Electronic Supplementary Information

Structure-Property Correlation of Hydrogels Obtained via Radical Polymerization Using Central Cores of Multiarm Star Polymers as Crosslinkers

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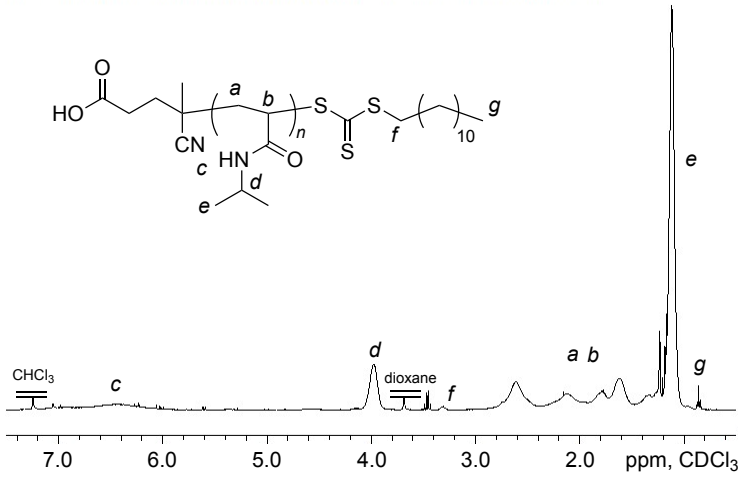

Fig. S1 Typical ^{1}H NMR spectrum of linear PNIPAAm (**LP$_{50}$**) obtained by RAFT polymerization. The DP_n and M_n were calculated from the integral ratio of peaks *d* and *g*. Reaction conditions: see Table 1.

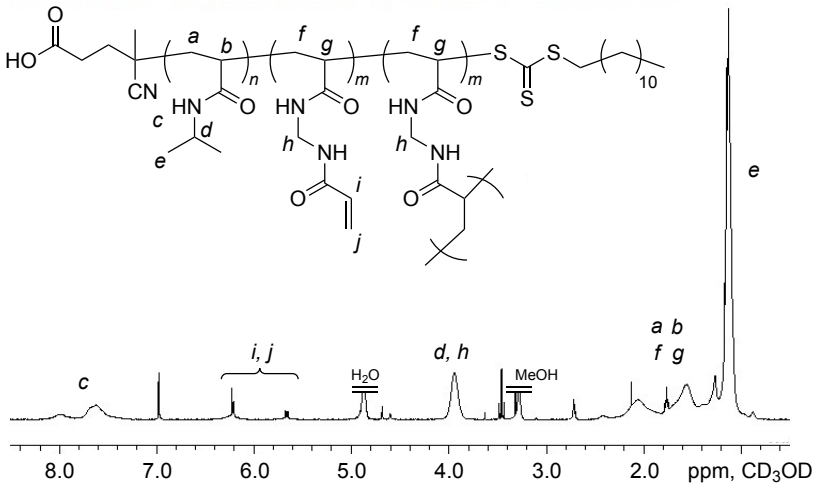

Fig. S2 Typical ^{1}H NMR spectrum of star PNIPAAm (**SP$_{50}$**) obtained by RAFT polymerization. The ratio of the unreacted vinyl groups was calculated from the integral ratio of peaks *i* and *j*. Reaction conditions: see Table 2.

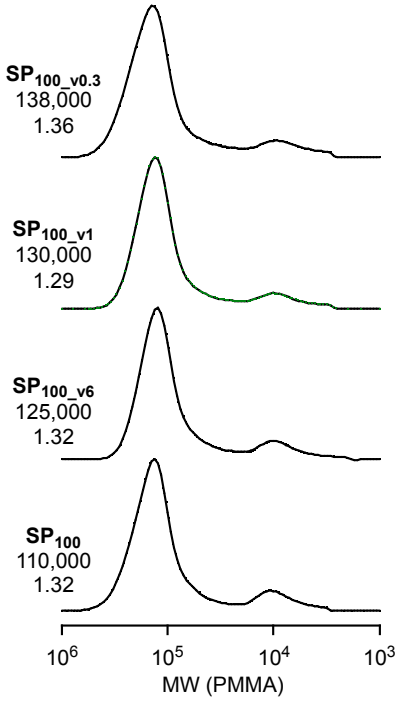

Fig. S3 SEC curves of star PNIPAAms with different amount of unreacted vinyl groups in the core (**SP$_{100_v0.3}$**, **SP$_{100_v1}$**, **SP$_{100_v6}$**, and **SP$_{100}$**). Reaction conditions: see Table 2.

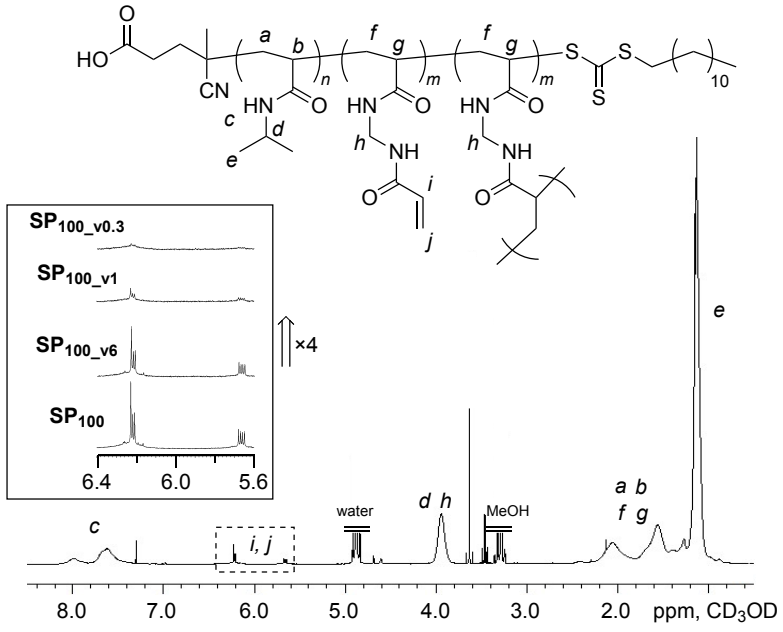

Fig. S4 ^{1}H NMR spectrum of **SP$_{100}$**. The inset shows the spectra in range of 6.4-5.6 ppm attributable to vinyl bonds in the core of star PNIPAAms (**SP$_{100_v0.3}$**, **SP$_{100_v1}$**, **SP$_{100_v6}$**, and **SP$_{100}$**).

Table S1. Results of uniaxial tensile tests of the gels prepared with star PNIPAAms with different amount of vinyl groups in the core.[a]

Entry	Young's modulus (kPa)	Breaking Stress (kPa)	Breaking Strain (%)
SG_{100}	8.81 ± 0.41	8.20 ± 0.87	204 ± 31
SG_{100_v6}	6.31 ± 0.7	8.04 ± 0.99	322 ± 84
SG_{100_v1}	2.70 ± 0.39	8.69 ± 0.16	420 ± 49

[a] Preparation conditions: see Table 3. The representative stress-strain curves are shown in Fig. 3.

Table S2. Analysis of SAXS profiles of the gels prepared with star PNIPAAms with different arm molecular weights.[a]

Gel	q_{max} (nm^{-1})	d_{star} (nm)[b]
$SG_{100\_2.5}$	0.314	20.0
$SG_{200\_2.5}$	0.307	20.5
$SG_{200\_5.0}$	0.295	21.3
$SG_{300\_2.5}$	0.310	20.3
$SG_{300\_7.5}$	0.298	21.1
$SG_{400\_2.5}$	0.307	20.5

[a] Preparation conditions: see Table 4. The SAXS profiles are shown in Fig. 5. [b] Calculated by the following equation: $d_{star} = 2\pi/q_{max}$.

Table S3. Results of uniaxial tensile tests of the gels prepared with star PNIPAAms with different arm molecular weights under the same weight fraction (2.5 wt%) of star crosslinkers.[a]

Gel	Young's Modulus (kPa)	Breaking Stress (kPa)	Breaking Strain (%)
$SG_{50\_2.5}$	11.9 ± 1.1	11.9 ± 2.7	187 ± 35
$SG_{100\_2.5}$	8.81 ± 0.41	8.20 ± 0.87	204 ± 31
$SG_{150\_2.5}$	9.74 ± 0.88	10.0 ± 1.5	465 ± 65
$SG_{200\_2.5}$	5.58 ± 0.63	12.7 ± 2.1	662 ± 80
$SG_{250\_2.5}$	5.71 ± 0.67	10.4 ± 1.7	738 ± 84
$SG_{300\_2.5}$	4.57 ± 0.45	12.7 ± 1.5	766 ± 110
$SG_{400\_2.5}$	5.00 ± 0.66	4.00 ± 0.67	219 ± 29

[a] Preparation conditions: see Table 4. The representative stress-strain curves are shown in Fig. 6a.

Table S4. Results of uniaxial tensile tests of the gels prepared with star PNIPAAms with different arm molecular weights under a similar molar concentration of star crosslinkers.[a]

Gel	Young's Modulus (kPa)	Breaking Stress (kPa)	Breaking Strain (%)
$SG_{50\_1.25}$	6.15 ± 0.17	8.18 ± 1.32	359 ± 61
$SG_{100\_2.5}$	8.81 ± 0.41	8.20 ± 0.87	204 ± 31
$SG_{150\_3.75}$	16.1 ± 1.5	16.3 ± 2.1	398 ± 56
$SG_{200\_5.0}$	13.0 ± 1.1	11.2 ± 2.3	257 ± 56
$SG_{250\_6.25}$	10.4 ± 1.5	8.65 ± 1.76	210 ± 88
$SG_{300\_7.5}$	8.92 ± 0.72	2.64 ± 0.86	47.8 ± 16.2

[a] Preparation conditions: see Table 4. The representative stress-strain curves are shown in Fig. 6c.

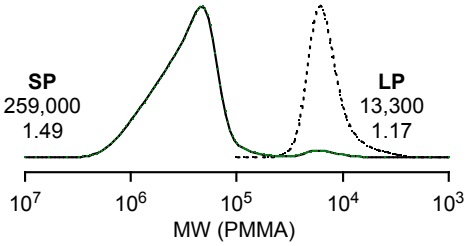

Fig. S5 SEC curves of star PNIPAAm (**SP**) employed for gel synthesis with a variety of AAm concentration and the linear PNIPAAm precursor (**LP**) obtained by RAFT polymerization. The preparation conditions were identical with **SP$_{150}$** and **LP$_{150}$** (**LP**: $DP_{n,\,NMR}$ = 163, $M_{n,\,NMR}$ = 18,900; **SP**: $R_{C=C}$ = 9.3%).

Table S5. Results of uniaxial tensile tests of the gels prepared with star PNIPAAms under various monomer concentrations.[a]

Gel	Young's Modulus (kPa)	Breaking Stress (kPa)	Breaking Strain (%)
SG$_{M20}$	46.0 ± 3.4	35.0 ± 4.8	508 ± 147
SG$_{M30}$	104 ± 5	91.5 ± 17.9	459 ± 90
SG$_{M40}$	218 ± 16	173 ± 17	368 ± 80

[a] Preparation conditions: see the caption of Fig. 8. The representative stress-strain curves are shown in Fig. 9.

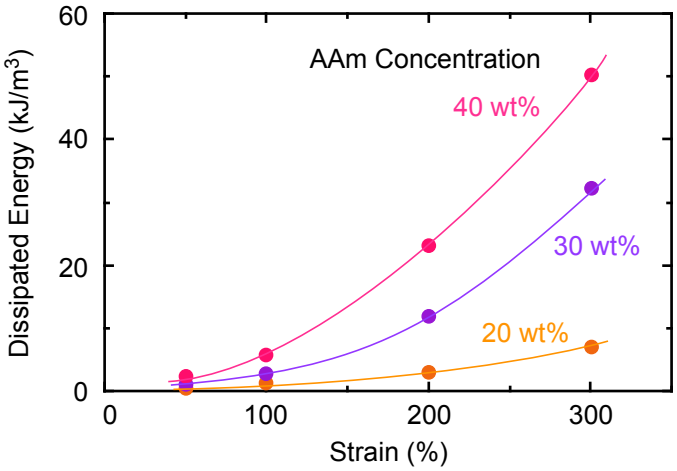

Fig. S6 Effect of AAm concentration on the dissipated energy during cyclic tensile tests of star-crosslinked gels at varying strain levels. The dissipated energies were calculated from the area of the hysteresis loop in the stress-strain curves shown in Fig. 10.