Electronic Supplementary Information (ESI)

Anisotropic hierarchical porous hydrogels with unique water losing/absorbing and mechanical properties

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Content:

Experimental Part

Measurements of melting points of ice in HEMA/AAm aqueous solutions

The melting points of ice crystals in the frozen HEMA/AAm aqueous solutions were investigated by differential scanning calorimetry (DSC). The HEMA/AAm aqueous solutions were put into the standard aluminum hermetic DSC pans and hermetically sealed to prevent solvent evaporation. The DSC studies were performed with a differential scanning calorimeter (DSC 1, Mettle Toledo AG, Switzerland) in the temperature range of -30–20°C at a heating rate of 2°C min^{-1} in a nitrogen atmosphere with a flow rate of 50 mL min^{-1}.

Swelling properties

The as-prepared P(HEMA-*co*-AAm) hydrogels were cut into round disks (the diameter is 10 cm and the height is 4 mm) and were vacuum dried at 60 °C for 24 h. The swelling rates were measured by weighing the hydrogel samples which were immersed in deionized water at room temperature for varying periods of time. The masses of the swollen gel samples (m_t, g) were determined immediately after wiping off excess water on them with paper tissues. The swelling ratio (SR) is calculated as: SR = $(m_{\mathrm{wet}}-m_{\mathrm{dry}})/m_{\mathrm{dry}}$, where m_{wet} and m_{dry} are the masses of the swollen samples and the dried samples, respectively.

Results and Discussion

Table S1. The size of the micro-pores on the lamellae of hydrogels synthesized with different HEMA/AAm molar ratios.

HEMA/AAm	Average Feret's Diameter (μm)	Diameter Range (μm)
2/1	1.11	0.5-1.5
1/1	1.46	0.5-3
1/2	2.86	1-5
1/5	3.89	2-6

*The pore sizes were analyzed with the image analysis software (ImageJ) based on SEM images.

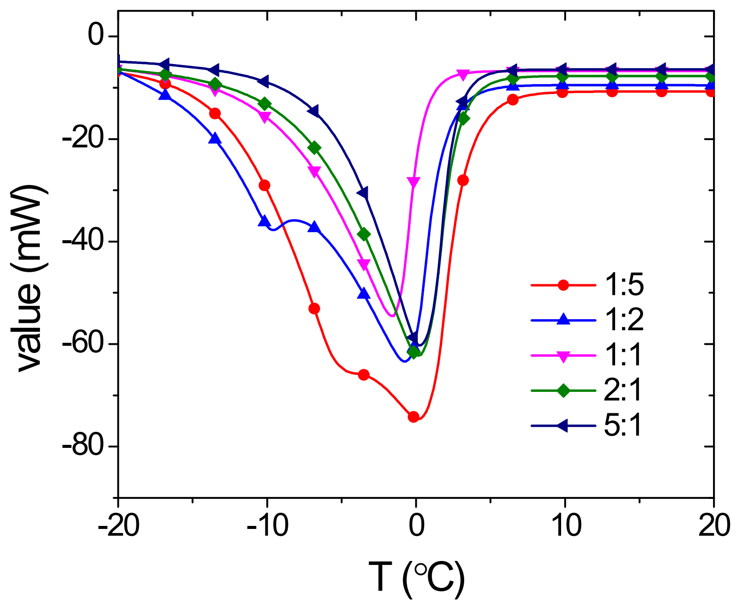

Figure S1. DSC curves of the HEMA/AAm aqueous solutions with different monomer ratios.

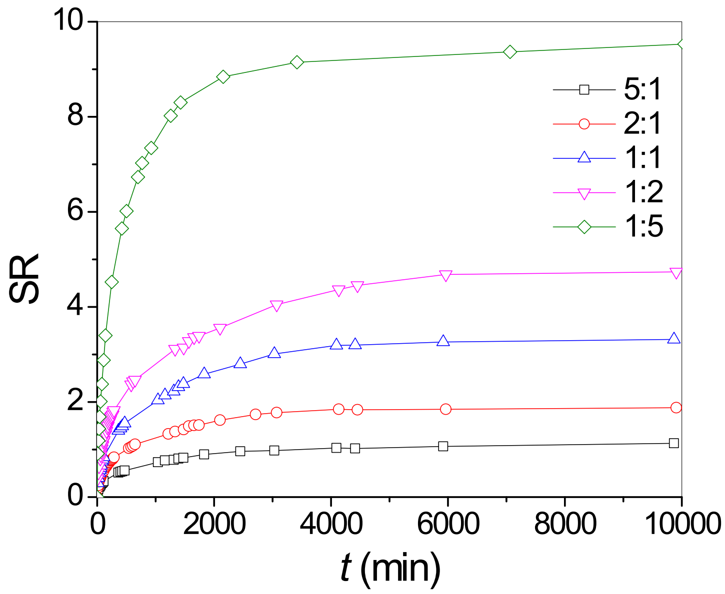

Figure S2. Swelling kinetics of the P(HEMA-*co*-AAm) hydrogels at room temperature.

The swelling kinetics of the hydrogels is shown in Fig. S1. The swelling rates of the P (HEMA-co-AAm) hydrogel increased with decreasing x/y.

The equilibrium swelling ratios (ESRs) of the as-prepared hydrogels can be calculated from the equilibrium water contents (EMC) of the HEMA/AAm hydrogels listed in Table 1, and they are 4.10, 6.69, 8.52, 12.16 and 21.73 for the as-prepared hydrogels, respectively.

The ESRs of the dried hydrogels are 1.13, 1.88, 3.32, 4.74 and 9.53 (Fig. S1), respectively, which are lower than those of the as-prepared hydrogels.

The ratio of the two ESRs is more obvious for the hydrogel with a higher HEMA molar ratio. The possible reason is that the close contact of polymer chains in the dried state leads to stronger hydrophobic interactions and hydrogen bonding among them and they cannot be fully broken during the swelling process.

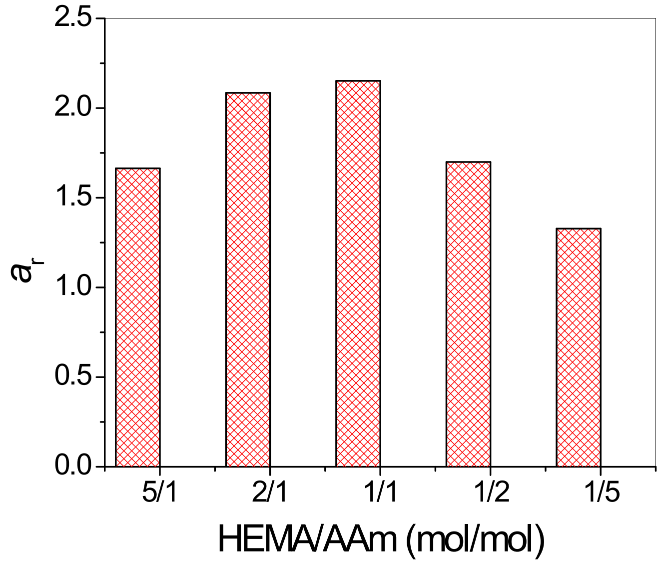

Figure S3. The anisotropy ratio (a_r) of E_c in the parallel direction to that in the vertical direction.

To compare the extent of anisotropy in the hydrogels, here we used anisotropy ratio, a_r, which is defined as the ratio of E in the parallel (p) direction to that in the vertical (v) direction. The biggest difference in the ratio of E_c in the parallel direction to that in the vertical direction is found at the molar ratio of 1/1 (Fig. S3).

Movie S1. The losing of water under compression and the absorbing of water by the hydrogel.

Movie S2. The fast water-absorbing of the squeezed Gel-1-1 hydrogel sample immersed into water.