Electronic Supporting Information for:

Tuning the hydroxyl functionality of block copolymer worm gels modulates their thermoresponsive behavior

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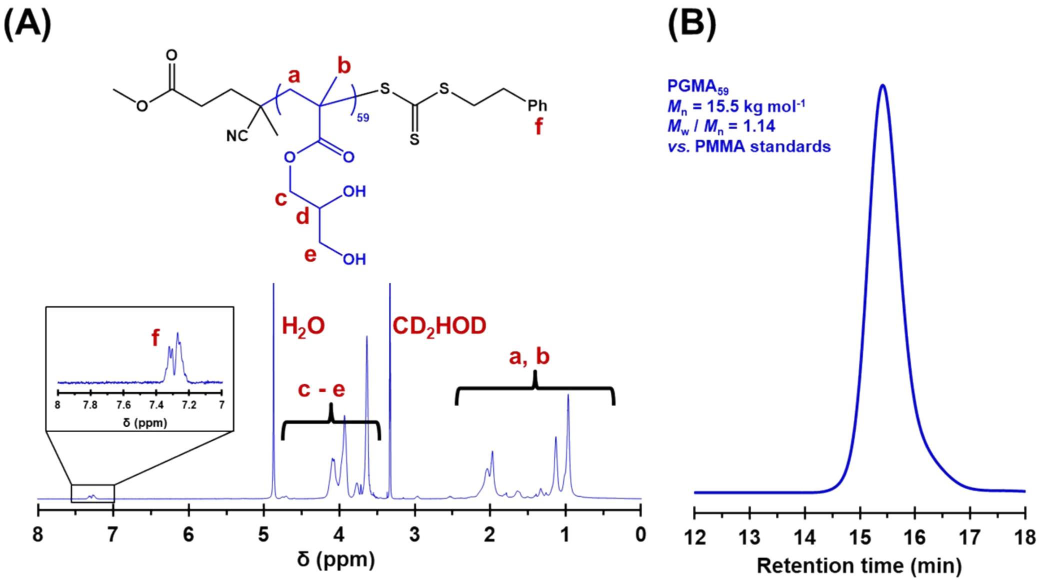

Figure S1. (A) Chemical structure and ^{1}H NMR spectrum for the $PGMA_{59}$ precursor. A mean DP of 59 was calculated by comparing the integrated aromatic signals at 7.2–7.4 ppm to that of the methacrylic backbone at 0.0–2.5 ppm. (B) DMF GPC curve obtained for this $PGMA_{59}$ precursor. Molecular weight data are expressed relative to poly(methyl methacrylate) calibration standards

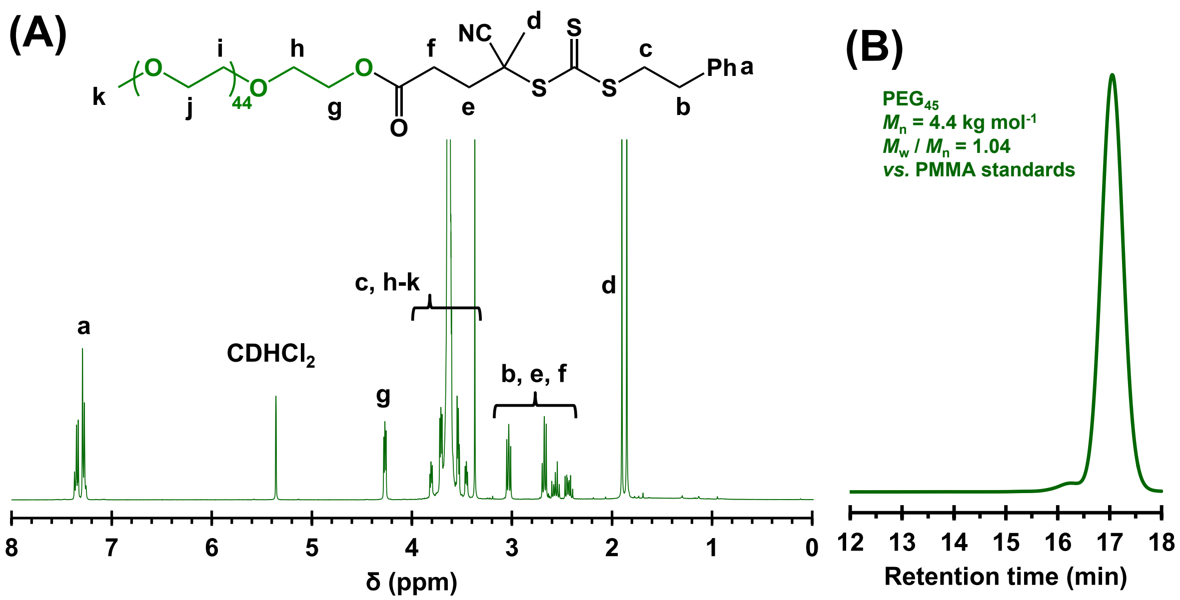

Figure S2. (A) Fully assigned [1]H NMR spectra recorded in CD_2Cl_2 at 298 K for the PEG_{45} precursor A mean degree of esterification of 94% was calculated by comparing the integrated aromatic proton signals (a) at 7.2–7.4 ppm against the PEG backbone (c, h-k) at 3.3-3.9 ppm. (B) THF GPC curve recorded for this PEG_{45} precursor. Molecular weight data are expressed relative to PMMA calibration standards.

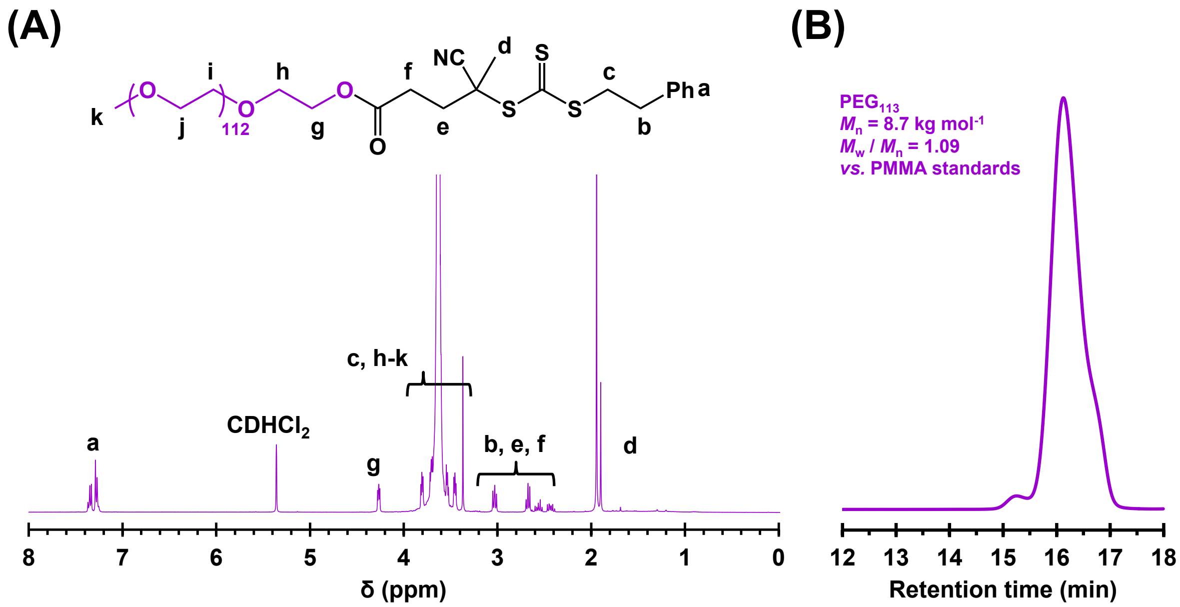

Figure S3. (A) Fully assigned [1]H NMR spectra recorded in CD_2Cl_2 at 298 K for the PEG_{113} precursor. A mean degree of esterification of 95% was calculated by comparing the integrated aromatic proton signals (a) at 7.2–7.4 ppm against the PEG backbone (c, h-k) at 3.3-3.9 ppm. (B) THF GPC curve recorded for this PEG_{113} precursor. Molecular weight data are expressed relative to PMMA calibration standards.

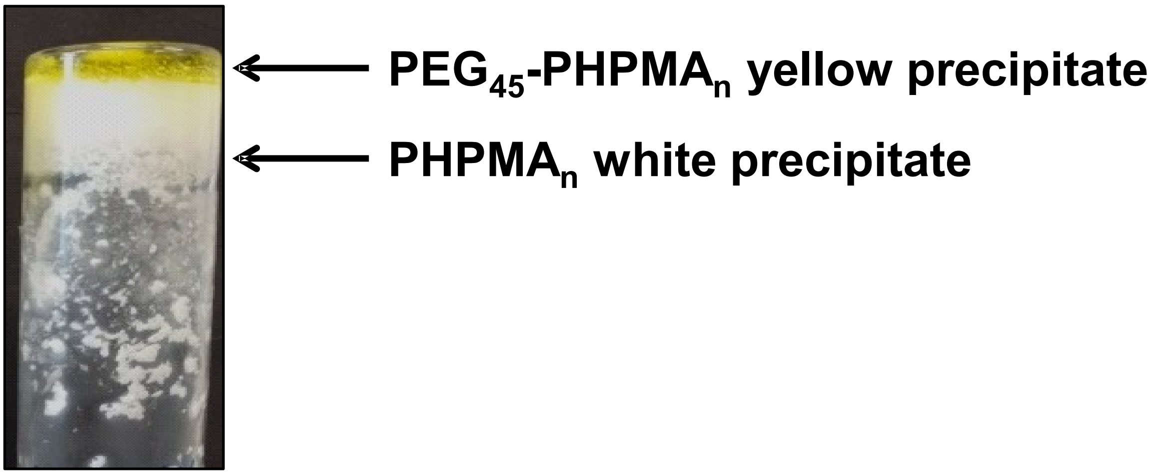

Figure S4. Digital photograph recorded after the attempted PISA synthesis of PEG_{45}-$PHPMA_{130}$ diblock copolymer nanoparticles at 50 °C targeting 10% w/w solids. Both a yellow PEG_{45}-$PHPMA_n$ precipitate and a white precipitate of PHPMA homopolymer are formed owing to colloidal instability and conventional free radical polymerization respectively.

Table S1. Summary of the target diblock copolymer compositions, GPC molecular weight data and copolymer morphologies for [x PEG_{45} + y $PGMA_{59}$]-$PHPMA_n$. [a] Calculated by ^1H NMR spectroscopy. [b] Molecular weight data were determined by DMF GPC analysis and are expressed relative to PMMA standards. [c] Determined by TEM analysis. [Abbreviations: S = spheres, W = worms, V = vesicles, P = precipitate].

Mol fraction of PEG_{45} (x)	Target PHPMA DP (n)	Conversion[a] (%)	M_n (kg mol^{-1})[b]	M_w / M_n[b]	Morphology[c]
0.20	90	> 99	30.9	1.12	S
0.40	90	> 99	29.4	1.15	S
0.60	90	> 99	24.9	1.14	S
0.80	90	> 99	21.9	1.18	S
1.00	90	> 99	25.3	1.91	P
0.00	110	> 99	33.3	1.12	S
0.20	110	> 99	31.3	1.14	S
0.40	110	> 99	31.1	1.15	S
0.60	110	> 99	30.9	1.12	S&W
0.80	110	> 99	28.3	1.11	V
1.00	110	> 99	23.1	1.61	P
0.00	130	> 99	36.8	1.14	S&W
0.20	130	> 99	33.6	1.13	S&W
0.40	130	> 99	33.3	1.13	S&W
0.60	130	> 99	33.0	1.12	V
0.80	130	> 99	31.6	1.10	V
1.00	130	> 99	29.4	2.14	P
0.00	140	> 99	37.4	1.13	S&W
0.00	150	> 99	43.6	1.15	W
0.20	150	> 99	38.4	1.14	W&V
0.40	150	> 99	36.7	1.15	V
0.60	150	> 99	34.5	1.13	V
0.80	150	> 99	36.6	1.50	V
1.00	150	> 99	37.1	6.97	P
0.00	160	> 99	40.0	1.10	W
0.00	170	> 99	46.0	1.18	W&V
0.20	170	> 99	45.7	1.14	W&V
0.40	170	> 99	43.7	1.20	V
0.60	170	> 99	34.4	1.16	V
0.80	170	> 99	35.6	1.52	V
1.00	170	> 99	27.2	1.40	P

Table S2. Summary of the target diblock copolymer compositions, GPC molecular weights and copolymer morphologies for [z PEG_{113} + y $PGMA_{59}$]-$PHPMA_n$. [a] Calculated by ^{1}H NMR spectroscopy. [b] Molecular weight data were determined by DMF GPC analysis and are expressed relative to PMMA standards. [c] Determined by TEM analysis.

Mol fraction of PEG_{113} (z)	Target PHPMA DP (n)	Conversion[a] (%)	M_n (kg mol^{-1})[b]	M_w / M_n	Morphology[c]
0.00	140	> 99	35.4	1.13	W&S
0.20	140	>99	34.8	1.15	W&S
0.40	140	>99	34.6	1.14	W&S
0.60	140	>99	34.1	1.15	S
0.80	140	>99	33.6	1.14	S
1.00	140	>99	33.4	1.12	S
0.00	160	> 99	39.2	1.15	W
0.10	160	> 99	42.5	1.12	W
0.20	160	> 99	34.5	1.17	W
0.30	160	> 99	39.8	1.12	W&S
0.40	160	> 99	32.8	1.19	W&S
0.50	160	> 99	40.3	1.12	W&S
0.60	160	> 99	33.5	1.18	W&S
0.70	160	> 99	40.0	1.13	W&S
0.80	160	> 99	33.2	1.16	W&S
0.90	160	> 99	39.0	1.10	S
1.00	160	> 99	37.5	1.11	S
0.00	180	> 99	46.9	1.25	W&V
0.10	180	> 99	39.0	1.17	W
0.20	180	> 99	32.0	1.24	W
0.30	180	> 99	37.4	1.16	W
0.40	180	> 99	34.7	1.17	W
0.50	180	> 99	42.2	1.13	W
0.60	180	> 99	36.8	1.17	W
0.70	180	> 99	39.0	1.14	W&S
0.80	180	> 99	36.0	1.17	W&S
0.90	180	> 99	38.6	1.13	W&S
1.00	180	> 99	42.6	1.12	W&S
0.00	200	> 99	40.1	1.20	V
0.10	200	> 99	37.9	1.27	V
0.20	200	> 99	32.6	1.23	V
0.30	200	> 99	45.4	1.16	V
0.40	200	> 99	39.9	1.20	M
0.50	200	> 99	45.0	1.16	M
0.60	200	> 99	45.9	1.14	M
0.70	200	> 99	32.3	1.42	W
0.80	200	> 99	29.6	1.19	W
0.90	200	> 99	29.5	1.23	W
1.00	200	> 99	28.7	1.18	W
0.00	220	> 99	49.3	1.21	V
0.10	220	> 99	44.2	1.20	V
0.20	220	> 99	45.8	1.18	V
0.30	220	> 99	46.8	1.16	V
0.40	220	> 99	40.6	1.21	V
0.50	220	> 99	47.0	1.17	M
0.60	220	> 99	38.8	1.16	W

0.70	220	> 99	48.4	1.14	W
0.80	220	> 99	42.2	1.17	W
0.90	220	> 99	54.5	1.12	W
1.00	220	> 99	42.5	1.15	W
0.00	240	> 99	52.8	1.17	V
0.10	240	> 99	51.5	1.18	V
0.20	240	> 99	53.3	1.21	V
0.30	240	> 99	44.6	1.19	V
0.40	240	> 99	43.8	1.22	V
0.50	240	> 99	43.9	1.22	M
0.60	240	> 99	52.1	1.14	M
0.70	240	> 99	40.9	1.21	M
0.80	240	> 99	44.9	1.18	W
0.90	240	> 99	44.1	1.19	W
1.00	240	> 99	42.2	1.13	W