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## **Supporting Information**

## Synergic Influences of Network Topologies and Associative Interactions on Microstructures and Bulk Performances of Hydrogels

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**Figure S1.** Absorbance spectra of DMSO solutions used for soaking the as-prepared organogels of GN-2-1.5 and IPN-2-1.5 until reaching the swelling equilibrium at room temperature. The organogels with a mass of 3 g is swelled in 10 mL DMSO for 7 days; the soaking solution is used for the measurement of UV-vis spectrum. DMSO solution of 1 wt% PNIPAm is also measured for comparison. The black line represents the characteristic absorbance peak of PNIPAm.



**Figure S2.** Tensile stress-strain curves (a) and corresponding mechanical parameters (b) of SN-2-1.5, IPN-2-1.5, and GN-2-1.5 gels with the same water content of 40 wt%. The water content of SN-2-1.5 and IPN-2-1.5 gels is controlled by solvent evaporation in air at room temperature. Tensile tests are performed to the gels at room temperature with a constant stretching rate of 100 mm/min.



Figure S3. Frequency-sweep spectra of storage modulus G', loss modulus G'', and loss factor  $\tan \delta$  of equilibrated SN-2-1.5 gel (a), IPN-2-1.5 gel (b), and GN-2-1.5 gel (c) at room temperature.



**Figure S4.** Tensile stress-strain curves (a,c,e) and corresponding mechanical parameters (b,d,f) of equilibrated SN-2-1.5 gel (a,b), IPN-2-1.5 gel (c,d), and GN-2-1.5 gel (e,f). Tensile tests are performed to the gel samples at room temperature with different stretching rate.



**Figure S5.** TEM image (a) and corresponding element distributions of carbon (b), nitrogen (c), and oxygen (d) of the IPN-2-1.5 gel. The sample is observed after a freeze-drying process.



**Figure S6.** SEM images of the equilibrated gel of IPN-2-1.5 before (a) and after (b) three cycles of heating-cooling treatment. The gel is incubated in 60 °C water bath for 12 h and then in 4 °C water bath for another 12 h; this process is repeated for three times, and the gel is freeze-dried before the SEM observation. In contrast, the gel sample before the heat-treatment is directly freeze-dried for SEM observation.



**Figure S7.** (a,b) DSC thermograms of the s-IPN gels (a) and GN gels (b) with constant  $C_a$  (2 M) yet different  $C_n$ . The gel samples are heated from 20 °C to 80 °C with a heating rate of 5 °C/min. (c,d) Corresponding transition temperature  $T_{tr}$  noted in the thermograms as a function of  $C_n$  (c) and the water content q (d) of the s-IPN gels and GN gels.



**Figure S8.** Variation of the swelling ratio in length of GN-2-1.5 hydrogel during the cyclic heating-cooling process. The gel is repeatedly incubated in 75 °C water bath for 12 h and then in 4 °C water bath for another 12 h for three cycles to examine the reversibility of the thermoresponse of the gel. Error bar represents the standard deviation of the mean.



**Figure S9.** SEM images of IPN-2-1.5 gel with a mechanical strain of 200%. The samples are prapred by freeze-drying of the stretched gel before the SEM observation. The arrows show the stretching direction of the gel.



**Figure S10.** Tensile stress-strain curves (a,c) and corresponding mechanical parameters (b,d) of the equilibrated s-IPN gels and GN gels with interpenetrated PNIPAm chains or grafted PNIPAm segments that have different degree of polymerization (DP). The gels are prepared with constant feeding concentration of AAc ( $C_a = 2$  M) and fixed density (0.04 M) of linear or grafted PNIPAm chains, while varying DP and the feeding concentration of NIPAm ( $C_n$ ). Water content (q) of the hydrogels is also presented in (b,d). Error bar represents the standard deviation of the mean.



**Figure S11.** Tensile stress-strain curves (a,c) and corresponding mechanical parameters (b,d) of the equilibrated s-IPN gels and GN gels with interpenetrated PNIPAm chains or grafted PNIPAm segments that have different degree of polymerization (DP). The gels are prepared with constant feeding concentration of AAc ( $C_a = 2$  M) and NIPAm ( $C_n = 1$  M) of linear or grafted PNIPAm chains, while varying DP and the density of linear or grafted PNIPAm chains. Water content (q) of the hydrogels is also presented in (b,d). Error bar represents the standard deviation of the mean.



**Figure S12.** Appearance of PNIPAm-OH aqueous during heating at 60 °C (above the LCST of PNIPAm).



**Figure S13.** Molecular weight distributions of PNIPAm-OH with different degree of polymerization (DP) measured by size exclusion chromatography.



Figure S14. <sup>1</sup>H NMR spectrum of PNIPAm-OH by using  $D_2O$  (4.70 ppm) as the deuterated reagent.



Figure S15. <sup>1</sup>H NMR spectrum of PNIPAm-macromonomer by using  $D_2O$  (4.70 ppm) as the deuterated reagent.



Figure S16. FTIR spectrum of PNIPAm-macromonomer.

Scheme S1. Synthesis of PNIPAm-OH and PNIPAm-macromonomer.



Table S1. Elemental analysis result of the equilibrated SN-2-1.5, IPN-2-1.5, and GN-2-1.5 gels.

Hydrogel	N (wt%)	C (wt%)	H (wt%)	
SN-2-1.5	6.34±0.06	51.41±0.35	7.70±0.01	
IPN-2-1.5	6.61±0.13	50.28±0.04	7.73±0.03	
GN-2-1.5	6.42±0.08	51.91±0.47	7.90±0.01	
Theoretical	6.70	57.42	7.82	

**Table S2.** Elemental analysis result of equilibrated IPN-2-1.5 gel before and after incubation in 60 °C water for 12 h.

Hydrogel	N (wt%)	C (wt%)	H (wt%)
Before	6.61±0.13	50.28±0.04	7.73±0.03
After	6.65±0.11	48.32±0.11	7.35±0.03
Theoretical	6.70	57.42	7.82

DP	NIPAm (g)	HEBIB (µL)	Me <sub>6</sub> TREN (µL)	CuBr (mg)	$M_{th}^{a}$ (g·mol <sup>-1</sup> )	$M \frac{b}{tr}$ (g·mol <sup>-1</sup> )	Polymer dispersity index
15	2.14	181	130	70	1908	1831	1.21
20	2.85	181	130	70	2474	2368	1.19
25	3.56	181	130	70	3040	3003	1.18

**Table S3.** Recipes of precursor solutions for the synthesis of PNIPAm-OH with different degree of polymerization (DP).

<sup>*a*</sup> The theoretical number-average molecular weight of PNIPAm-OH. <sup>*b*</sup> The measured numberaverage molecular weight of PNIPAm-OH.