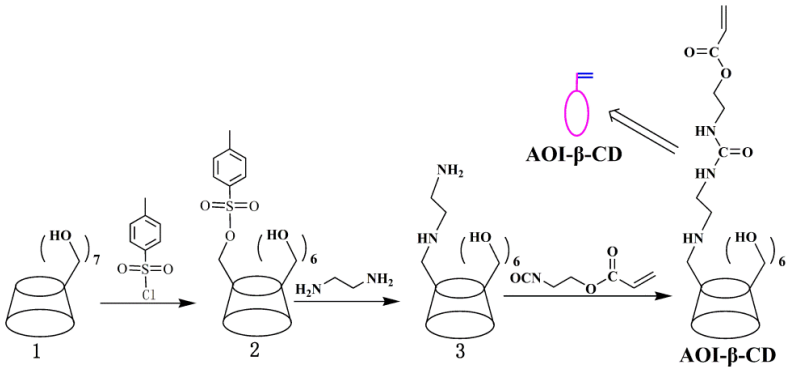


Scheme S1. Synthetic procedure for H_2N-PEG-PPG-PEG-NH_2[1]

Pluronic F-127 (12.6 g, 1 mmol) was dissolved in dry THF (20 mL) and added dropwise to excess amount of CDI (1.78 g, 11 mmol) in THF (15 mL) at room temperature for 4 h under a nitrogen atmosphere. Then the mixed solution was further stirred for another 2 h at room temperature resulting in a clear slight yellow solution. After the solvent was evaporated, the resulting mixture was poured into excess diethyl ether under vigorously magnetic stirring, yielding 10.9 g (86%) white precipitate of CDI-activated Pluronic F-127. Then, the obtained CDI-activated Pluronic F-127 in dry THF (35 mL) was slowly added for 6 h dropwise into excess ethylenediamine (30 mL) at room temperature. Unreacted ethylenediamine was removed by evaporation, and the resulting viscous oil was dialyzed for 3 days against water.

Finally, the dialyzed solution was freeze-dried to give 6.4 g (58%) of H_2N-PEG-PPG-PEG-NH_2 as a white powder.

Synthesis of AOI-β-CD



Scheme S2. Synthetic procedure for AOI-β-CD

AOI-β-CD was synthesized according to our previous report from compound 3 as shown in Scheme 2.[2]

To dry DMF solution (9 mL) containing compound 3 (1.0 g, 0.8 mmol), 2-isocyanatoethylacrylate (AOI, 0.12 g, 0.9 mmol) was added slowly at 15 ° C and stirred for 30 min under nitrogen atmosphere. After the reaction was completed, 30 mL cold acetone was added. The produced precipitate was washed with acetone and dried under vacuum at room temperature. ^{1}H NMR (400 MHz, DMSO-d6), (ppm): 8.26 (d, 1H), 5.80 (m, 3H), 4.83 (s, 1H), 4.46 (d, 7H), 3.98 (s, 2H), 3.81 (d, 1H), 3.49 (d, 6H),3.15 (m, 48H), 2.90 (s, 2H), 2.68 (m, 7H), 2.01 (m, 4H), 1.24 (s, 1H).

Synthesis of OCN-PEG-NCO

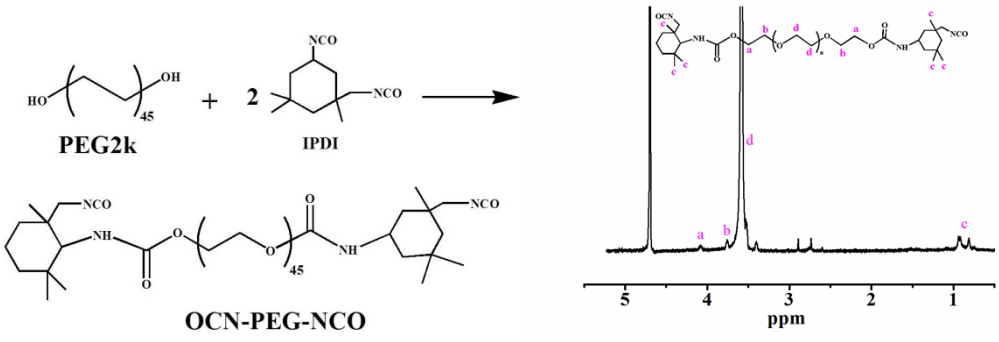


Fig S1. Synthetic procedure (left) and ^{1}H NMR (right) of OCN-PEG-NCO.

1.0 mmol PEG 2k was dissolved in 15 mL DMF, and the solution was stirred at 65 ºC until the polymer was fully dissolved. Then 2.0 mmol IPDI and 5 μL of DBTDL were added into the solution, and the mixture was stirred at 65 ºC under nitrogen for another 3 h. The resulting

solution was cooled to room temperature and precipitated in excess of diethylether under vigorously magnetic stirring, yielding white OCN-PEG-NCO powder. The powder was collected and dried at 40 ºC under high vacuum.

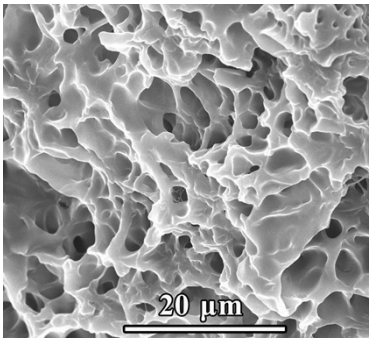


Fig S2. SEM micrograph showing the cross section of the freeze-dried 1.0%-15CD hydrogel sample.

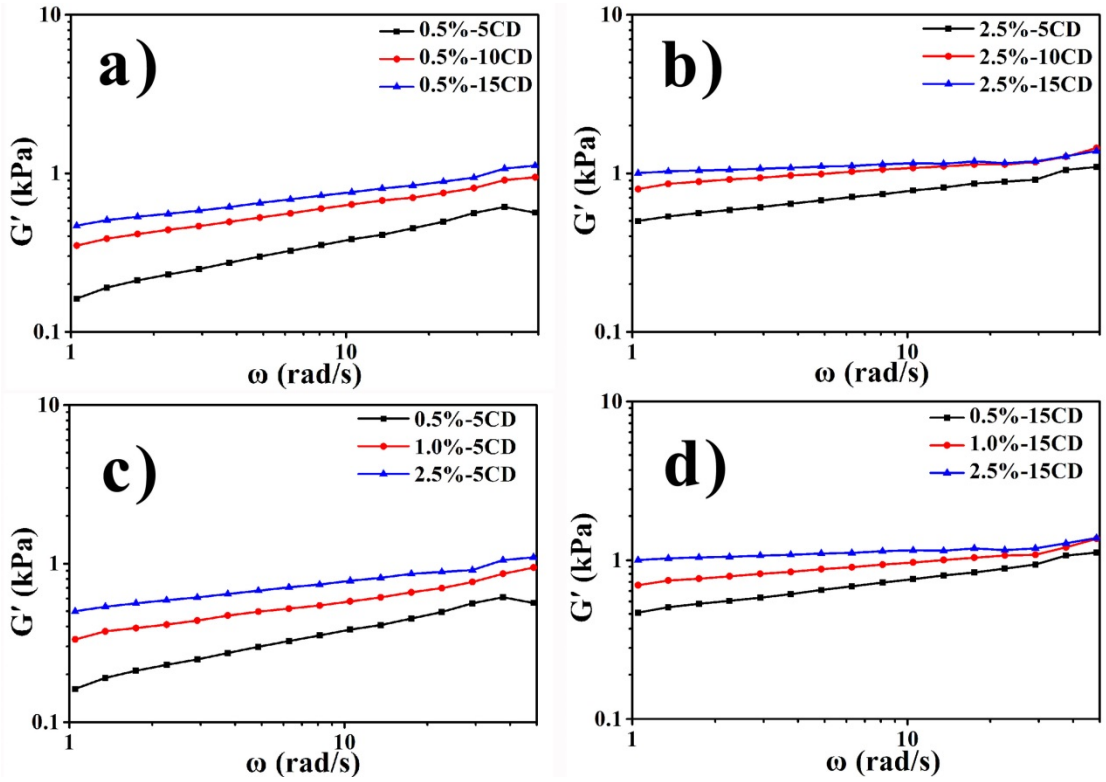


Fig S3. Shear storage modulus of the obtained hydrogels with various concentrations of H_2N-PEG-PPG-PEG-NH_2 and AOI-β-CD.

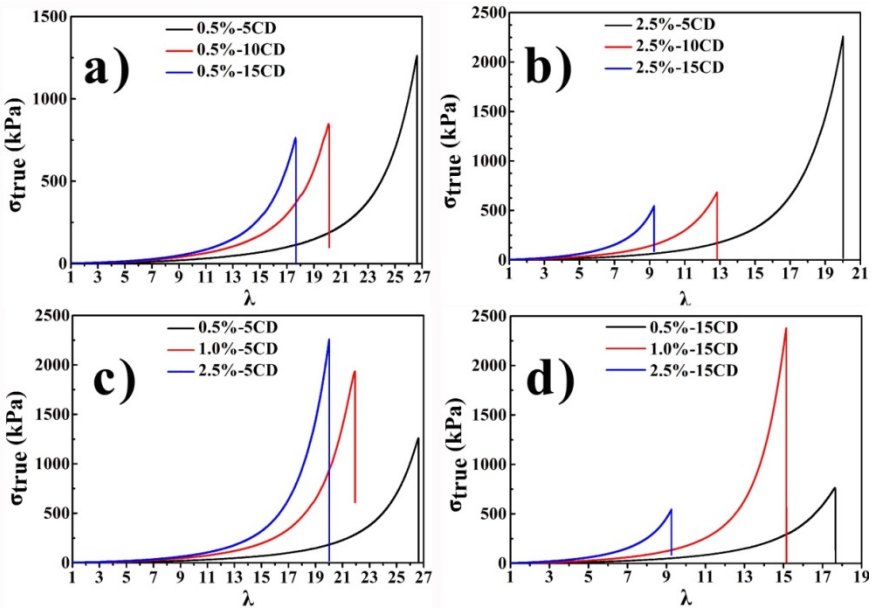


Fig S4. Stretching tensile tests of the hydrogels with various concentrations of H_2N-PEG-PPG-PEG-NH_2 and AOI-β-CD.

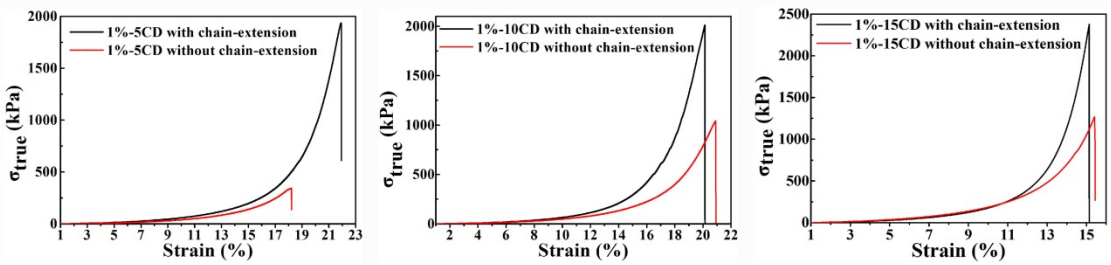


Fig S5. Tensile tests of hydrogels with and without chain-extension.

References

(1) Fujita, H.; Ooya, T.; Yui, N. *Macromolecules* **1999**, *32*, 2534.

(2) Yuan, C.; Guo, J.; Tan, M.; Guo, M.; Qiu, L.; Yan, F. *Acs Macro Letters* **2014**, *3*, 271.