Electronic Supplementary Information

Thermoresponsive "Irreversible" Property Change of POSS-Crosslinked PNIPAAm Hydrogels

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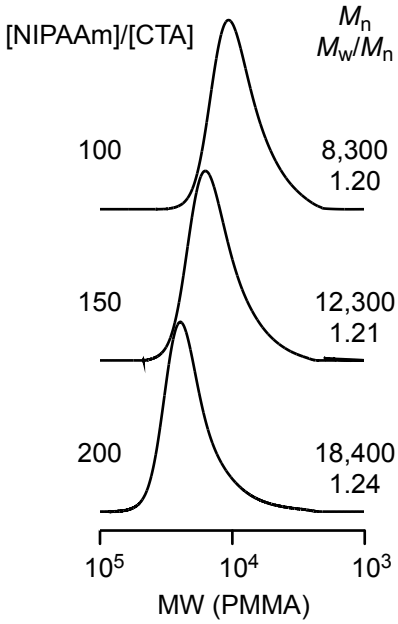

Fig. S1 SEC curves of PNIPAAm with various molecular weights obtained by RAFT polymerization. Reaction condition: [NIPAAm] = 2000 mM, [CTA]/[V-501] = 10 in 1,4-dioxane at 60 ˚C for 25 h.

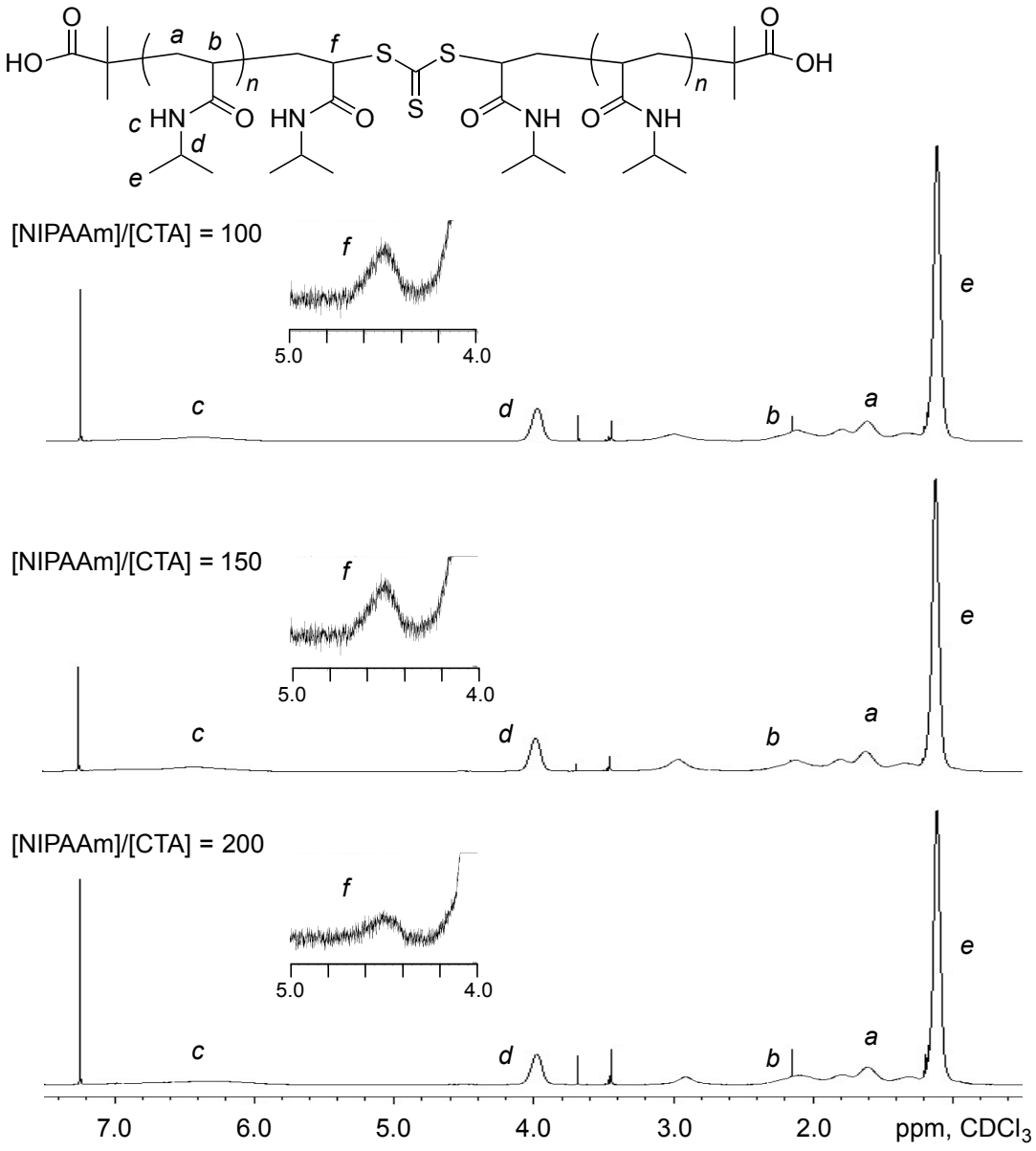

Fig. S2 ^{1}H NMR spectra of PNIPAAm obtained by RAFT polymerization. Reaction condition: see Fig. S1. DP_n and $M_{n,\,NMR}$ were calculated from the ratio of integral values between *d* and *f*.

Table S1. RAFT polymerization of NIPAAm.[a]

Entry	[NIPAAm]/[CTA]	Conv. (%)	$DP_{n,\,NMR}$	$M_{n,\,NMR}$	$M_w/M_{n,\,SEC}$
1	100	90	102	11,800	1.20
2	150	88	152	17,500	1.21
3	200	78	197	22,600	1.24

[a] Reaction conditions: see Fig. S1.

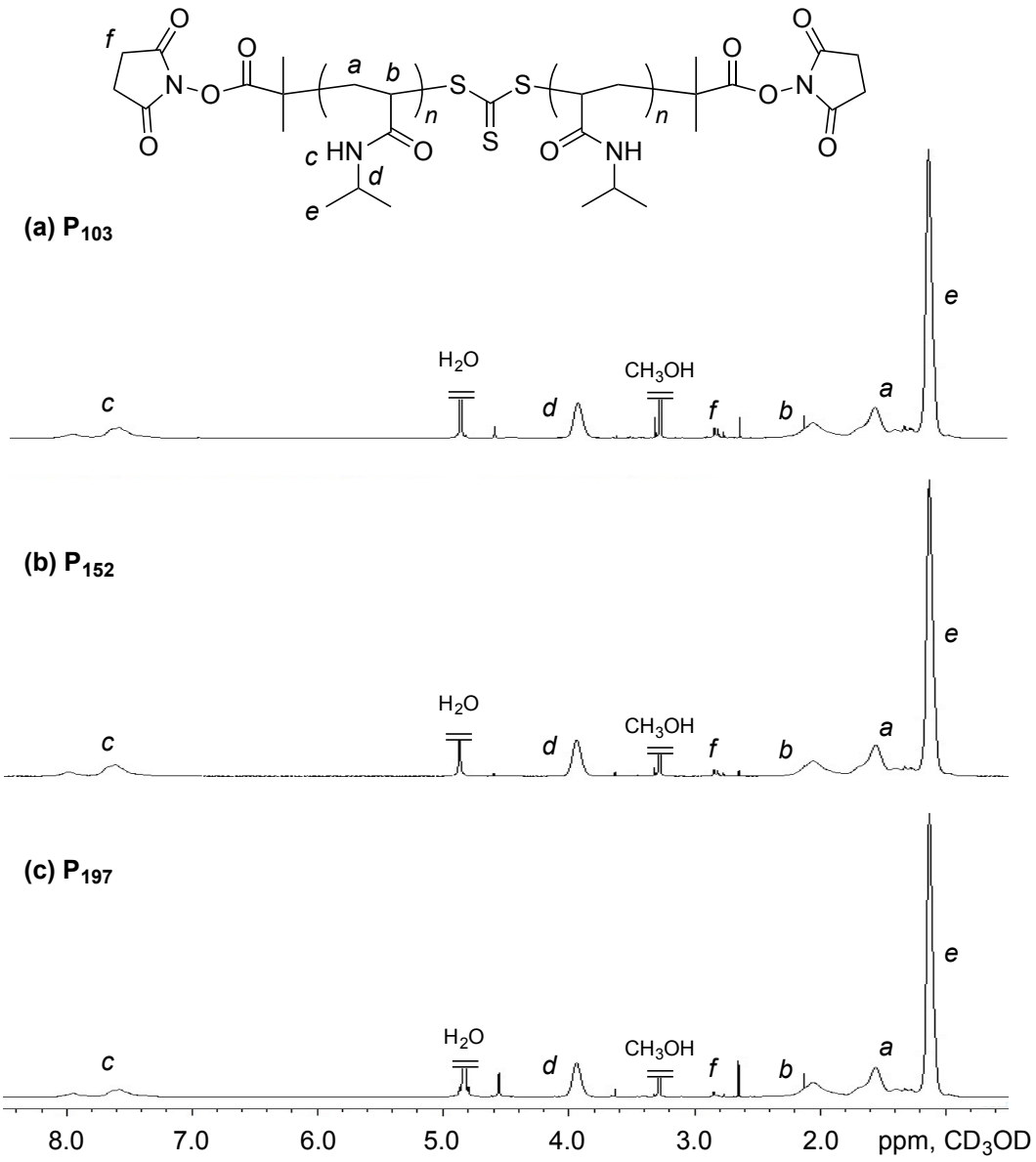

Fig. S3 ^{1}H NMR spectra of telechelic PNIPAAms obtained by esterification with NHS. Reaction condition: see Table 1.

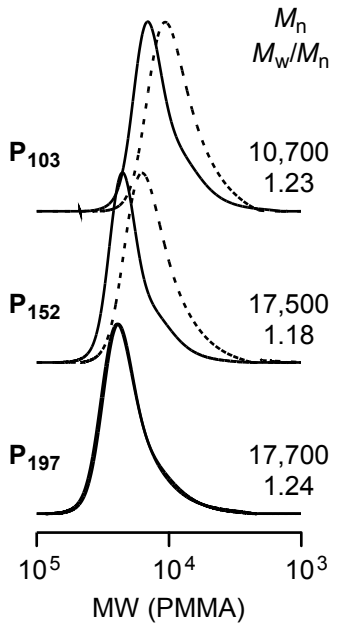

Fig. S4 SEC curves of telechelic PNIPAAms with activated ester end groups (dashed line: PNIPAAms with carboxy ends). Reaction condition: see Table 1.

Fig. S5 Appearance of a mixture of **POSS-CL** (12.5 mM) and TEA (2.4 M) in DMF/H_2O (H_2O: 22 vol%).

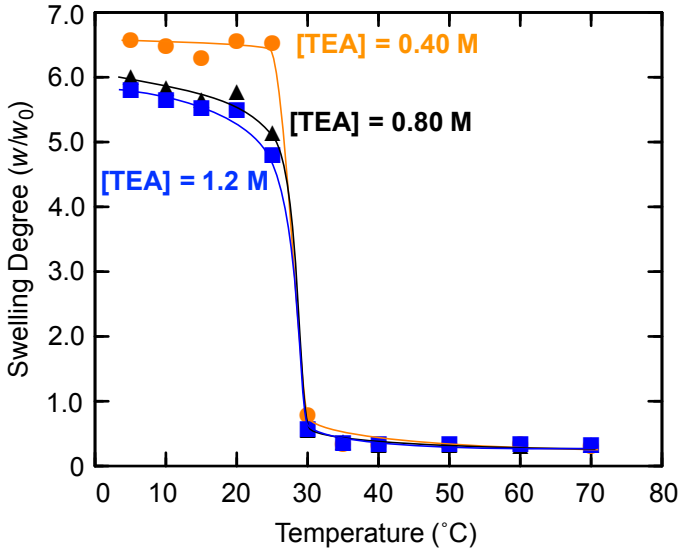

Fig. S6 Effect of feed TEA concentration on swelling behavior in water of POSS-crosslinked PNIPAAm gels. Reaction condition: see Fig. 3.

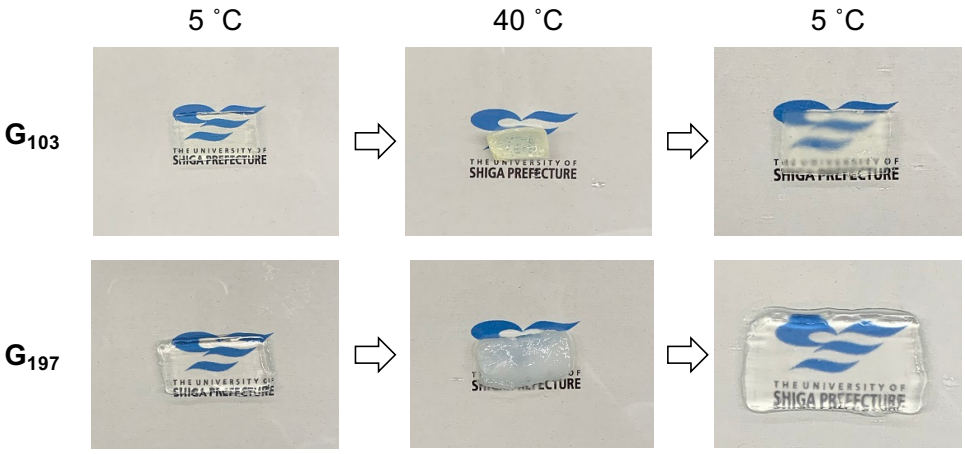

Fig. S7 Appearance of POSS-crosslinked PNIPAAm gels prepared from prepolymers with different molecular weights against heating/cooling cycle in water.

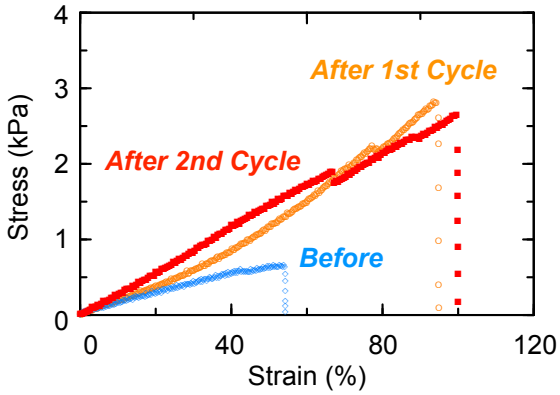

Fig. S8 Representative stress-strain curve obtained by uniaxial tensile test of $\mathbf{G_{197}}$ after applying 2nd heating/cooling cycle (in red line; Young's modulus: 2.40 ± 0.31 kPa, breaking strain: 91 ± 12%). Blue and orange markers are corresponded to the data in Fig. 5c (before and after applying 1st heating/cooling cycle).

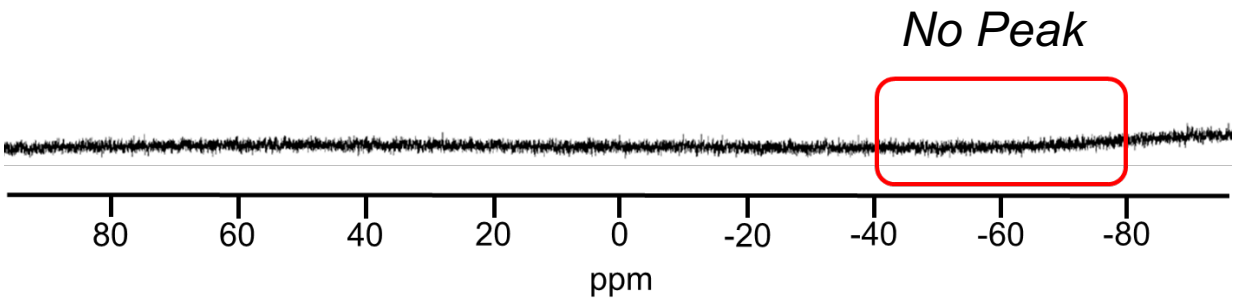

Fig. S9 ^{29}Si NMR spectrum of a degradation product from $\mathbf{G_{103}}$.

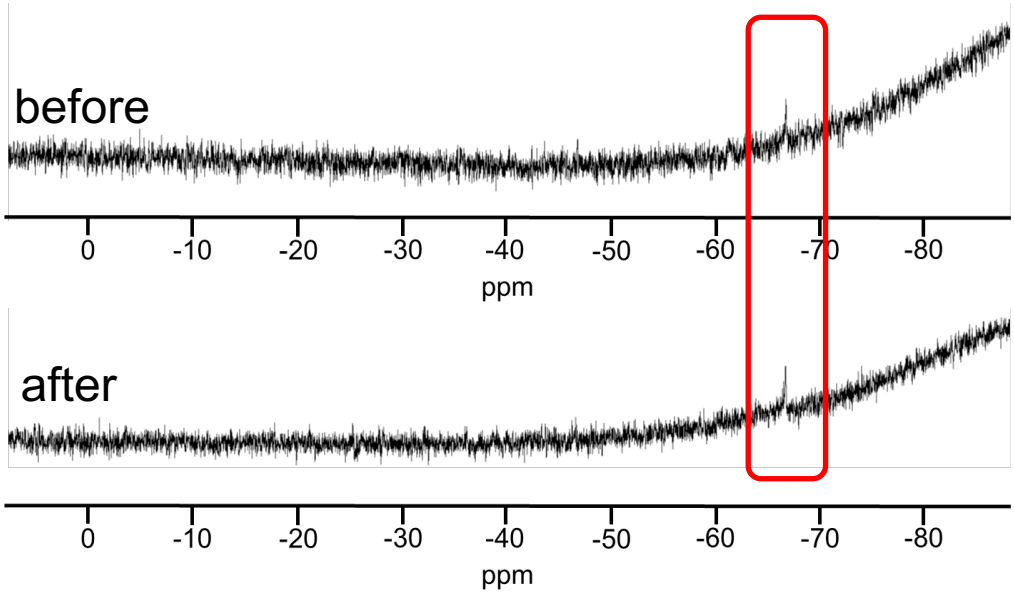

Fig. S10 ^{29}Si NMR spectrum of a degradation product from POSS-crosslinked gel prepared with short PNIPAAm (DP_n = 25) before and after applying a heating/cooling cycle.

Table S2. Normalized transmittance (T_n) of 500 nm light of gel films immersed in various solvents after a heating/cooling cycle.[a]

Sample	T_n (%)
Initial State	81.7 ± 6.0
After a heating/cooling cycle in H_2O	28.4 ± 1.9
DMSO	50.0 ± 0.8
DMF	41.2 ± 1.6
MeOH	43.0 ± 7.7
1,4-dioxane	20.1 ± 0.8
THF	24.5 ± 8.6

[a] T_n was normalized transmittance at the sample thickness of 3.0 mm. The value is calculated from the following equation: $T_n = T_{exp}^{d/3}$, where T_{exp} is the transmittance of 500 nm light of gel samples and d (mm) is the thickness of the sample.

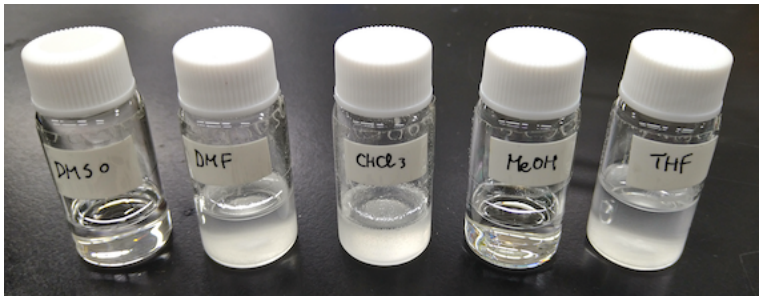

Fig. S11 Solubility of **POSS-CL** (0.50 wt%) in the presence of excess Et_3N (5 wt%) in various solvents: (from left to right) DMSO, DMF, chloroform, methanol, and THF. **POSS-CL** was well soluble in DMSO and methanol.

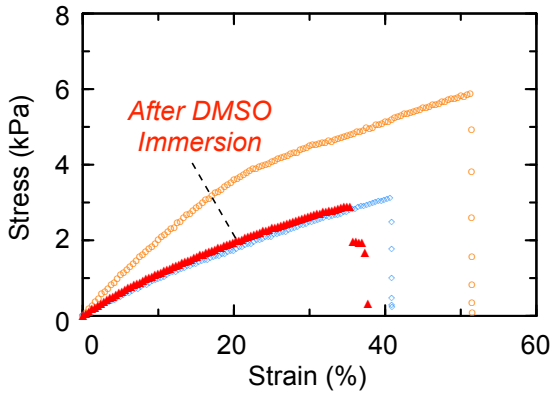

Fig. S12 Representative stress-strain curve obtained by uniaxial tensile test of $\mathbf{G_{103}}$ after applying a heating/cooling cycle and immersion in DMSO, followed by the solvent substitution into water (in red line; Young's modulus: 12.3 ± 3.1 kPa, breaking strain: 35 ± 16%). Blue and orange markers are corresponded to the data in Fig. 5a (before and after a heating/cooling cycle, respectively).