## Supporting Information for Secondary Structure-Governed Polypeptide Cross-Linked Polymeric Hydrogels

Chongyi Chen\*<sup>†</sup>, Jun Lan<sup>†</sup>, Yuanchao Li<sup>‡</sup>, Dongran Liang<sup>†</sup>, Xiuquan Ni<sup>†</sup>, Qiao Liu<sup>§</sup>

<sup>†</sup> Ningbo Key Laboratory of Specialty Polymers, Faculty of Materials Science and Chemical Engineering, Ningbo University, Ningbo 315211, China.

<sup>‡</sup> Key Laboratory of Polymeric Composite and Functional Materials of Ministry of Education, School of Materials Science and Engineering, Sun Yat-Sen University, Guangzhou, 510275, China.

<sup>§</sup> Institute of Materials, Ningbo University of Technology, Ningbo, 315016 Ningbo, China.

**Materials.** Tetrahydrofuran (THF), hexane, dichloromethane (DCM) and *N*,*N*'-dimethylformamide (DMF) were purified by first purging with dry nitrogen, followed by passage through columns of activated alumina. All commercially obtained reagents were used as received without further purification.

Instruments. <sup>1</sup>HNMR spectra were recorded on Bruker AVANCEII 400 MHz NMR spectrometer (at 400 MHz). Circular dichroism spectra (CD) were recorded on an Applied Photophysics Chirascan CD Spectrometer.

**Rheology measurement.** The strain sweep and recovery experiments were conducted by using a rotational rheometer (ARES-G2, TA Instruments) equipped with 25 mm parallel plates. A typical hydrogel sheet with a thickness of 2 mm was cut into a circle 25 mm in diameter and then put on the bottom plate of the rheometer for the time and strain sweep measurements at 25 °C,  $\omega = 1$  Hz.

**Tensile test.** The hydrogel tensile test was performed on a Shenzhen Kaiqiangli Testing Instruments KDIII-0.05 tensile testing machine. All the cylindrical hydrogel samples with a diameter of 4.6 mm were tested with a crosshead speed of 50 mm·min<sup>-1</sup> at 25 °C. The engineering tensile stress ( $\sigma$ ) was calculated as  $\sigma = L/(\pi R^2)$ , where *L* is the load and *R* is the original radius of the specimen. The engineering tensile strain ( $\varepsilon$ ) was defined as the change in length (*I*) relative to the initial gauge length ( $I_0$ ) of the specimen,  $\varepsilon = I/I_0 \times 100\%$ . The toughness was calculated by integrating the area under the stress-strain curve at fracture. Work of extension was calculated by integrating the area under the loading curve. Tensile modulus (*E*) was calculated from stress-strain curve between elongations of 10% and 100%. At least three specimens per experimental point were tested in all mechanical measurements to obtain reliable values. Cyclic tests were performed by performing subsequent trials immediately following the initial loading with the same specimen at a strain speed of 50 mm·min<sup>-1</sup>. The waiting time was the recovery time from the end of the first cycle to the second cycle stretch. The hysteresis during the cyclic tensile test was determined by the integration of the area between the loading and unloading curves. The hysteresis ratio for a certain cycle was calculated by the equation hysteresis ratio = 1 -  $A_2/A_1$ , where  $A_1$  and  $A_2$  represent the areas beneath the loading and the unloading curves, respectively. Work of extension recovery ratio was defined by evaluating the

ratio of the integrated area of the 2nd or later extension curves to that of the 1st one.



Figure S1. <sup>1</sup>H NMR spectra of <sub>DL</sub>-PHPG in D<sub>2</sub>O and acryl-<sub>DL</sub>-PHPG in DMSO-*d*.



Figure S2. (A) L0.5 with diameter of 4.6 mm lifts up a ca. 100 g weight. (B) High strain is applied to L0.5.



**Figure S3.** Circular dichroism spectra of (blue solid line) acryl-L-PHPG (1.8 mg/mL) and (red solid line) acryl-DL-PHPG (1.8 mg/mL) aqueous solutions, (green solid line) PAAc (0.05 g/mL) aqueous solutions, PAAc hydrogels (0.05 g/mL) cross-linked by (blue dot line) acryl-L-PHPG (1.8 mg/mL) and (red dot line) acryl-DL-PHPG (1.8 mg/mL).



Figure S4. Tensile mechanical properties of Bx synthesized as a function of  $M_{link}$ .