Supporting Information

Anisotropic volume change of poly(*N*-isopropylacrylamide)-based hydrogels with an aligned dual-network microstructure

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Materials

N-isopropylacrylamide (NIPA, 99%, Acros Organics, New Jersey) was used after recrystallization from n-hexane. Poly(ethylene glycol) diacrylate (PEGDA, Mw=700, 98%, Aladdin Chemistry Co. Ltd, China), *N,N,N′,N′*-tetramethylethylenediamine (TEMED, 99%, Acros Organics, New Jersy), ammonium persulfate(APS, 98%, Sinopharm Chemical Reagent Co. Ltd, China), fluorescein isothiocyanate isomer I (FITC, 95%, Alfa Aesar) and Rhodamine B (>90%, Acros Organics) were used as received.

Experimental Methods

Formation of the aligned porous PEG scaffold:

0.5 g PEGDA was dissolved in 5 mL deionized water to form solutions with predetermined concentration at room temperature. The solution was firstly cooled to 0 °C, followed by adding APS (4% aqueous solution, 200 μL) and TEMED (20 μL). This precursory solution was poured into a polypropylene tube(17 mm diameter × 50 mm height), which was kept closely at the surface of the liquid nitrogen(-196 °C). After freezing the precursory solution completely, the solidified sample was transferred into a freezer to complete the polymerization at -15 °C for 12 hours. The resulted hydrogel was immersed in

excessive deionized water for 48 h, and the water was refreshed every several hours to remove the unreacted materials. At last, the samples were freeze-dried and preserved for further use. To prepare a conventional porous PEG hydrogel with randomly distributed spherical pores as a control, the before mentioned precursory solution was solidified in a freezer at -15 ℃. After preserved at this temperature for 12 h, the samples were thawed and washed with deionized water in the same way.

Microstructure morphology of the PEG scaffold:

The microstructures of the cylindrical PEG scaffold with both aligned pores and conventional random-distributed pores were observed by scanning electron microscopy (SEM, Ultra 55, ZEISS, Deutschland). The freeze-dried samples were coated with gold by a sputter coater (IB-5 ION coater, EIKO, Japan) for 10 min in advance. The samples were cut in both axial and radial directions.

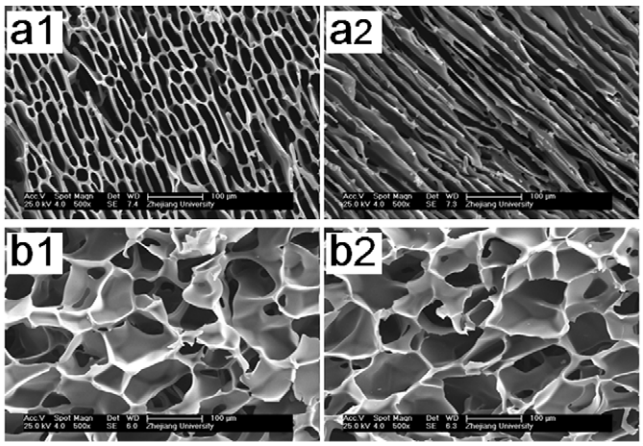

Fig S1. SEM micrographs of the PEG scaffold with aligned pores (a1 and a2) and normal pores (b1 and b2). Cross section along the radial direction: a1, b1 and vertical section along the axial direction: a2, b2

Formation of the aligned dual-network PEG/PNIPA hydrogel:

0.6 g NIPA and 8mg BIS was dissolved in 6 mL deionized water. After adding 10 μL TEMED and 100 μL APS, the freeze-dried PEG scaffold was put into this precursory solution. The polymerization occurs at room temperature and lasts for 12 h. The polymerized PNIPA outside the PEG scaffold was cut off before further test.

Confocal laser scanning microscope observation of the aligned dual-network PEG-PNIPA hydrogel:

For CLSM (LSM 510, ZEISS, Deutschland) observation, the deionized water used for PEG scaffold preparation was replaced with 5mg. L-1 FITC aqueous solution, and the PEG hydrogel was immersed in excessive water to remove the FITC existing in the pores. The deionized water used for NIPA polymerization was replaced with 5mg. L-1 Rhodamine B aqueous solution. The obtained PEG/PNIPA hydrogel was cut into slices with a thickness of approximately 0.5mm to be ready for observing the aligned dual-network microstructure.

Swelling ratio of the PEG/PNIPA hydrogel:

Both of the PEG-PNIPA dual-network hydrogel and the conventional PNIPA hydrogel were measured gravimetrically after wiping off the excessive water with wet filter paper at each given temperature ranging from 20 °C to 50 °C. Before making the measurement, the gel samples were immersed in the deionized water for 12 h to reach the equilibrium swollen or shrunken states at each given temperature. The swelling ratio (SR) was calculated as W_s/W_d, where W_s was the weight of swollen gel sample at each given temperature, and W_d was the weight of dry sample.

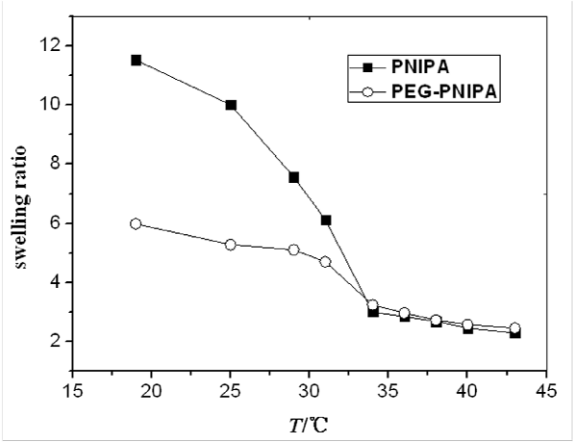

Fig S2. Equilibrium swelling ratio of PEG-PNIPA dual-network hydrogel and conventional PNIPA hydrogel as a function of temperature.

Deswelling and reswelling kinetics of the PEG/PNIPA hydrogel:

The equilibrated gel samples at a temperature of 20 °C were quickly transferred into hot deionized water of 45 °C, and then the deswelling kinetics were measured gravimetrically after removing excessive water from the surface of samples with filter paper. The reswelling kinetics of the shrunken samples that were immersed in the hot water of 45 °C for at least 48 h were determined gravimetrically at 20 °C.

The deswelling and reswelling kinetics were defined as temporal weight changes for the samples. The change of weight was converted to the normalized swelling degree, which indicated the volume changes of the samples between equilibrium swollen (100%) and equilibrium shrunken (0%) states. The swelling degree is defined as $100 \times (W_t - W_{20})/(W_{45} - W_{20})$, where W_t is the weight of sample at a given time, W_{20} and W_{45} are the weights of samples that reached equilibrium at 20 °C and at 45 °C, respectively.

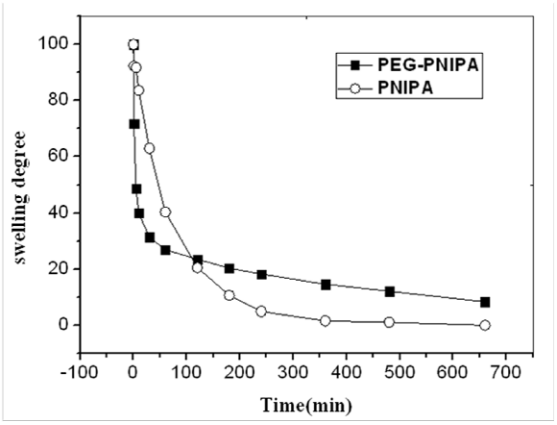

Fig S3. Deswelling kinetics of PEG/PNIPA dual-network hydrogel and conventional PNIPA hydrogel at 45 °C from the equilibrium swollen state at 20 °C.

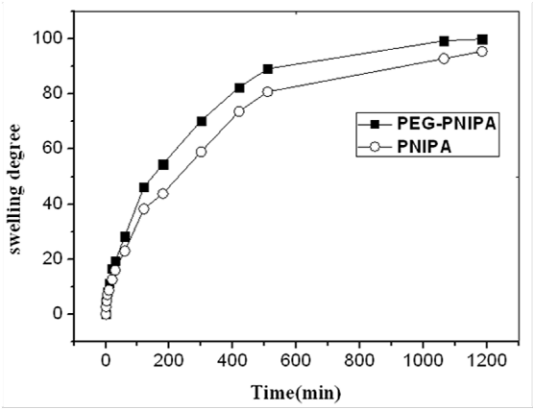

Fig S4. Reswelling kinetics of PEG/PNIPA dual-network hydrogel and conventional PNIPA hydrogel at 20 °C from the equilibrium shrunken state at 45 °C.