Supplementary Information

Temperature-sensitive bending of bigel strip bonded by macroscopic molecular recognition

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Materials

β-Cyclodextrin (β-CD) and 1-adamantylamine were purchased from Aladdin Chemistry Co. Ltd. N-isopropylacrylamide (NIPA, 99%, Acros Organics, Fairlawn, NJ) was used after further recrystallization from n-hexane. NaHCO₃, NaOH, acetone, methanol, 2,2'-azobis(isobutyronitrile), ammonium peroxodisulfate (APS), triethylamine, THF and dimethyl sulfoxide were obtained from Sinopharm Chemical Reagent Co. Ltd., China. N,N,N',N'-tetramethylethylenediamine (TMEDA, 99%, Acros Organics), N,N'-methylenebisacrylamide (BIS, ≥98%, Fluka Chemika), Acrylamide (AAm, 99%, Shanghai Third Chemical Reagent Factory, China), Acryloyl chloride (TCI Development Co., Ltd., Shanghai) were used as received.

Measurements

1H-NMR spectra were recorded on a Bruker DRX-400 (400 MHz) instrument with CDCl₃ as the solvent (with tetramethylsilane (TMS) as an internal standard). The electro spray ionization-mass spectrometry (ESI-MS) analyses were measured on a Bruker Esquire-LC-0075 spectrometer.

Preparation of monomers

(i) 6-Acrylamido-β-CD

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6-Amino-β-CD was prepared according to the literature\(^1\)\(^2\) previously reported.

6-Amino-β-CD (0.34 g, 0.30 mmol) was dissolved in 25 mL of NaHCO\(_3\) aq. (0.25 g) and pH of the solution was adjusted to around 10 with NaOH. Acryloyl chloride (50 μL, 0.6 mmol) was added to the solution of 6-amino-β-CD in ice bath. The solution was stirred for 6 hours in ice bath. After the prescribed time, the solution was evaporated to around 15 ml and poured into acetone (250 mL). The obtained crude product was collected by centrifugation, and purified by following method: The white solid was dissolved in methanol/H\(_2\)O=3:1 aqueous solution (20 mL), then added the solution into acetone (300 mL). The product was obtained after filtration, and dried with vacuum oven for an overnight. Yield: 59%. H\(^1\)-NMR (400MHz, CDCl\(_3\)): δ= 7.92(brs, 1H), 6.22(dd, 1H), 6.02(d, 1H), 5.94-5.47(d, 1H and m, 15H), 4.99-4.65(m, 7H), 4.62-4.21(m, 6H), 3.91-2.98(m, overlaps with HOD). (ESI-MS): m/z =1210.7 [M+Na]\(^+\).

( ii) Adamantyl (Ad) acrylamide

1-Adamantylamine (0.75 g, 5.0 mmol) and triethylamine (770 μL, 5.5 mmol) was dissolved in 20 mL of dried THF in ice bath. Subsequently acryloyl chloride (450 μL, 5.5 mmol) in 20 mL of dried THF was added dropwise to the solution of 1-adamantylamine. After that, the solution was stirred for 4 hours in ice bath. The precipitate was removed by filtration, and the supernatant was concentrated under the reduced pressure. The obtained crude product was purified by column chromatography (hexane/ethyl acetate 3:1) and dried in vacuum. Yield: 77%. H\(^1\)-NMR (400MHz, CDCl\(_3\)): δ= 1.69 (m, 6H), 2.05 (m, 6H), 2.09 (m, 3H), 5.28 (br. s, 1H), 5.56 (d, 1H), 6.04 (dd, 1H), 6.20 (d, 1H). (ESI-MS): m/z =228.6 [M+Na]\(^+\).

**Preparation of gels**

( i) PNIPAAm-CD gel

PNIPAAm-CD hydrogel was prepared by copolymerization of N-isopropylacrylamide, 6-acrylamido-CD and N, N'-methylenebis(acrylamide) by radical polymerization initiated by a redox pair of APS and TMEDA in water.

NIPAAm (52 mg), 6-acrylamido-β-CD (98 mg), BIS (8 mg) were dissolved in deionized water (1.5 mL) in a glass vessel. Then APS (100 μL) and TMEDA (10 μL) were added to the solution. The polymerization was carried out overnight at room temperature. After the reaction, the resulted
gel was immersed in deionized water for 24 h, and then the sample was refreshed by deionized water every 4 h to remove unreacted monomers. The chemical structure of gel was shown in Figure S1.

Figure S1. Chemical structure of PNIPAAm-CD gel

( ii) PAAm-CD gel

PAAm-CD gel was prepared by copolymerization of acrylamide, N-(1-adamantyl) acrylamide, and N,N'-methylenebis(acrylamide) initiated by AIBN in DMSO at 70°C.

AM (154 mg), adamantyl acrylamide (46 mg), BIS (22 mg) were dissolved in DMSO (2 ml) in a glass vessel, and then AIBN (9 mg) was added into the solution. After expelling nitrogen out, the reaction precursory was initiated at 70°C. The resulted gel was obtained, followed by repeated leaching of the organic solvent with deionized water. The chemical structure of gel was shown in Figure S2.

Figure S2. Chemical structure of PAAm-CD gel
Fig.S3 (a) Deswelling kinetics of PNIPAAm-CD gels at 60 °C from the equilibrium swollen state at 20 °C. (b) Reswelling kinetics of PNIPAAm-CD gels at 20 °C from the equilibrium shrunk state at 60 °C.
References
