Electronic Supporting Information (ESI)

Structural evolution of dispersed hydrophobic association in hydrogel analyzed by tensile behavior

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Materials

Poly(vinyl alcohol) (PVA (99+%hydrolyzed); M_w: 146,000-186,000; Product number:363065) were purchased from Sigma Aldrich. Octylamine, *N,N′*-carbonyldiimidazole (CDI), Dimethylsulfoxide (DMSO) and *N,N'*-Dimethylformamide (DMF) and 28% Ammonium hydroxide were supplied by Energy Chemical, China, and were used without further purification.

Synthesis of PVA-C8-DS series

The synthesis of PVA-C8-DS has been generally described in our previous work.[1] Typically, PVA (1 g, 22.75 mmol based on -OH group) was dissolved in 40 mL dry DMSO in a 125 mL round bottom flask under vigorous stirring. The obtained PVA solution was cooled down to 20 ^{o}C, then 3.73 g CDI (1 equiv/hydroxyl) was quickly added and kept vigorous stirring for 3 h at 20 ^{o}C. Afterwards, 3.76 mL *n*-octyl amine (1 equiv/hydroxyl) was added to CDI/PVA solution drop by drop during a course of half hour. After additional stirring for about *t* h, 28% ammonia solution was added and the reaction mixture was stirred for 2 h to hydrolyze all CDI activated hydroxyls which did not react with octyl amine. The product, namely PVA-C8-DS, precipitated out by adding 10-fold diluted HCl aqueous solution (pH~5-6) at 40 °C and resolved in DMSO. This process was repeated for at least three times. The precipitate was collected by centrifugation, and washed with water. At last, a final product as white powder was obtained after freeze-drying. During the reaction course of *t* h, ^{1}H nuclear magnetic response (NMR) spectra were used to monitor the DS value. Figure S1 shows a ^1H NMR spectra of PVA-C8-DS with a DS value of 0.1 to 0.5.

Gelation of PVA-C8-DS

PVA-C8-DS was dissolved in DMF to form a 100 mg/mL homogeneous solution. The solution of PVA-8-DS/DMF was sonicated in an ultrasonic cleaning tank, operating at a frequency of 40 kHz with power of 180 W and then vacuumed with a water pump to remove the trapped bubble. Subsequently, the solution was casted into a Teflon mold and then exposed to saturated water vapor at 24 °C for about 24 h to trigger gelation upon solvent-nonsolvent exchange. The gel was immersed in a large amount of water to extract residual DMF, resulting in as-C8-DS. The as-C8-DS was immersed in water at 90 °C for 12 h and naturally cooled down to 24 °C to produce C8-DS.

Measurement Methods

Nuclear magnetic resonance spectroscopy (NMR)

The NMR spectrum of PVA-C8-DS was recorded by using d_6-DMSO as solvent on a Bruker 400 MHz spectrometer.

X-ray Diffraction (XRD)

X-ray diffraction (XRD) patterns were recorded on the wet PVA-C8-based hydrogels by using a Bruker Advance D8 diffractometer with a lynxeye detector at 40 kV and 40 mA at a scanning rate of 1 ^{o}/min from $2\theta=1^{o}$-60^{o}.

Differential scanning calorimeter (DSC)

The thermal behavior of wet PVA-C8 based hydrogels were investigated by DSC (TA, Q20) from -30 ^{o}C to 250 ^{o}C under N_2 flow at a ramping rate of 10 ^{o}C/min.

Water content of hydrogel

The water content of the as-C8-DS and C8-DS was calculated by the weight change upon drying: A piece of as-C8-DS or C8-DS with rectangle shapes was weighed and recorded as W_{wet}. Then, the same piece of hydrogel was fully dried using a freeze-drying process until the weight became constant, and recorded as W_{dry}. Accordingly, the water content of the hydrogel is calculated from the equation:

$$C = (W_{\mathrm{wet}} - W_{dry}) / W_{\mathrm{wet}}$$

Volume fraction of hydrogel

The volume fraction of polymer in hydrogel, φ, was defined as the ratio of polymer's volume in hydrogel to the total volume (*V*) of hydrogel. The *V* of hydrogel can be directly measured. Thus, the volume fraction of polymer, φ, can be calculated from equation:

$$\varphi = (V - V_W) / V$$

V_w is the volume of water in the gel and can be calculated by $V_w=W/\rho_w$, W is the water content in the gel with a volume V, and the density of the water is 0.998 g/mL.

Mechanical properties

The stretch test was carried out on an electronic universal tensile machine (Zhuhai SANS (CMT2203)). The test was conducted on a rectangle sample with width of approximate 4 cm and thickness of approximate 0.1 cm. During the test, the sample was immersed in a water bath at a constant temperature of 24 ^{o}C. Nominal stress (σ), elongation (λ) and elastic modulus (E) are all derived from the stress-elongation curve: σ is the Force (F) divided by the cross-sectional area is calculated, and λ is the length of the extended sample divided by the original length; E is calculated from the slope of the stress-elongation curve (1% to 5%) elongation. For single edge crack testing, two identical samples with length of 10 mm and width of 7 mm for tensile testing were used. A notch with length of 3 mm along the width was introduced by a razor blade cutting into one of these two samples, with A as the area of cross section of the unnotched sample and L_0 as the initial distance between the clamps. A force-extension curve was measured for both the notched sample and an unnotched sample with the same initial dimensions. ΔL_c was defined as the critical extension where the crack propagation starts, and $U(\Delta L_c)$ was the work of extension to reach ΔL_c extension (calculated as the integral of the force-extension curve). The fracture energy based on single edge crack method was given by:

$$\Gamma_{notch} = U(\Delta L_c)/A$$

Supporting Figures

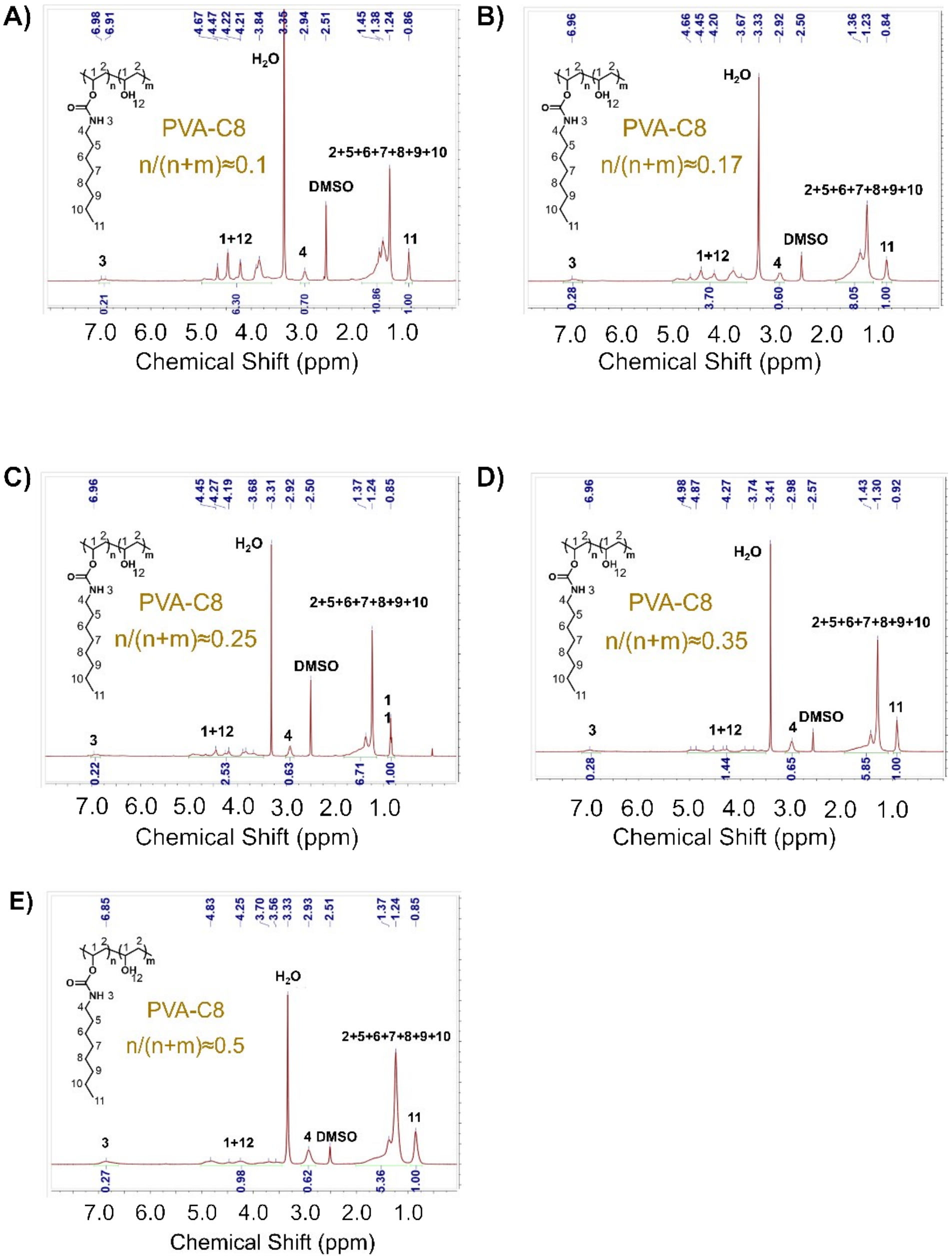

Figure S1. Liquid ^{1}H NMR spectrum of representative PVA-C8-DS (Solvent: d_6-DMSO) with various DS.

Using the peak area of the ^{1}H NMR spectrum, we calculated the molar ratio of the octyl carbamate group on the PVA to the initial -OH group, which is defined as the degree of substitution (DS). We suppose that the -OH groups *in* initial PVA is normalized to be 1 and the DS=X. Thus, the normalized number of protons from the terminal -CH_3 of octyl-carbamate should be 3X. The total amount of protons from -CH_2- on PVA backbone and -CH_2- on side octyl-carbamate groups should be 2*1+4*2X. The value of (2*1+4*2X)/3X should be the ratio of integrated area of the peak between 1.37-1.94 ppm to that of the peak at 0.9 ppm.

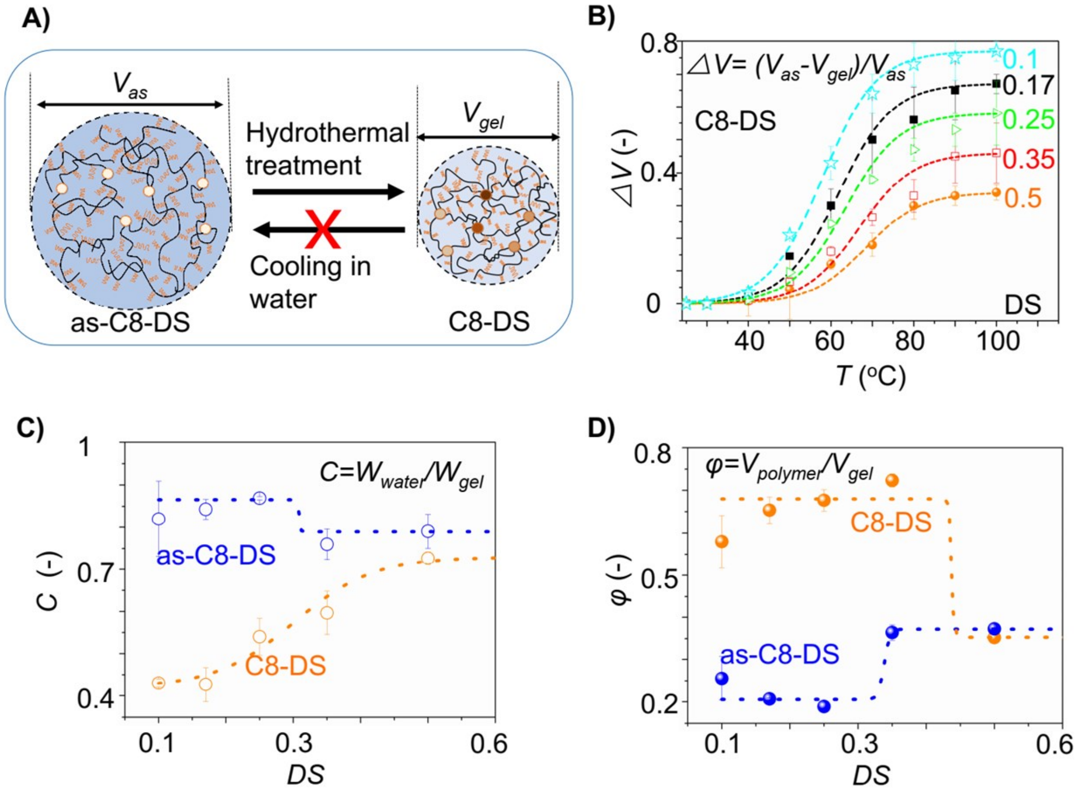

Figure S2. (A) Schematic diagram of the volume shrinkage of as-C8-DS caused by hydrothermal treatment; (B)the degree of volume shrinkage at different temperatures of hydrothermal treatment for as-C8-DS series; (C)water content and (D) volume fraction of as-prepared as-C8-DS hydrogel and hydrothermally treated C8-DS hydrogel.

Our previous works have phenomenally exhibit that as-prepared as-Cn-DS hydrogels experience irreversible volume shrinkage and dehydration upon hydrothermal treatment (Figure S2A), and thus mechanical properties are collectively enhanced. We further elucidate the hydrothermal treatment effects on as-C8-DS series. During solvent-non-solvent induced gelation process, solvent mixing and assembly of hydrophobic alkyl chains release energy. Most of this energy is dissipated as heat, but a small portion may remain in the as-Cn-DS network in the form of strain energy. Thus, there may exist some residual stress in as-Cn-DS. The hydrothermal treatment induces the internal rotation of the chain segment to release the residual stress. Driven by free energy, some adjacent dangling alkyl side chains spontaneously form hydrophobic clusters, resulting in an increase in the number density of polymer chains in the network.

Figure S2B shows the degree of volume shrinkage ($\triangle V$) of as-C8-DS upon hydrothermally treatment at different temperatures for 12 h. Below 40^{o}C, the volume shrinkage is negligible, indicating that energy input at this temperature may not be sufficient to overcome potential barrier of internal rotation of polymers. As the temperature of hydrothermal treatment increases from 40^{o}C to 90^{o}C, $\triangle V$ gradually increases and eventually saturates in the temperature range of 90^{o}C-100^{o}C. This result implies the number density of hydrophobic association get maximized upon the hydrothermal treatment at 90 ^{o}C.

Under any given hydrothermal conditions, the degree of volume shrinkage of as-C8-DS becomes less pronounced as the DS becomes larger. For example, when DS is 0.1, degree of volume shrinkage is as high as 75%, while for DS =0.5, the volume shrinkage is only 28%. The inverse correlation between DS and $\triangle V$ may suggest that higher modification density of alkyl chains may have higher potential barrier to suppress the internal rotation .

Figures S2C-S2D exhibits the water content and volume fractions of the as-prepared (as-C8-DS) and hydrothermally treated C8-DS hydrogel (90 ^{o}C, 12 h). The water content (*C*) of the as-prepared as-C8-DS series hydrogels is around 0.8-0.75. In line with the volume contraction, the water content of C8-DS is lower than that of as-C8-DS. Notably, water content in C8-DS increases with the increase of DS. For example, the water content of C8-0.1 is 0.41, while it increases to 0.72 for C8-0.5. This result is unexpected since the hydrophilicity of PVA-C8-DS should lower with an increase of DS. When DS is around 0.35, the volume fraction of as-C8-DS abruptly increases from 0.2 to 0.35, while the volume fraction of C8-DS abruptly decrease from 0.7 to 0.35.

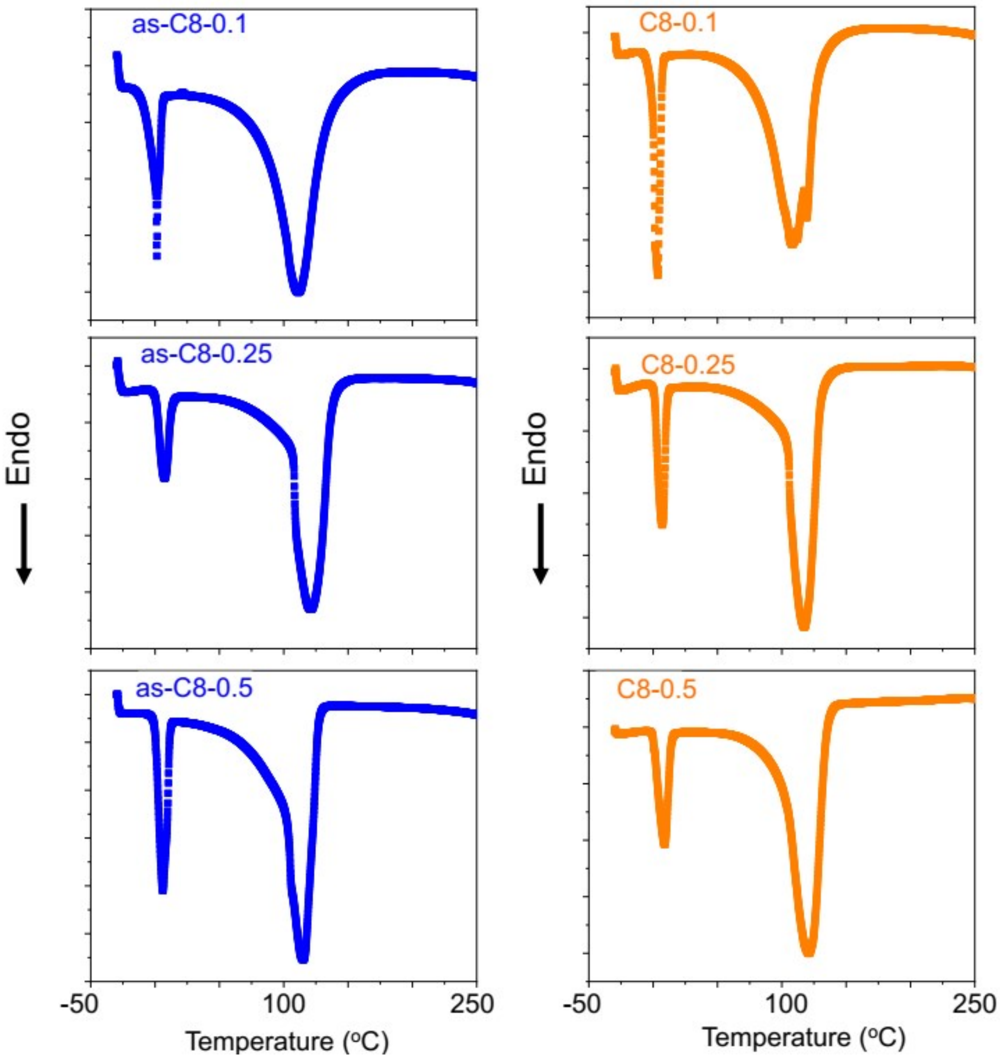

Figure S3. DSC traces for typical as-C8-DS and C8-DS hydrogels in wet state.

In Figure S3, the first peak in DSC curves for these hydrogels at approximately 2.5 ^{o}C is due to the melting of water. The second peak at about 100~112 ^{o}C is due to the boiling of water.[2] Clearly, there is no melting point for the hydrophobic association of octyl chains. This thermal behaviour is significantly different from that of semi-crystalline hydrogels crosslinked by hydrophobic association of very long alkyl chains,[3] which exhibits a well-defined endothermal peak due to the melting of alkyl crystals. These DSC results suggest that there exists no crystalline phase, either from PVA backbone nor from the octyl side chains.

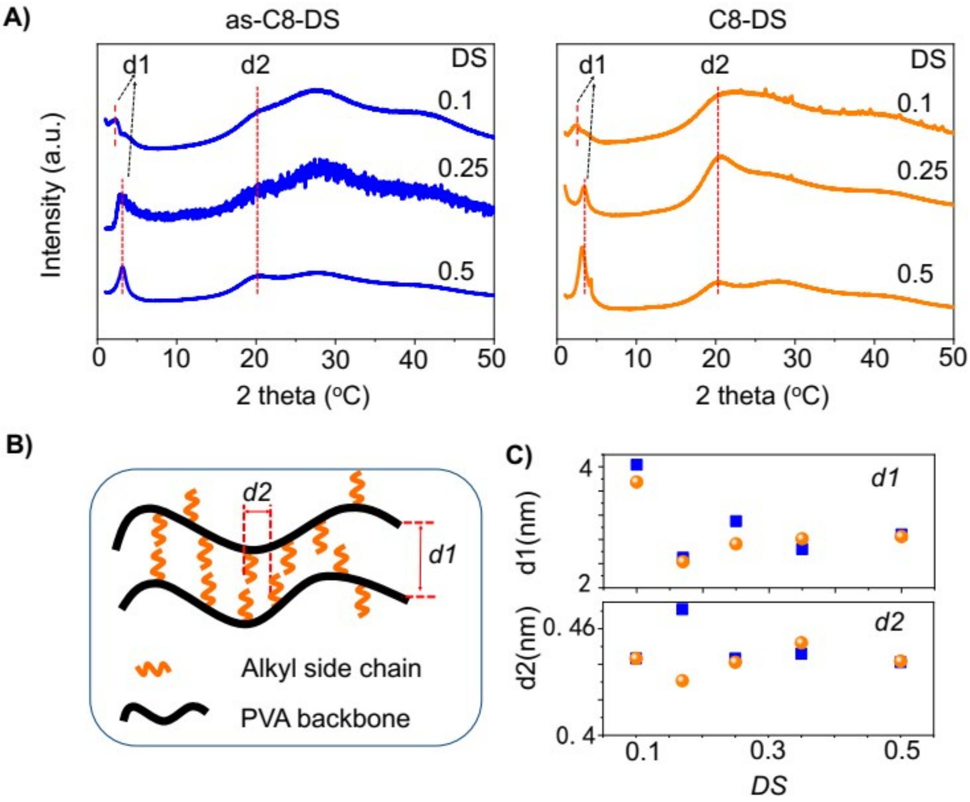

Figure S4. (A) XRD patterns for as-C8-DS and C8-DS hydrogels; (B) molecular arrangement of octyl side chains and PVA backbone in hydrogels; (C) characteristic length of hydrophobic association.

We perform XRD to probe the molecular arrangement of octyl side chains in PVA-C8-based hydrogel in Figure S4A. The characteristic length of the peaks in the X-ray diffraction (XRD) patterns can characterize the backbone-to-backbone distance (d_1) and side-chain spacing (d_2) of side alkyl chains for the polymer systems with alkyl side chains as schemed in Figure S4B . Based on the equation of (2(d1 or d2)sinθ=0.154 nm, where 0.154 nm is the wavelength of X-ray used for XRD collection), the average value of d1 and d2 can be estimated as shown in Figure S4C.

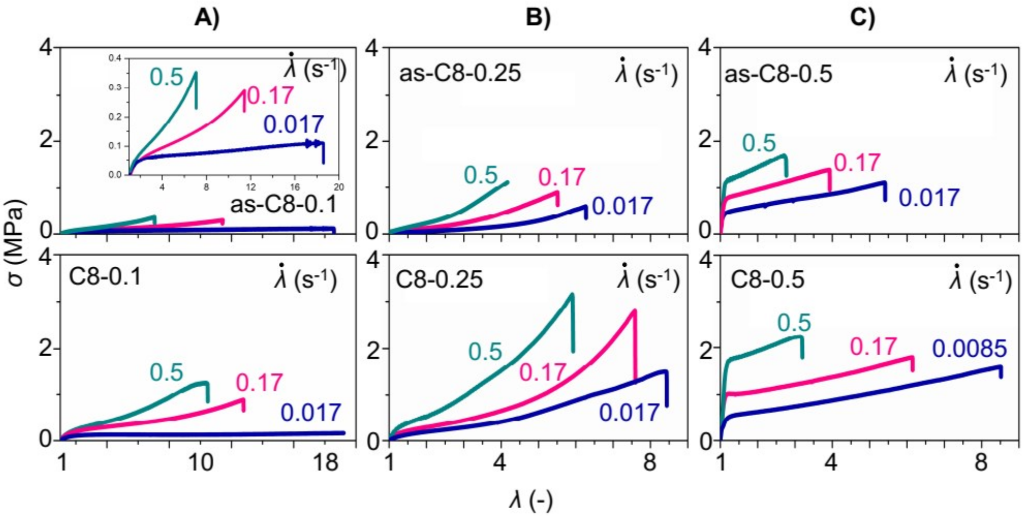

Figure S5. Representative stress-elongation curves of as-C8-DS (top) and C8-DS (bottom) series of stretch curves at different elongation rates for different DS (A) 0.1; (B) 0.25; and (C) 0.5.

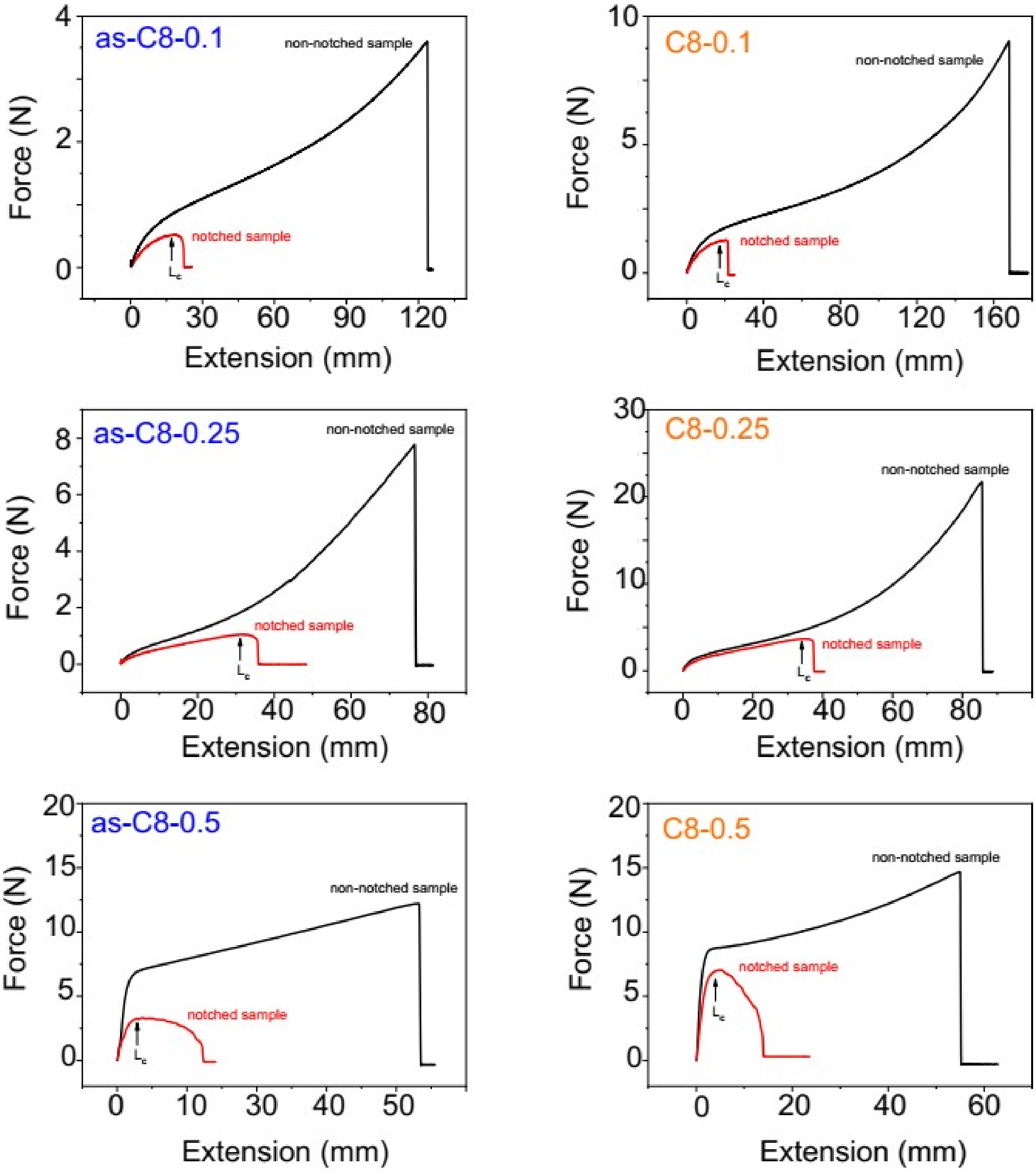

Figure S6. Typical force-extension curves for single-edge notched and non-notched PVA-C8 based hydrogels for the calculation of fracture energy (tensile rate=0.17 s^{-1} and 24 ^{o}C).

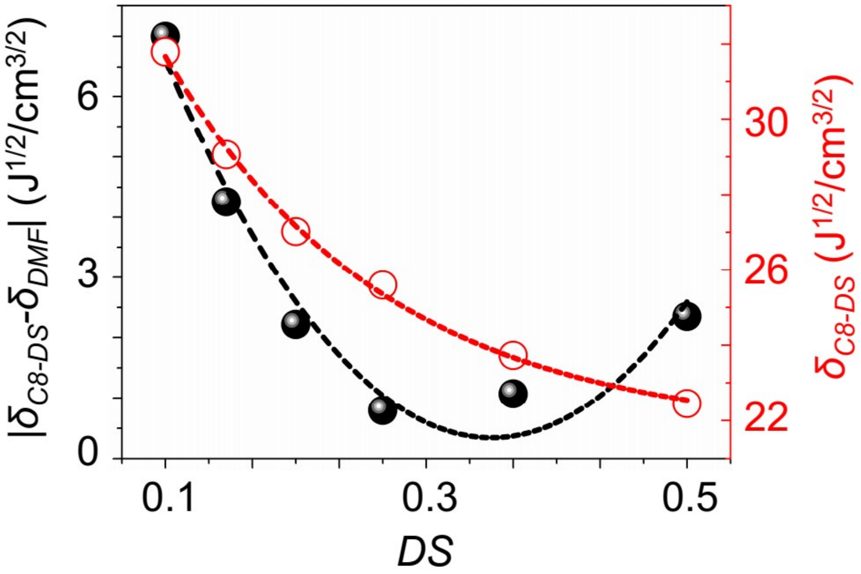

Figure S7. The calculated solubility parameter of PVA-C8-DS ($\delta_{C8\text{-}DS}$) (black sphere) and the difference between the solubility parameter (δ_{DMF}) of DMF solvent and $\delta_{C8\text{-}DS}$ (red circle).

On one hand, similar to the brush and comb polymers, larger DS in PVA-C8-DS leads to larger intrinsic rigidity. On the other hand, the gelation via solvent-nonsolvent exchange process may mainly enhance the inter-chain interactions to form crosslinking knots due to the increase of the solvent interaction parameter-χ. Therefore, the intra-chain interaction of polymer may depend on the conformation of the PVA-C8-DS polymer in the solution, which is primarily affected by the solubility parameters of polymers at a given solvent. By using molar attraction method, the solubility parameter of PVA-C8-DS polymer can be estimated and summarized in Figure S7. Generally, when the DS increases from 0.1 to 0.25, the difference between the solubility parameter of the PVA-C8-DS and the DMF solvent is reduced from 7 to 0.74, and then further increases the DS, resulting in the increased difference in solubility parameters from 0.74 to 2.5. According to solubility parameter close principle, PVA-C8-0.25 and PVA-C8-0.35 in DMF can be relatively more extended than the other PVA-C8-DS. The intra-chain interaction in extended conformation should be minimized. Thus, as DS increases, the rigidity of PVA-C8-DS naturally increases. However, the intra-chain interaction undergoes of PVA-C8-0.1 should be higher than PVA-C8-0.25 and PVA-C8-0.35. The net effect is that the polymer chains in hydrogels with DS=0.25 and 0.35 show highest flexibility.

References for ESI

1. S. Wang, S. Li and L. Gao, *ACS Appl. Mater. Interface*, 2019, **11**, 43622-43630.
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