

Supporting Information

A Supramolecular Hydrogel with Identical Cross-linking Point Density but Distinctive Rheological Property

Chuang Li, Xu Zhou, Yu Shao, Ping Chen, Yongzheng Xing, Zhongqiang Yang, Zhibo Li and Dongsheng Liu*

1. Materials: All oligonucleotides (see Table S1) were synthesized using ABI 394 DNA synthesizer with a standard phosphoramidite DNA synthesis protocol and purified by HPLC. Water used in all experiments was Millipore Milli-Q deionized (18.2 M Ω cm⁻¹).

Table S1 DNA sequences for the preparation of polypeptide-DNA hydrogels

(A) Azido-DNA

L₁: 5'-azido-AAGTGTCCAGTT-3'

(B) SE12 (12-base long sticky ends)

12a: 5'-ACTATGCGTGAATCCGTTAGAACTGGACACTT-3'

12b: 5'-CTAACGGATTCACGCATAGTAACTGGACACTT-3'

(C) SE8 (8-base long sticky ends)

8a: 5'-ACTATGCGTGAATCCGTTAGAACTGGAC-3'

8b: 5'-CTAACGGATTCACGCATAGTAACTGGAC-3'

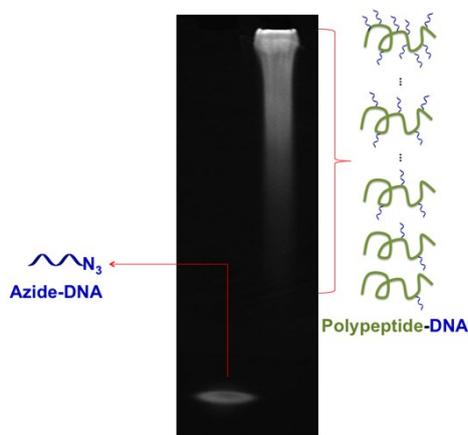
(D) SE8M (single mismatch in 8-base long sticky ends)

8M-a: 5'-ACTATGCGTGAATCCGTTAGAACAGGAC-3'

8M-b: 5'-CTAACGGATTCACGCATAGTAACAGGAC-3'

Red sequences are “sticky ends”; Blue base is single-base mismatch site.

2. Synthesis of polypeptide-DNA conjugate.



of azido-DNA and “sticky ends” of DNA linkers. The melting points are 68.5 °C (double strand region of DNA linker), 53.5 °C (SE12), 39.6 °C (SE8), and 20.8 °C (SE8M), respectively.

5. Rheological tests.

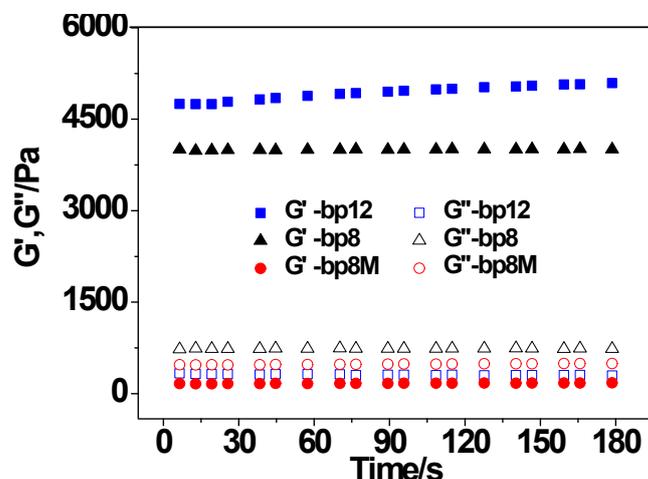


Figure S3. The mechanical strength of hydrogel samples (5 wt%) with different DNA linkers were characterized by time scan rheological test performed at a fixed frequency of 1 Hz and strain of 1 % at 25 °C.

The hydrogel could be also mechanically tuned by varying relative molar ratio of two components. In our study, DNA linker (SE12) and polypeptide-DNA were mixed together with different molar ratios of “sticky ends” at 0.6:1, 0.8:1, 1.0:1 and 1.2:1, respectively, with a fixed total mass content of 5 wt%. Theoretically, the mechanical property of the hydrogels should be the highest when the “sticky ends” from DNA linker and polypeptide-DNA are at the ratio of 1:1, i.e., the networks are fully cross-linked. In our experiment, shown in Fig. S5, the hydrogel at the ratio of 0.8:1 and 1.0:1 exhibited the highest mechanical strength, and beyond this range, when the system had either polypeptide-DNA or DNA-linker in excess, the hydrogel exhibited lower mechanical strength.

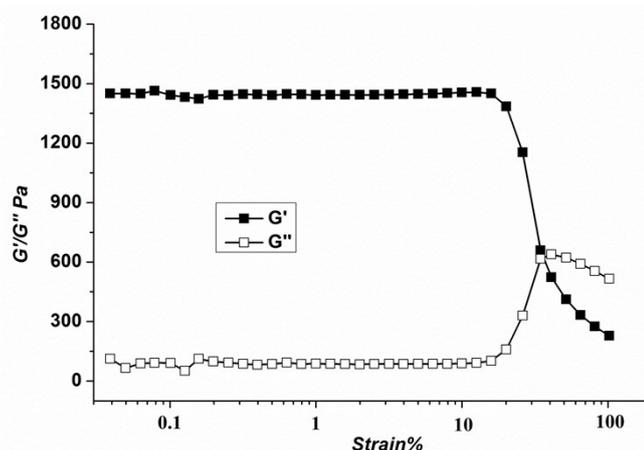


Figure S4. Rheological strain sweep of polypeptide-DNA hydrogels (3 wt%) which was performed between 0.04% and 100% at 25 °C with a fixed frequency of 1 Hz.

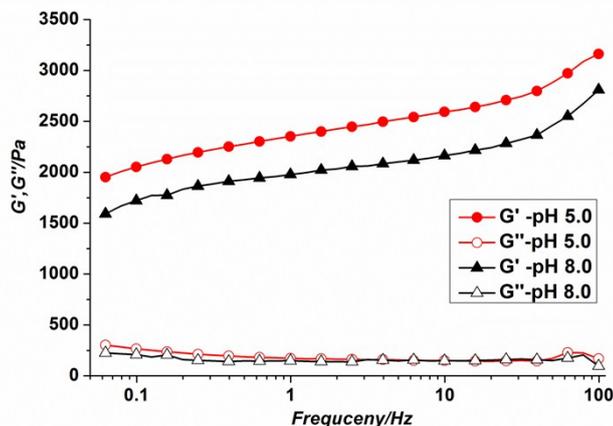


Figure S5. Rheological properties of polypeptide-DNA hydrogels with different pHs. Frequency sweep rheological tests were carried out between 0.05 Hz and 100 Hz at a fixed strain of 1% at 25 °C.

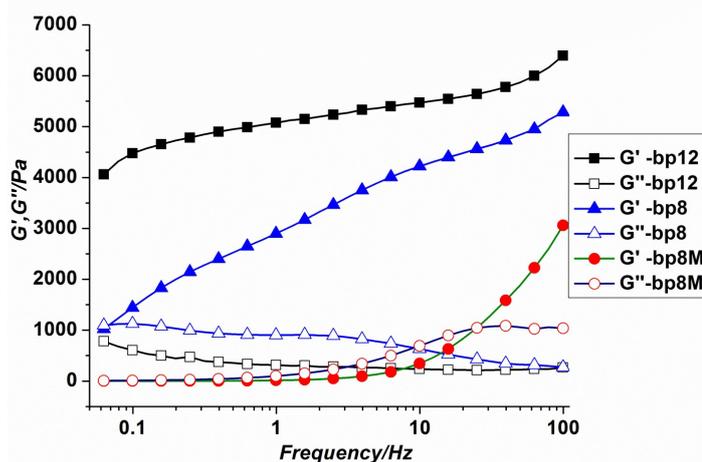


Figure S6. Rheological properties of polypeptide-DNA hydrogels with different DNA linkers. Frequency sweep rheological tests were carried out between 0.05 Hz and 100 Hz at a fixed strain of 1% at 25 °C.

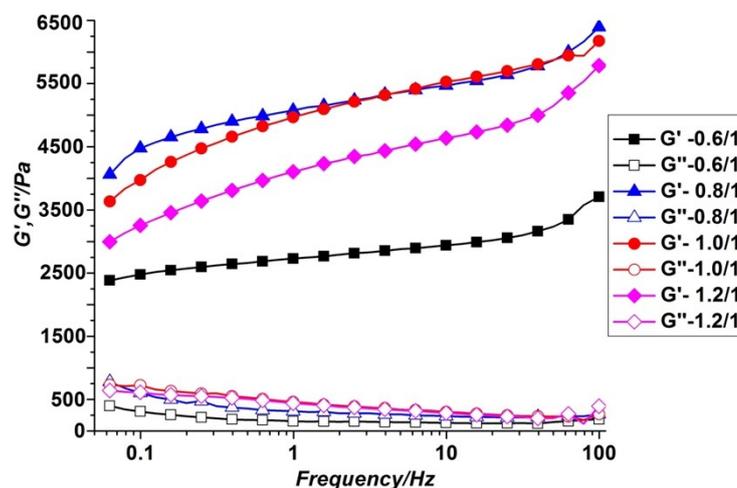


Figure S7. Rheological properties of polypeptide-DNA hydrogels with different molar ratios of linkers (sticky ends of DNA linker/polypeptide-DNA = 0.6:1, 0.8:1, 1.0:1, and 1.2:1). The total polypeptide and DNA content was 5 wt.% and the frequency sweep rheological tests were carried out between 0.05 Hz and 100 Hz at a fixed strain of 1% at 25 °C.

6. Circular dichroism spectroscopy.

The circular dichroism (CD) spectra were collected on an Applied Photophysics Chirascan spectropolarimeter which was carried out at the range of 180-350 nm at room temperature in a quartz cell of 1 mm optical length with a scanning speed of 60 nm·min⁻¹.

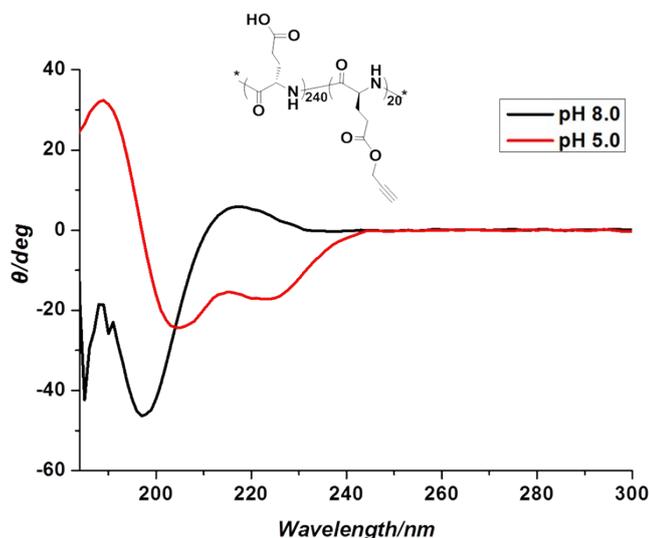


Figure S8. CD Spectroscopy of polypeptide in phosphate buffer (100 mM) with different pHs. Red line, CD curve of polypeptide in phosphate buffer of pH 5.0 (red line) and pH 8.0 (black line).