Electronic Supplementary Material (ESI) for Soft Matter

Supporting Information

Structure and Mechanical Response of Protein Hydrogels Reinforced by Block Copolymer Self-Assembly

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Table S1: MALDI-TOF of purified proteins

Protein	Expected Molar Mass (kDa)	Measured Molar Mass (kDa)
Proteins with near N- and C-terminal cysteines		
cys-C_{80}-cys	67.1	67.2
cys-$C_{20}(PC_{20})_2$-cys	61.1	60.9
cys-$C_{10}(PC_{10})_4$-cys	63.3	63.2
cys-$C_{10}(PC_{10})_2$-cys	37.0	37.0
Proteins with near C-terminal cysteines		
$C_{10}(PC_{10})_4$-cys	63.1	63.0

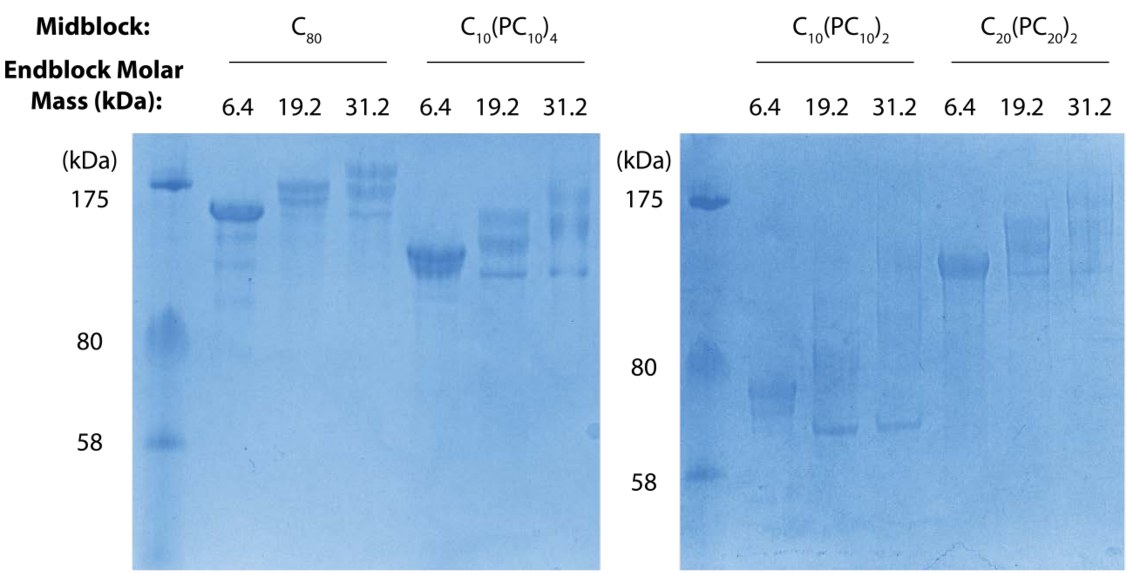

Figure S1: SDS-PAGE of hybrid block copolymers

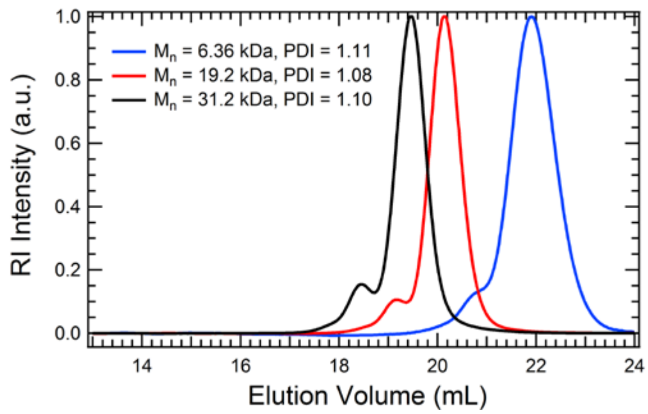

Figure S2: Gel permeation chromatograph of purified, maleimide-functionalized PNIPAM

Table S2: Effect of concentration on T_t (^oC) measured by DSC for gels in 100 mM phosphate, pH = 7.6

Block Copolymer	7.5%	15%	30%
$C_{20}(PC_{20})_2$ – 6.4 kDa	32.8	25.4	19.1
$C_{20}(PC_{20})_2$ – 19.2 kDa	29.5	26.0	21.1
$C_{20}(PC_{20})_2$ – 31.2 kDa	28.2	25.4	22.0

Table S3: Effect of triblock weight fraction (w_t) on T_t (^oC) measured by DSC for 30% (w/v) hydrogels in 100 mM phosphate, pH = 7.6

Block Copolymer	0.33	0.43	0.53
$C_{10}(PC_{10})_4$ – 18.4 kDa	32.8	25.4	19.1

SANS Modeling: SANS data were fit to the Percus-Yevick model for disordered hard spheres:

$$I(q) = K \cdot S(q)F(q) + C \tag{1}$$

The structure factor *S(q)* was computed using the formula:

$$S(q) = \frac{1}{1+24\,\eta\,G(2qR)} \tag{2}$$

$$G(x) = \frac{\alpha}{x^3}(\sin x - x\cos x) + \frac{\beta}{x^4}(2x\sin x + (2-x^2)\cos x - 2) + \frac{\gamma}{x^6}(-x^4\cos x + 4[(3x^2-6)\cos x + (x^3-6x)\sin x + 6]) \tag{3}$$

With the constants:

$$\alpha = \frac{(1+2\eta)^2}{(1-\eta)^4}, \beta = -6\eta\frac{(1+\eta/2)^2}{(1-\eta)^4}, \gamma = \frac{\eta}{2}\frac{(1+2\eta)^2}{(1-\eta)^4} \tag{4}$$

The form factor was computed for polydisperse spheres:

$$F(q) = \frac{\int P(r)\, f^2(q,r)dr}{\int P(r)dr} \tag{7}$$

Where the function *f(q,r)* for a single sphere is given by:

$$f(q,r) = \frac{4}{3}\pi r^3 \frac{3}{(qr)^3}(\sin qr - qr\cos qr) \tag{8}$$

And the lognormal probability distribution *P(r)* has the form:

$$P(r) = \sqrt{2\,\bar{\sigma}_p{}^2\pi}\;\exp\left(\frac{(-\ln r - \bar{r}_o)^2}{2\;\bar{\sigma}_p{}^2}\right) \tag{9}$$

The expected value (r_o) and standard deviation (σ_p) of the distribution are computed according to:

$$r_o = \exp\left(\bar{r}_o + \tfrac{1}{2}\,\bar{\sigma}_p{}^2\right) \qquad \text{and} \qquad \sigma_p = r_o\sqrt{\exp\,\bar{\sigma}_p{}^2 - 1}$$

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Table S4: Percus-Yevick fit parameters to SANS data from 30% (w/v) hydrogels at 35°C.

Sample	K	R_{HS} (nm)	η	r_o (nm)	σ_p (nm)	C
C_{80} – 6.4 kDa	2.8E-13 ± 8.6E-14	15.28 ± 0.06	0.455 ± 0.005	5.9 ± 0.9	1.5 ± 0.6	0.0096 ± 0.0308
C_{80} – 19.2 kDa	6.8E-13 ± 8.2E-4	22.11 ± 0.08	0.439 ± 0.005	12.9 ± 1.0	3.8 ± 0.8	0.0203 ± 0.1239
C_{80} – 31.2 kDa	4.8E-13 ± 3.9E-4	25.21 ± 0.10	0.361 ± 0.005	15.8 ± 0.8	3.6 ± 0.6	0.0434 ± 0.1717
$C_{20}(PC_{20})_2$ – 6.4 kDa	3.4E-12 ± 1.1e-12	15.01 ± 0.07	0.427 ± 0.005	5.7 ± 0.9	1.4 ± 0.5	0.0183 ± 0.0332
$C_{20}(PC_{20})_2$ – 19.2 kDa	7.3E-13 ± 7.4E-14	21.54 ± 0.07	0.432 ± 0.004	12.6 ± 0.7	3.0 ± 0.5	0.0319 ± 0.1018
$C_{20}(PC_{20})_2$ – 31.2 kDa	4.5E-13 ± 6.3E-14	27.21 ± 0.18	0.350 ± 0.008	15.7 ± 1.3	3.8 ± 0.9	0.0707 ± 0.3088
$C_{10}(PC_{10})_4$ – 6.4 kDa	2.7E-12 ± 3.7E-13	14.70 ± 0.04	0.395 ± 0.003	6.1 ± 0.4	1.2 ± 0.3	0.0453 ± 0.0131
$C_{10}(PC_{10})_4$ – 19.2 kDa	7.7E-13 ± 9.9E-14	21.87 ± 0.10	0.356 ± 0.005	11.8 ± 0.9	3.1 ± 0.7	0.0484 ± 0.1114
$C_{10}(PC_{10})_4$ – 31.2 kDa*	--	--	--	--	--	--
$C_{10}(PC_{10})_2$ – 6.4 kDa	1.74E-12 ±1.1E-12	13.34 ±0.05	0.479 ±0.005	5.2 ±1.5	1.7 ±0.9	0.7055 ±3.5284
$C_{10}(PC_{10})_2$ – 19.2 kDa	7.4E-13 ± 5.4E-14	20.43 ± 0.08	0.354 ± 0.005	13.5 ± 0.6	3.2 ± 0.5	0.0337 ± 0.0952
$C_{10}(PC_{10})_2$ – 31.2 kDa	7.1E-13 ± 5.1E-14	22.83 ± 0.11	0.317 ± 0.006	15.1 ± 0.6	3.4 ± 0.5	0.0633 ± 0.1653

**Fits not performed on this gel since cylindrical micelles were formed.*

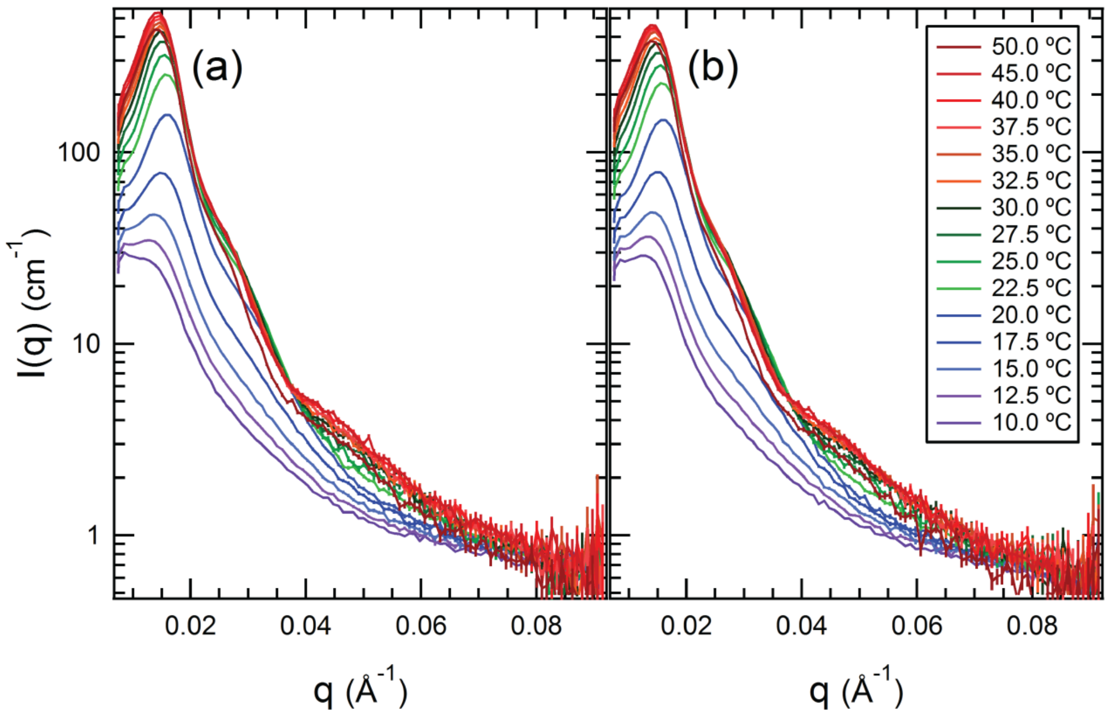

Figure S3: Thermal evolution of nanostructure measured by SANS for 30% (w/v) hydrogels with $C_{10}(PC_{10})_4$ midblocks and 18.4 kDa endblocks for (a) w_t = 0.43 and (b) w_t = 0.33

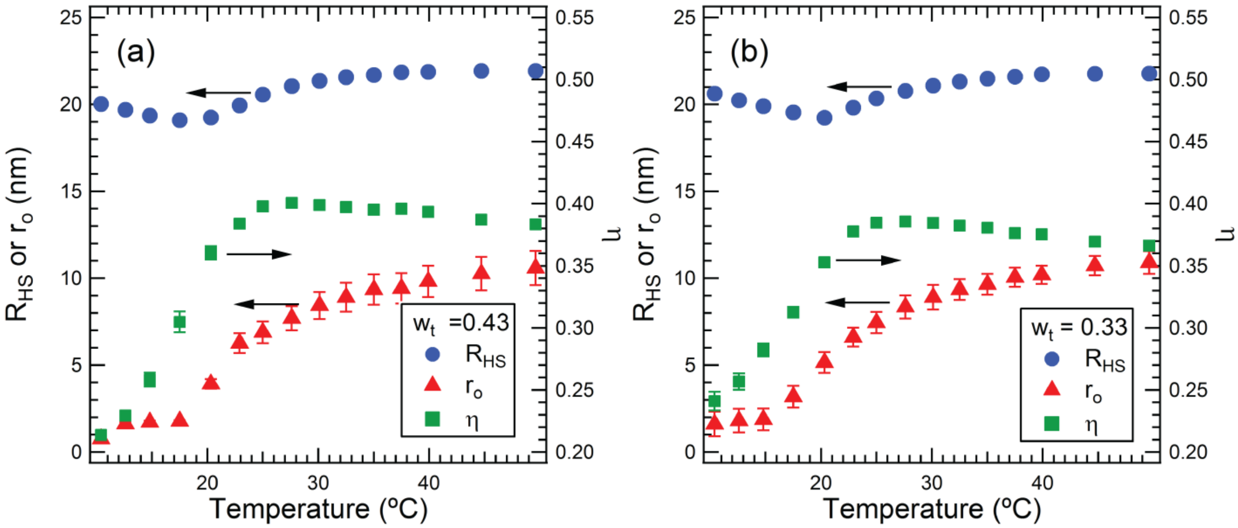

Figure S4: Percus-Yevick fit parameters for 30% (w/v) $C_{10}(PC_{10})_4$ gels with 18.4 kDa endblocks as a function of triblock weight fraction (w_t).

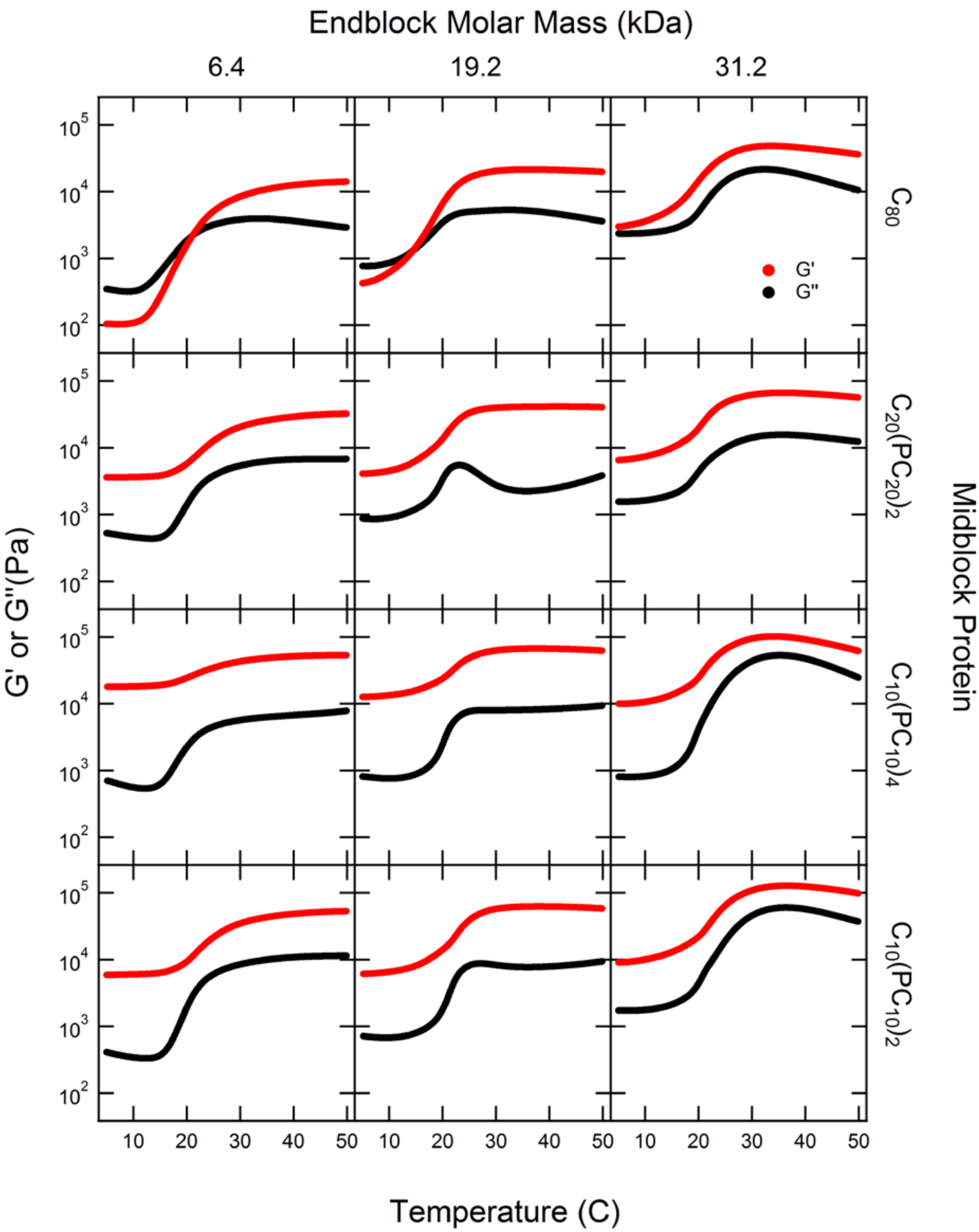

Figure S5: Temperature sweep linear oscillatory shear rheology showing G' and G'' during heating.

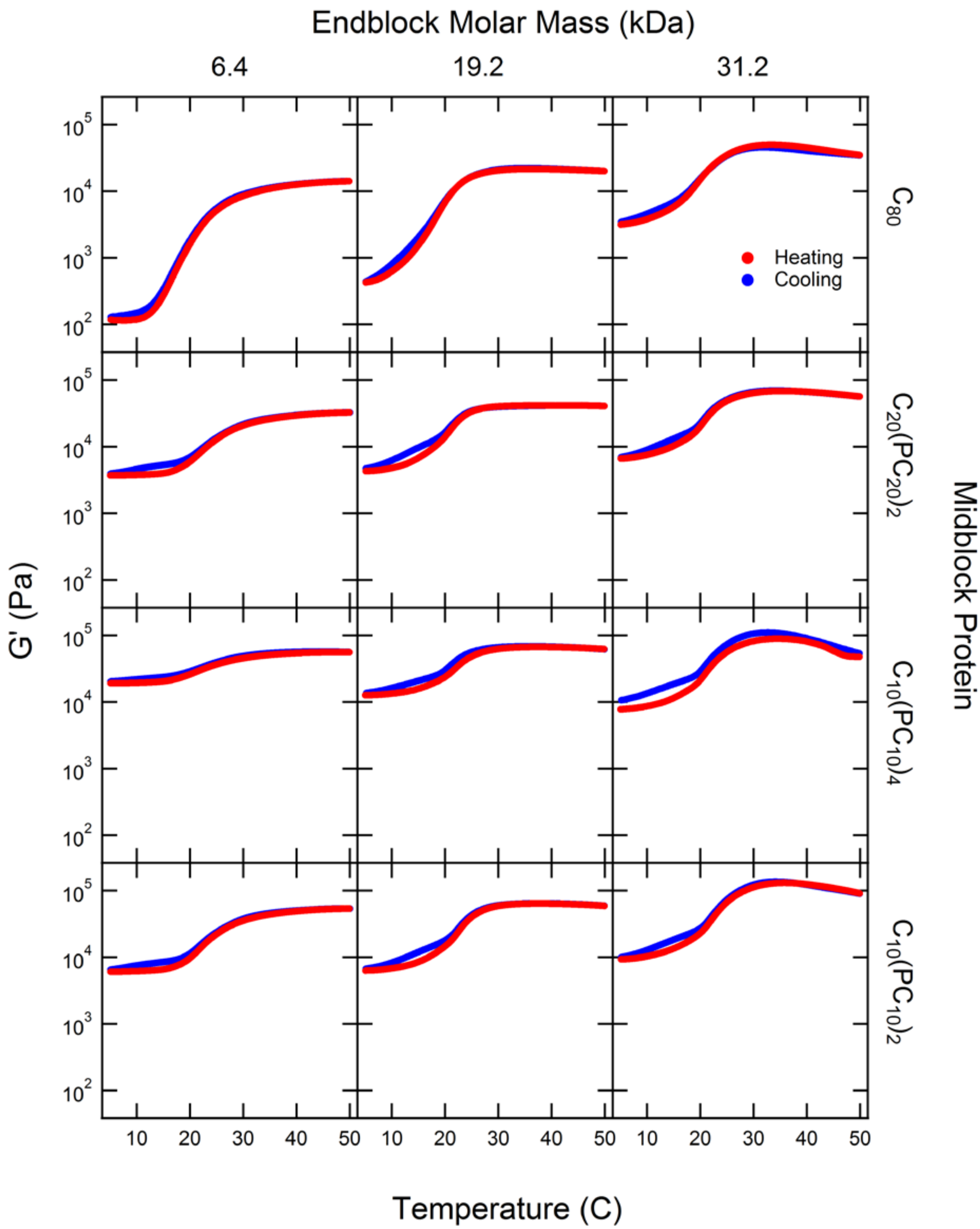

Figure S6: Temperature sweep linear oscillatory shear rheology showing G' upon heating and cooling.

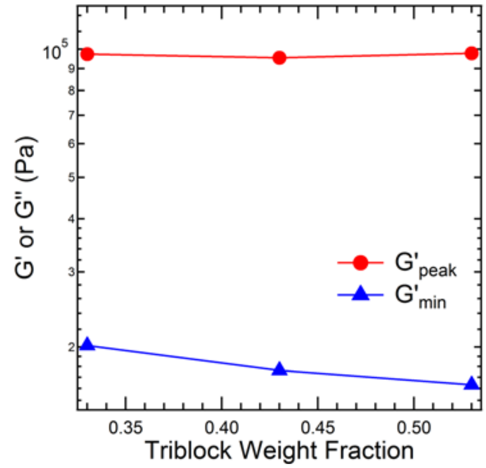

Figure S7: The peak (G'_{peak}) and minimum (G'_{min}) moduli from temperature sweep rheology for 30% (w/v) gels with $C_{10}(PC_{10})_4$ midblocks and 18.4 kDa endblocks, as a function of triblock weight fraction (w_t)