

Supporting Information

Hetero-Network Hydrogels Crosslinked with Silica Nanoparticles for Strategic Control of Thermal Responsive Property

M. Maria Rahman,^{a,b} Md. Ashraful Alam,^c Hirotaka Ihara,^{a,d} Makoto Takafuji^{a*}

^a *Department of Applied Chemistry and Biochemistry, Faculty of Advanced Science and Technology, Kumamoto University, 2-39-1 Kurokami, Chuo-ku, Kumamoto, Japan.*

^b *Department of Chemistry, Faculty of Science, Jagannath University, Dhaka-1100, Bangladesh.*

^c *Department of Applied Chemistry and Chemical Engineering, Faculty of Engineering and Technology, Noakhali Science and Technology University, Noakhali, Sonapur-3814, Bangladesh.*

^d *Okinawa College, National Institute of Technology, 905 Henoko, Nago, Okinawa, 905-2192, Japan.*

Corresponding author Email: takafuji@kumamoto-u.ac.jp

Figure S1

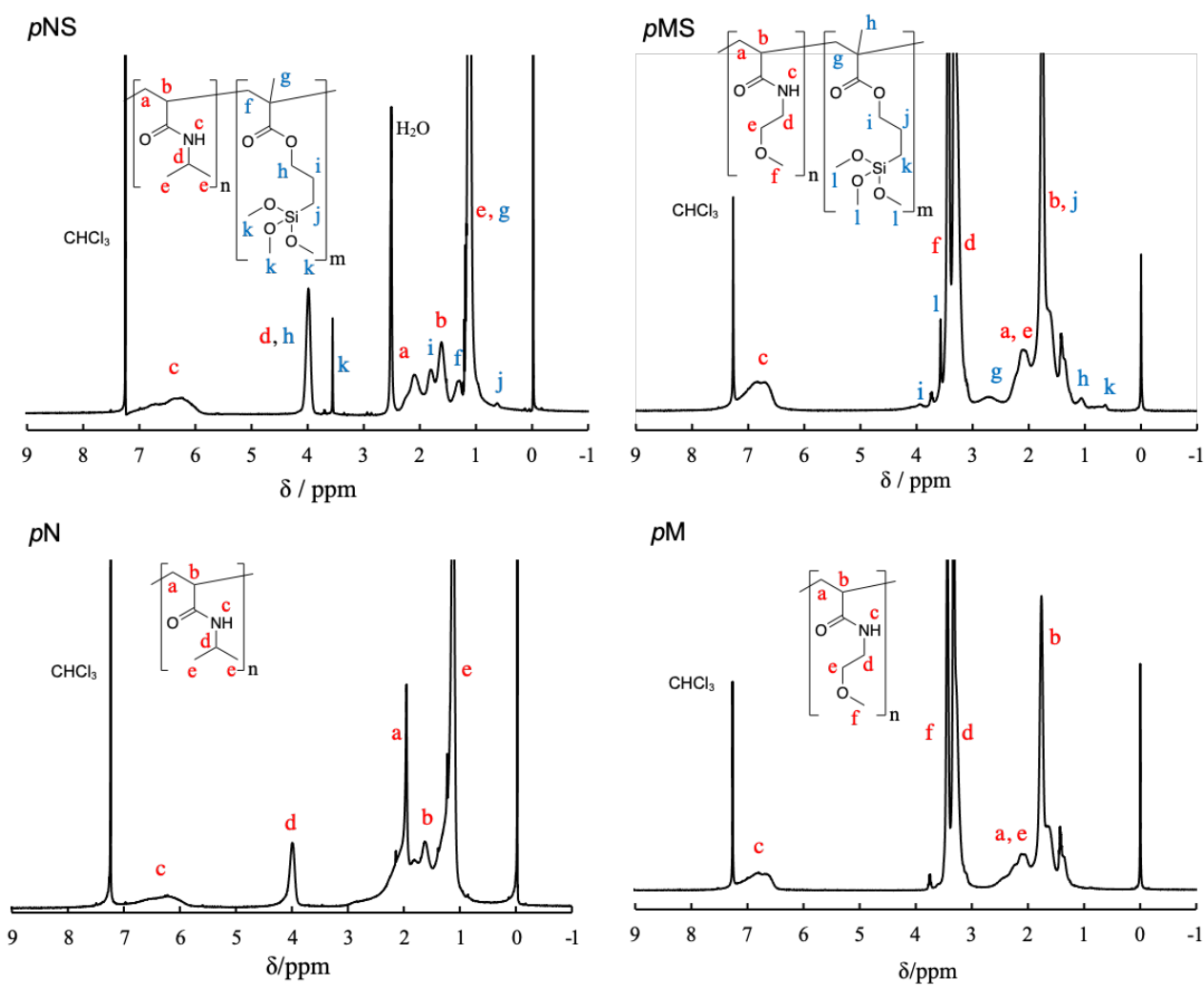


Fig. S1 ^1H NMR spectra of thermo-sensitive polymers (*pN*, *pM*) and co-polymers (*pNS*, *pMS*).

Figure S2

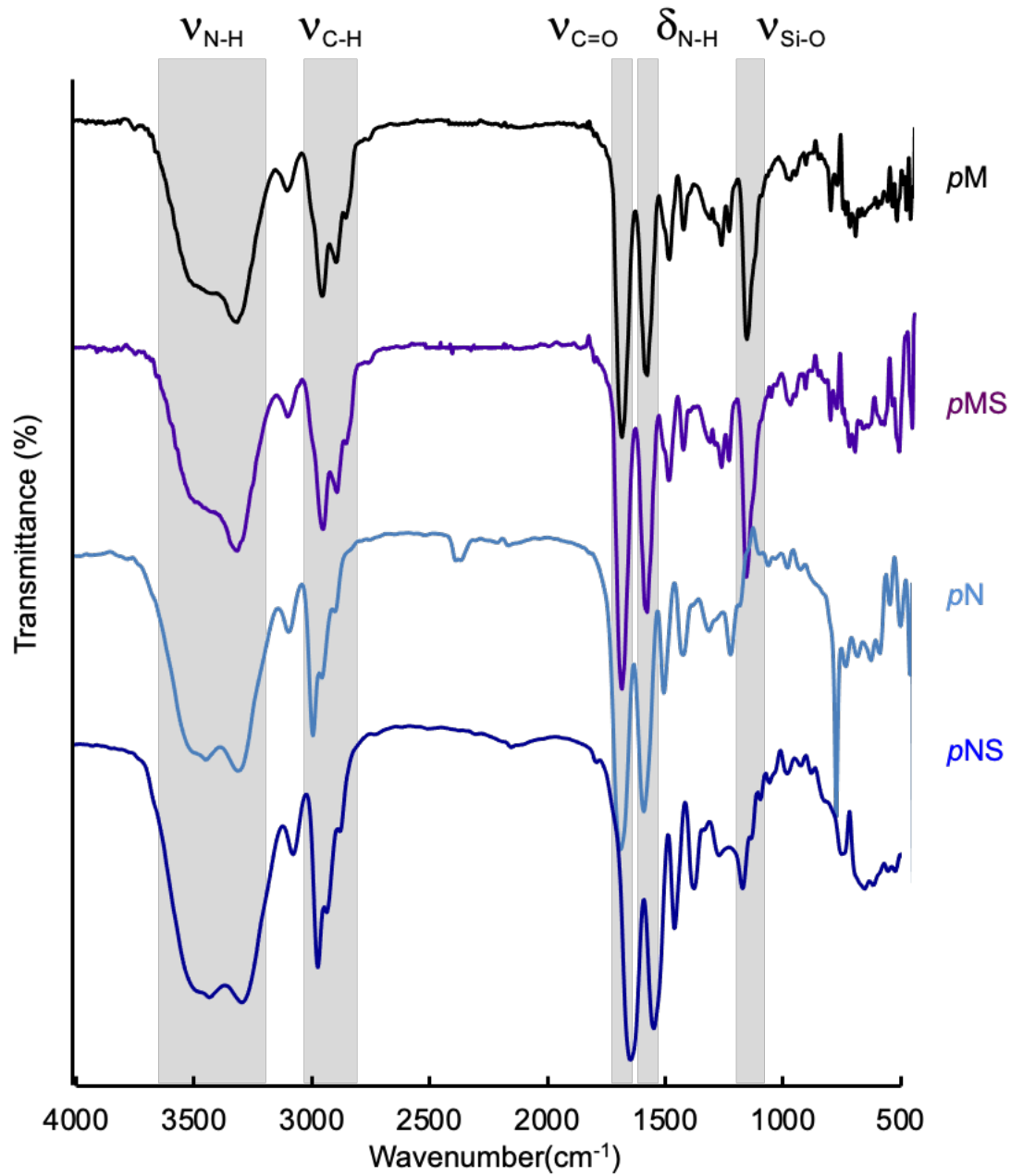


Fig. S2 FT-IR spectra of thermo-sensitive polymers (*pN*, *pM*) and co-polymers (*pNS*, *pMS*).

Table S1Table S1. Gelation time of aqueous solutions of *p*NS, *p*MS and mixture of *p*NS and *p*MS, with Si.^a

| Si (wt.%) | <i>p</i> NS (wt%) | | | | <i>p</i> MS (wt%) | | | | mixture of <i>p</i> NS and <i>p</i> MS ^b (wt%) | | | | <i>p</i> N (wt%) | <i>p</i> M (wt%) |
|-----------|-------------------|--------|--------|--------|-------------------|--------|--------|--------|---|--------|--------|--------|------------------|------------------|
| | 2 | 3 | 4 | 5 | 2 | 3 | 4 | 5 | 2 | 3 | 4 | 5 | | |
| 0.0 | NG | NG | NG | NG | NG | NG | NG | NG | NG | NG | NG | NG | | |
| 2.5 | 31.5 h | 28.4 h | 4.0 h | 90 min | 8.5 h | 6.0 h | 2.8 h | 50 min | 9.0 h | 7.2 h | 3.1h | 80 min | | |
| 5.0 | 8.2 h | 7.5 h | 2.1 h | 35 min | 6.2 h | 3.4 h | 65 min | 25 min | 7.2 h | 4.0 h | 76 min | 30 min | | |
| 10.0 | 5.8 h | 4.5 h | 70 min | 22 min | 4.0 h | 2.1 h | 30 min | 13 min | 4.6 h | 2.8 h | 40 min | 16 min | NG | NG |
| 15.0 | 2.7 h | 1.8 h | 45 min | 15 min | 2.2 h | 78 min | 20 min | 7 min | 2.0 h | 85 min | 28 min | 12 min | | |

^a Gelation time was measured at 25 °C by tube inversion method and Si nanoparticles size 12 nm (average diameter). NG indicates that no gelation was observed within 3 weeks. ^b Concentration were equal in mixture of *p*NS and *p*MS

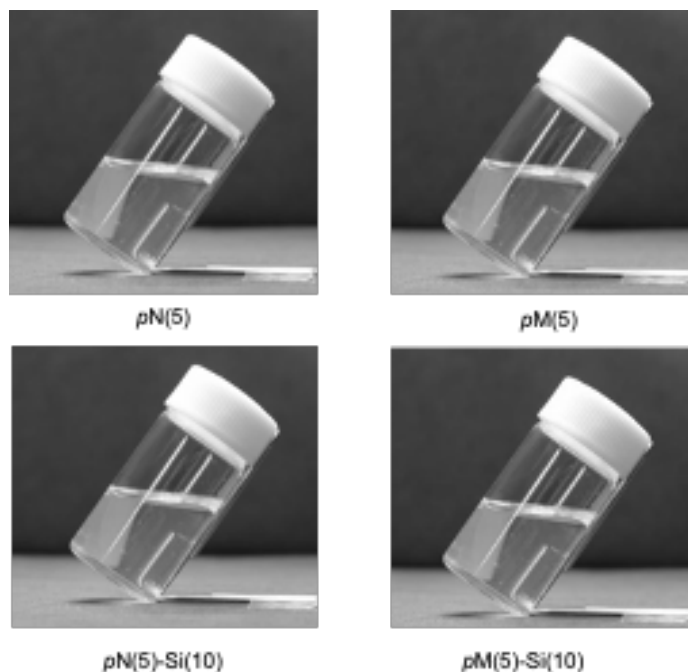
Figure S3**Fig. S3.** Photos of aqueous solution of homo-polymers (*p*N and *p*M) with and without Si suspension at 25 °C.

Figure S4

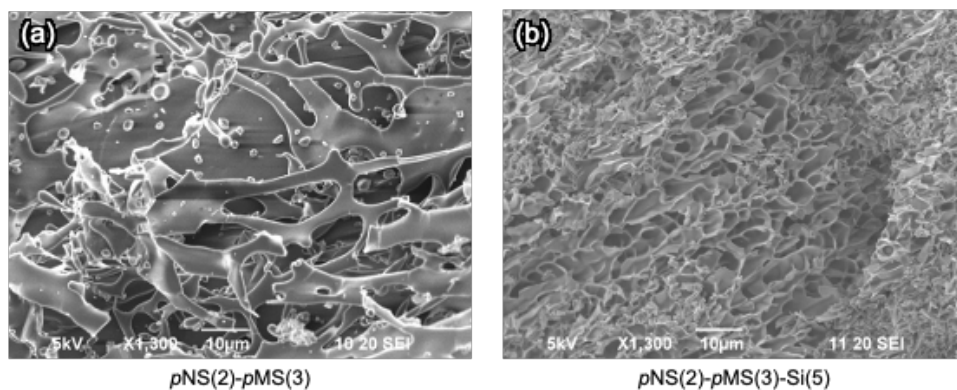


Fig. S4. FE-SEM microphotographs of cross-sectional morphology of freeze-dried (a) copolymers, $pNS(2)-pMS(3)$ solution and (b) $pNS(2)-pMS(3)-Si(5)$ hydrogel.

Figure S5

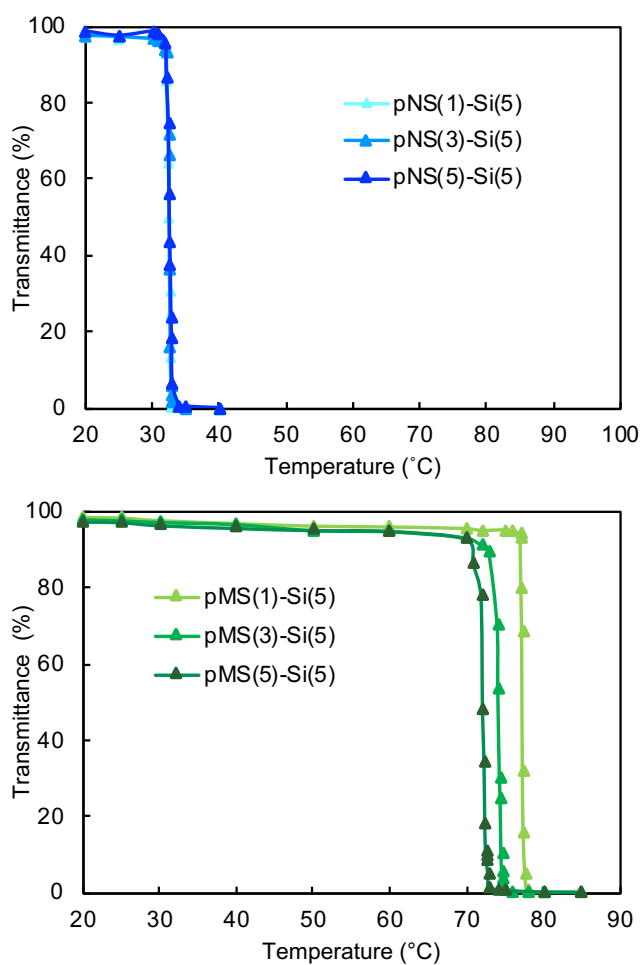


Fig. S5 Phase transition behavior of (a) $pNS-Si$ and (b) $pMS-Si$ in the cooling process.

Figure S6

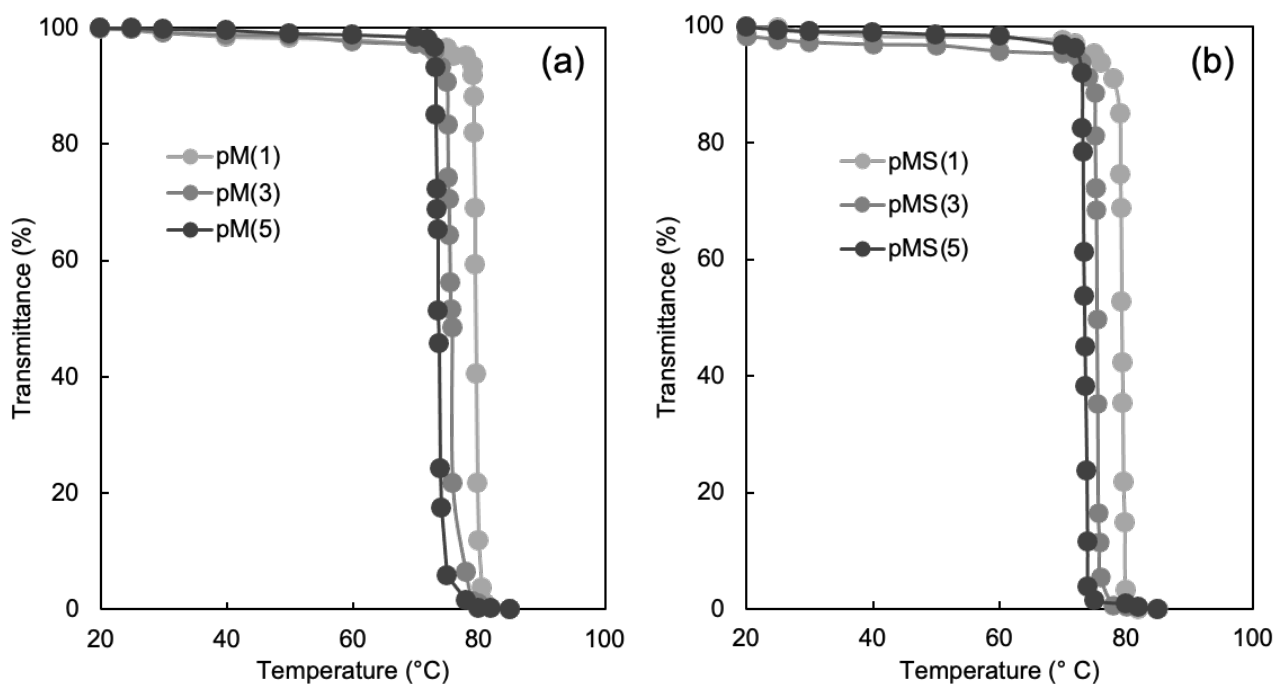


Fig. S6 Phase transition behavior of (a) *pM* and (b) *pMS* at different concentrations.

Figure S7

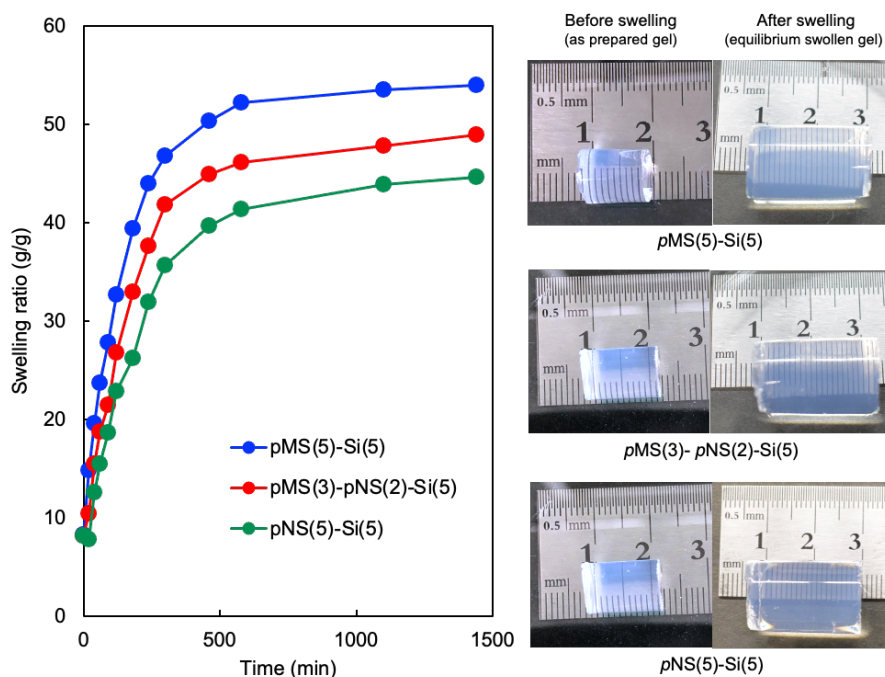


Fig. S7 Swelling profile of hydrogels in distilled water at 20 °C and photographs show the as prepared hydrogel and equilibrium swollen hydrogels at 20 °C after 24 h.

Figure S8

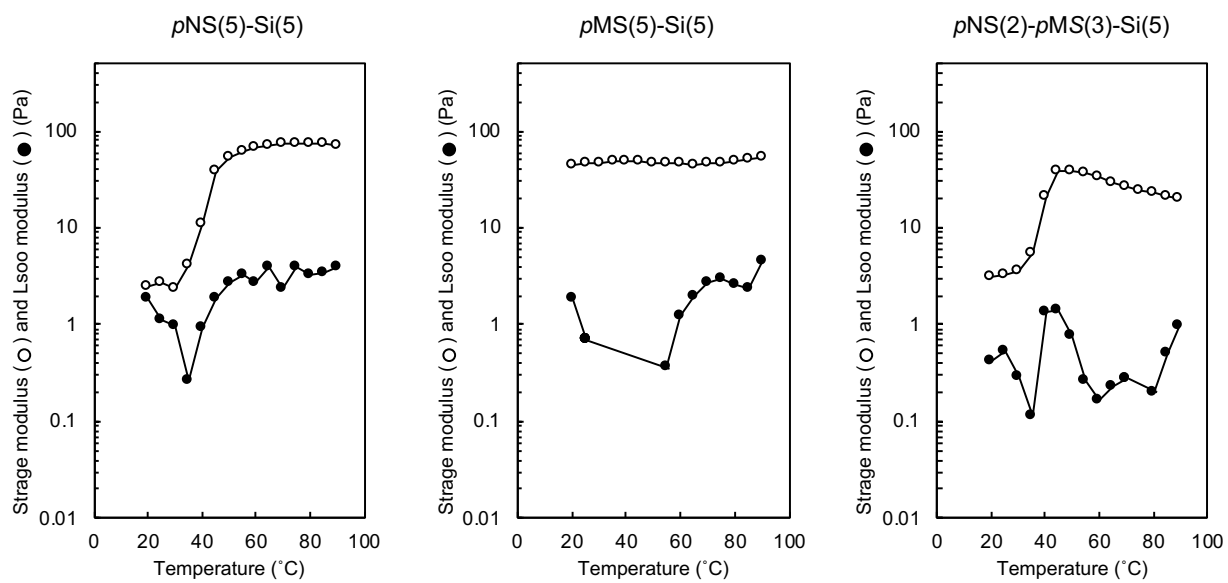


Fig. S8 Temperature dependencies of G' and G'' of the hetero-network hybrid hydrogels.