Supporting Information

Thermoresponsive Property of Poly(*N*,*N*-bis(2-ethoxyethyl)acrylamide) and Its Multi-Block Copolymers with Poly(*N*,*N*-dimethylacrylamide) Prepared by Hydrosilylation-Promoted Group Transfer Polymerization

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1. Monomer reactivity ratio

The monomer reactivity ratios of r_{EOEAm} and r_{DMAm} were determined using the Kelen–Tüdös equation of $\eta = (r_{\mathrm{EOEAm}} + r_{\mathrm{DMAm}}/\alpha) - r_{\mathrm{DMAm}}/\alpha)$, where η and ξ are mathematical functions of the comonomer molar fractions in the feed and in the copolymer, respectively: $\eta = G/(\alpha + F)$ and $\xi = F/(\alpha + F)$. Here, $G = x(y - 1)/y$ and $F = x^2/y$ with $x = M_{\mathrm{EOEAm}}/M_{\mathrm{DMAm}}$ and $y = m_{\mathrm{EOEAm}}/m_{\mathrm{DMAm}}$. F_{EOEAm} and F_{DMAm} are the mole fractions of EOEAm and DMAm in the monomer feed, respectively, M_{EOEAm} and M_{DMAm} are the mole fractions of EOEAm and DMAm in the residual monomer mixture, respectively, and m_{EOEAm} and m_{DMAm} are the mole fractions of EOEAm and DMAm units in the copolymer, respectively. The term $\alpha = \sqrt{F_m F_M}$ is a constant that is chosen appropriately to obtain a uniform spread of the data ($\alpha > 0$). F_{m} and F_{M} are the lowest and highest values obtained from the experimental data.

After terminating a random GTcoP of EOEAm and DMAm, remaining monomers and a resulting copolymer in a polymerization mixture were separated by dialysis against acetone. A mixture of residual monomers was purified using a short silica gel column, and M_{EOEAm} and M_{DMAm} were determined using the ^{1}H NMR spectrum of the monomer mixture. m_{EOEAm} and m_{DMAm} were determined using the ^{1}H NMR spectrum of the obtained copolymer. The monomer reactivity ratios r_{EOEAm} and r_{DMAm} were determined to be 0.66 and 15.83, respectively, from the least-squares method. The number-average sequence length of the EOEAm unit (l_{EOEAm}) was determined as a parameter that reflects the isolation tendency of the EOEAm–EOEAm diad. The $l_{\mathrm{EOEAm}n}$ was calculated from the monomer reactivity ratio of l_{EOEAm} using the equation $l_{\mathrm{EOEAm}} = 1 + r_{\mathrm{EOEAm}}[F_{\mathrm{EOEAm}}/(1 - F_{\mathrm{EOEAm}})]$.

Table S1. Random group transfer copolymerization (GTcoP) of EOEAm and DMAm using Me_2EtSiH and $B(C_6F_5)_3$

F_{EOEAm}	M_{EOEAm} [b]	conv. %	m_{EOEAm} [b]	ξ	η	l_{EOEAm}
0.3	0.36	0.25	0.08	0.23	−0.95	1.3
0.4	0.47	0.23	0.13	0.31	−0.76	1.4
0.5	0.55	0.19	0.18	0.36	−0.59	1.7
0.6	0.64	0.21	0.26	0.44	−0.40	2.0
0.7	0.76	0.20	0.39	0.57	−0.18	2.5
0.8	0.88	0.22	0.58	0.77	0.15	3.6

[a] $[SKA^{Et}]_0/[B(C_6F_5)_3]_0 = 1/0.2$; solvent, CH_2Cl_2; temperature, 25 °C. [b] Determined by ^1H NMR spectroscopy in $CDCl_3$.

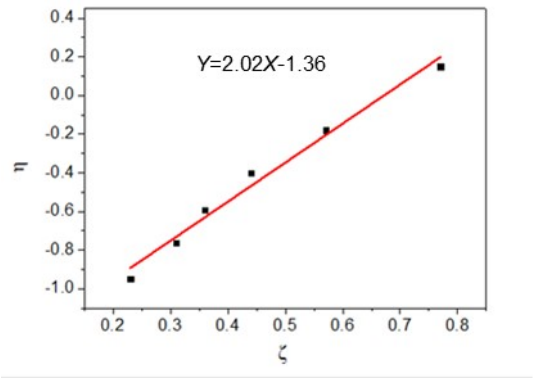

Figure. The equation obtained by fitting ξ and η.

2. T_{cp} of PMOEAm.

The T_{cp} of $PMOEAm_x$ prepare by the GTP of MOEAm with Me_2EtSiH using $B(C_6F_5)_3$: 56.5 °C for x = 25, 53.9 °C for x = 50, 51.2 °C for x = 75, 50.9 °C for x = 100, 50.5 °C for x = 150, 48.0 °C for x = 200.

3. ^{1}H and ^{13}C NMR spectra.

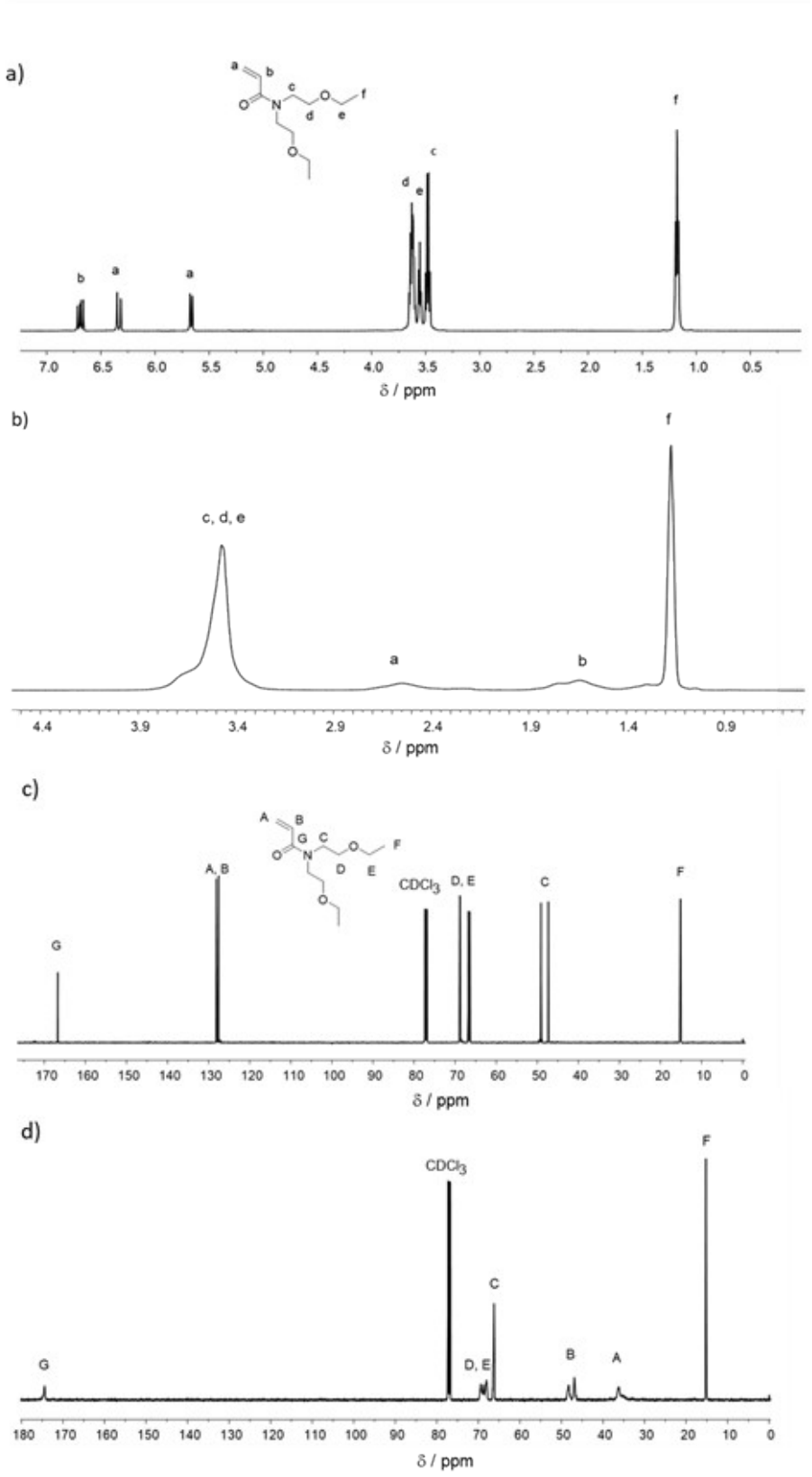

Figure 1S. ^{1}H NMR spectra of a) EOEAm and b) PEOEAm and ^{13}C NMR spectra of c) EOEAm and d) PEOEAm in $CDCl_3$.

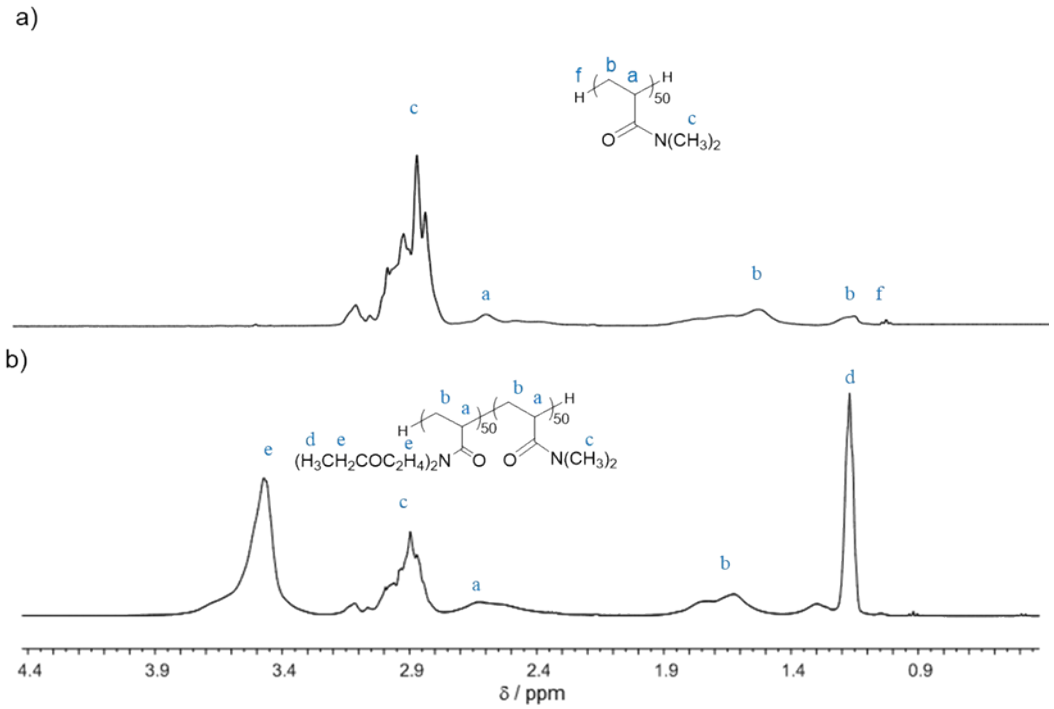

Figure S2. ^{1}H NMR spectrm of a) $PDMAm_{50}$ and b) $PEOAm_{50}$-*b*-$PDMAm_{50}$

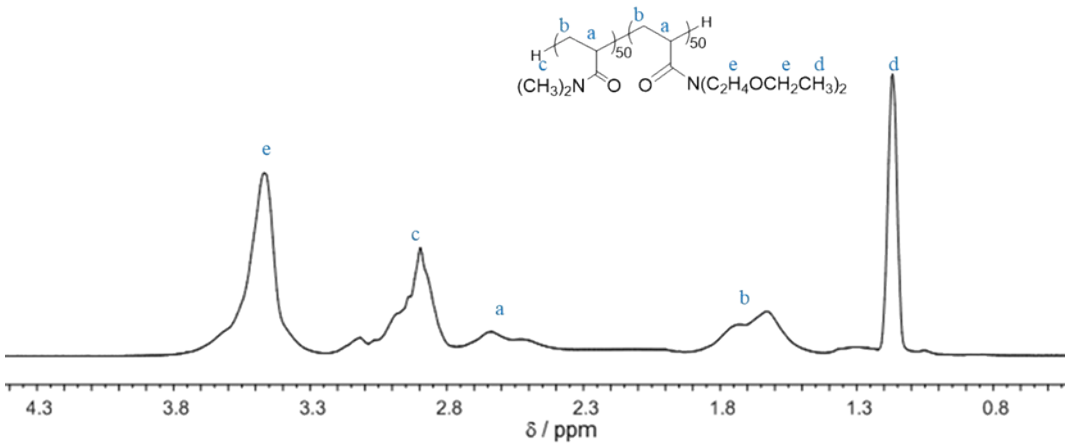

Figure S3. ^{1}H NMR spectrum of $PDMAm_{50}$-*b*-$PEOEAm_{50}$

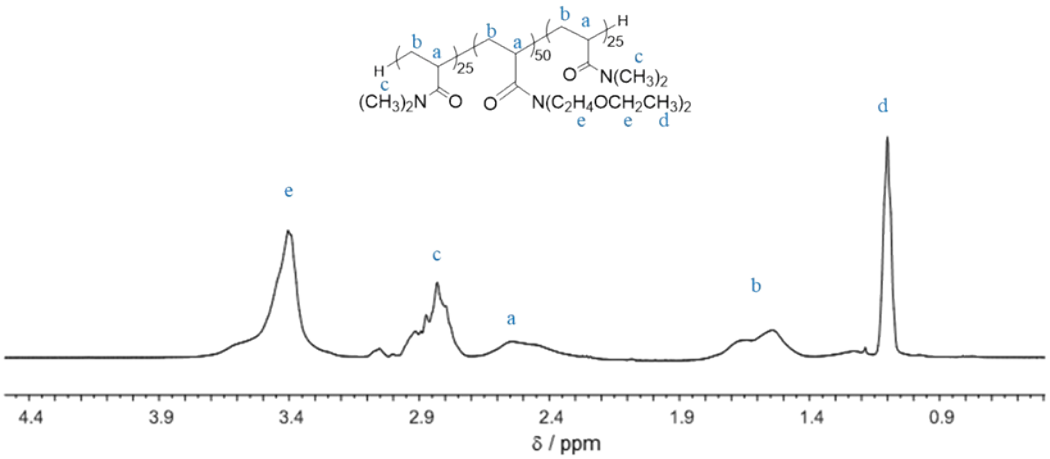

Figure S4. ^{1}H NMR spectrum of PDMAm$_{25}$-*b*-PEOEAm$_{50}$-*b*-PDMAm$_{25}$

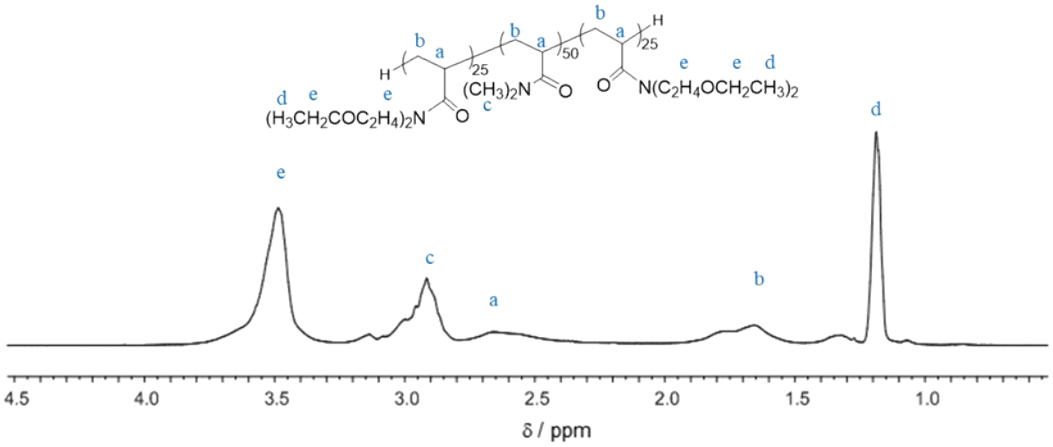

Figure S5. ^{1}H NMR spectrum of PEOEAm$_{25}$-*b*-PDMAm$_{50}$-*b*-PEOEAm$_{25}$

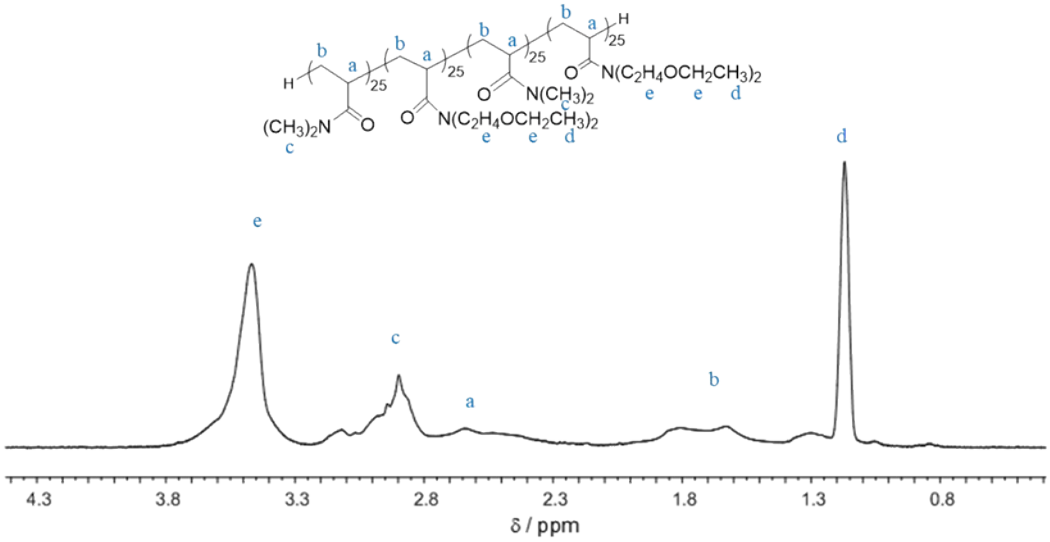

Figure S6. ^{1}H NMR spectrum of (PDMAm$_{25}$-*b*-PEOEAm$_{25}$)$_2$

4. Sec traces for di-, tri-, and tetra-block copolymers.

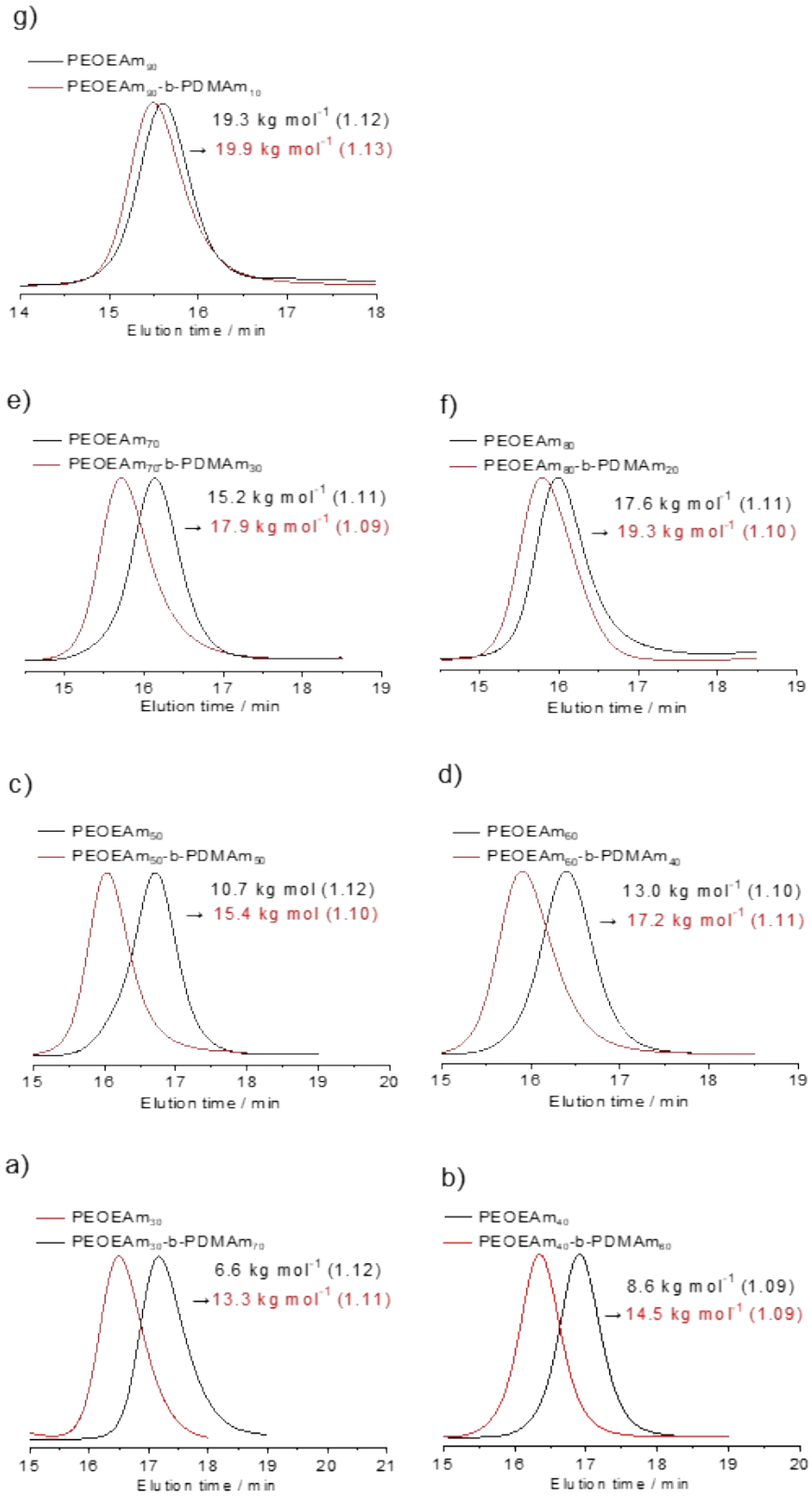

Figure S7. SEC traces of PEOEAm$_x$-*b*-PDMAm$_y$: (a) x/y = 40/10, (b) x/y = 35/15, (c) x/y = 30/20, (d) x/y = 25/25, (e) x/y = 20/30, and (f) x/y = 15/35 (runs 7 – 13, Table 2).

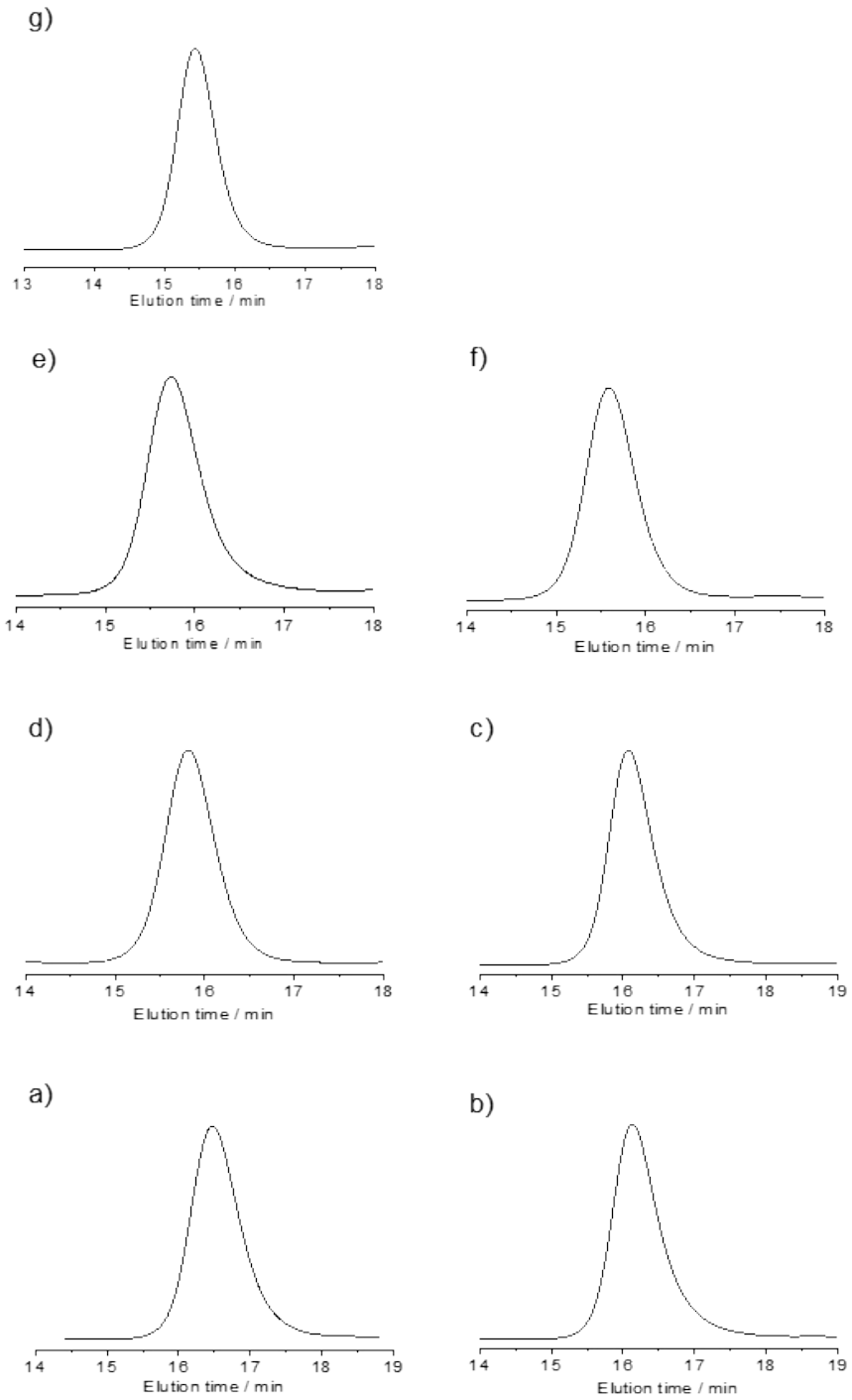

Figure S8. SEC traces of PDMAm$_y$-*b*-PEOEAm$_x$: (a) x/y = 30/70, (b) x/y = 40/60, (c) x/y = 50/50, (d) x/y = 60/40, (e) x/y = 70/30,(f) x/y = 80/20, (g) x/y = 90/10 (runs 14 – 20, Table 2).

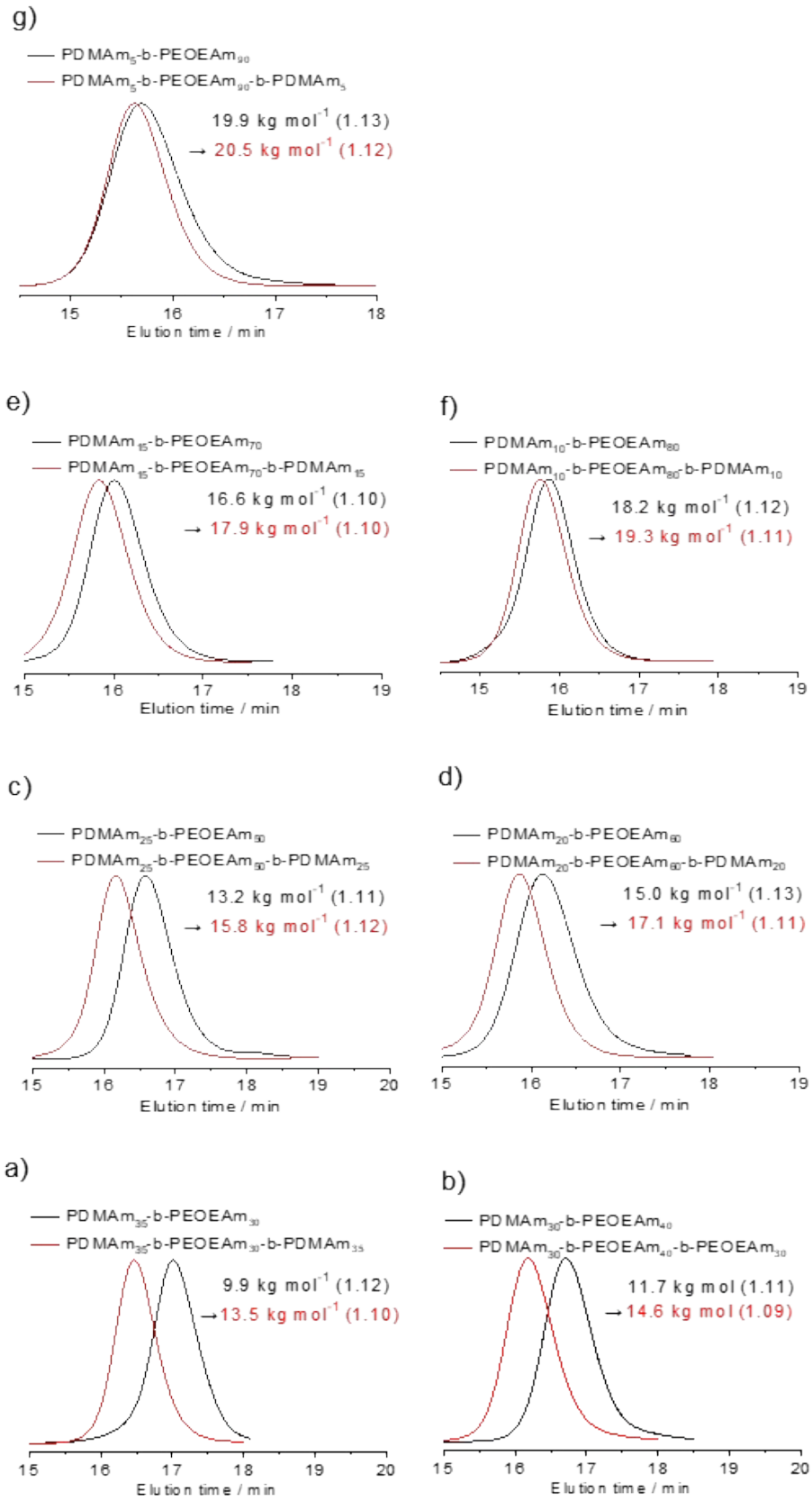

Figure S9. SEC traces of PDMAm$_y$-*b*-PEOEAm$_x$-*b*-PDMAm$_y$ (runs 21 – 27, Table 3).

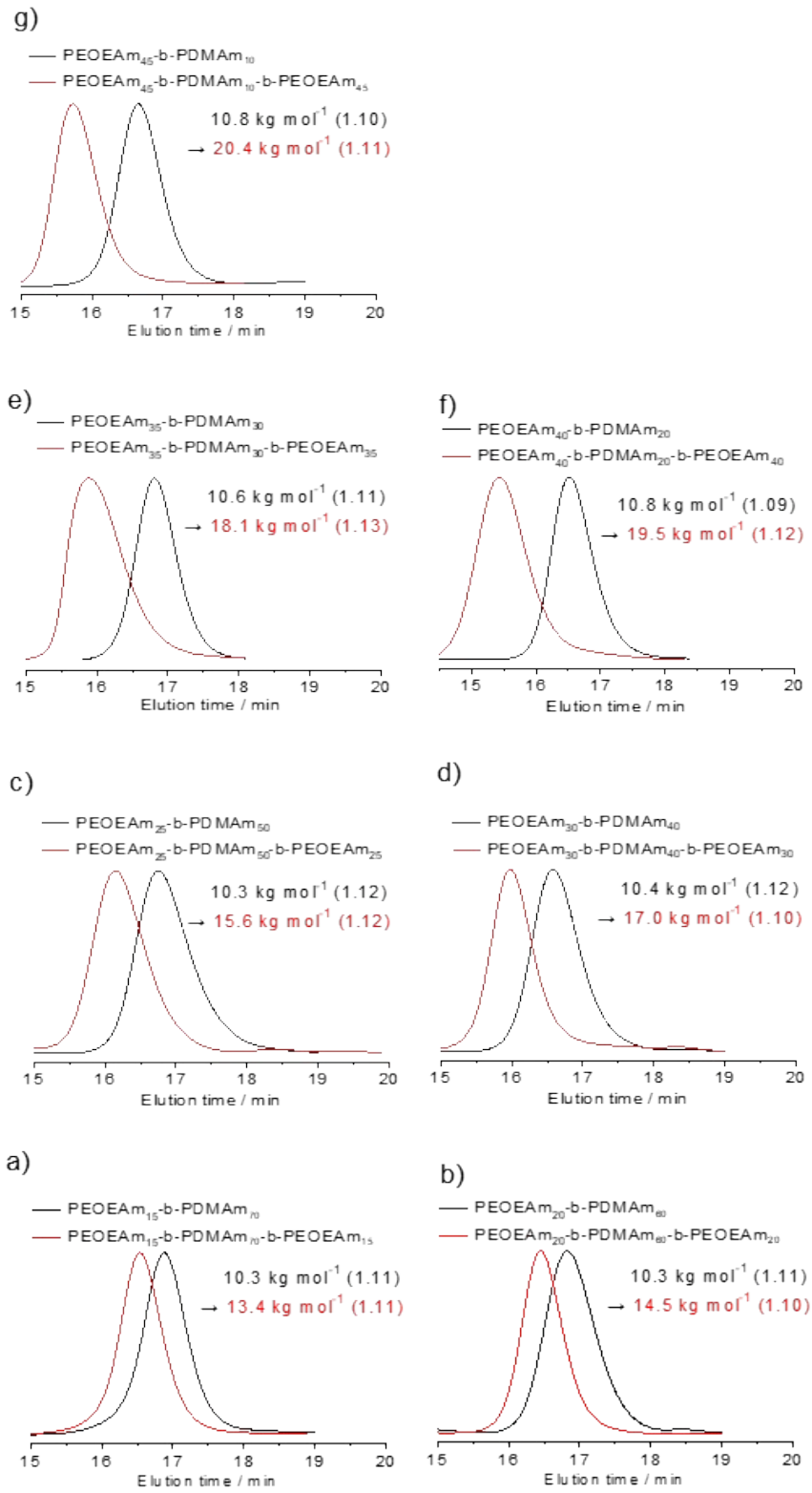

Figure S10. SEC traces of $PEOEAm_x$-*b*-$PDMAm_y$-*b*-$PEOEAm_x$ (runs 28 – 34,Table 3)

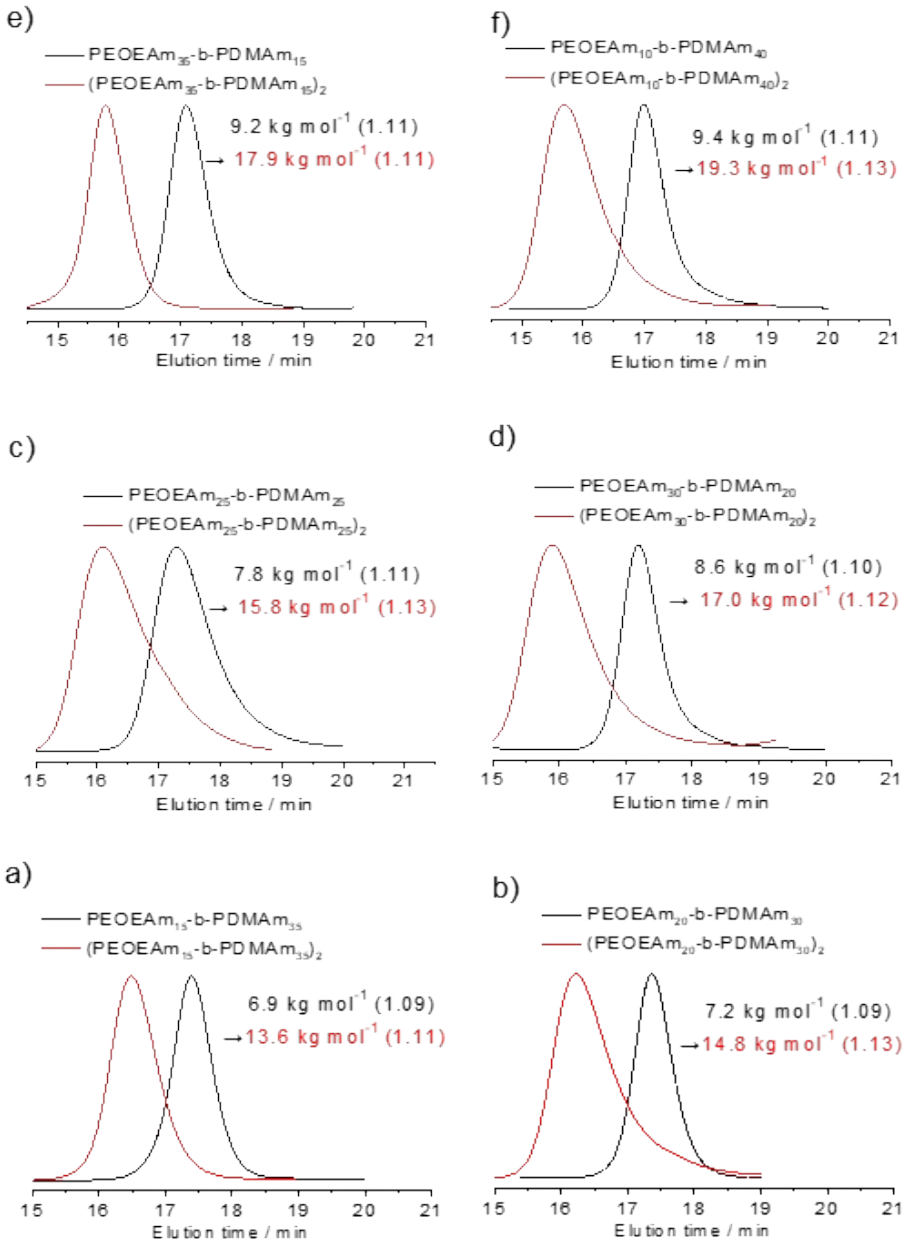

Figure S11. SEC traces of $(PDMAm_y\text{-}b\text{-}PEOEAm_x)_2$ (Table 4).

5. UV-vis absorption spectra of Block copolymers at different temperatures.

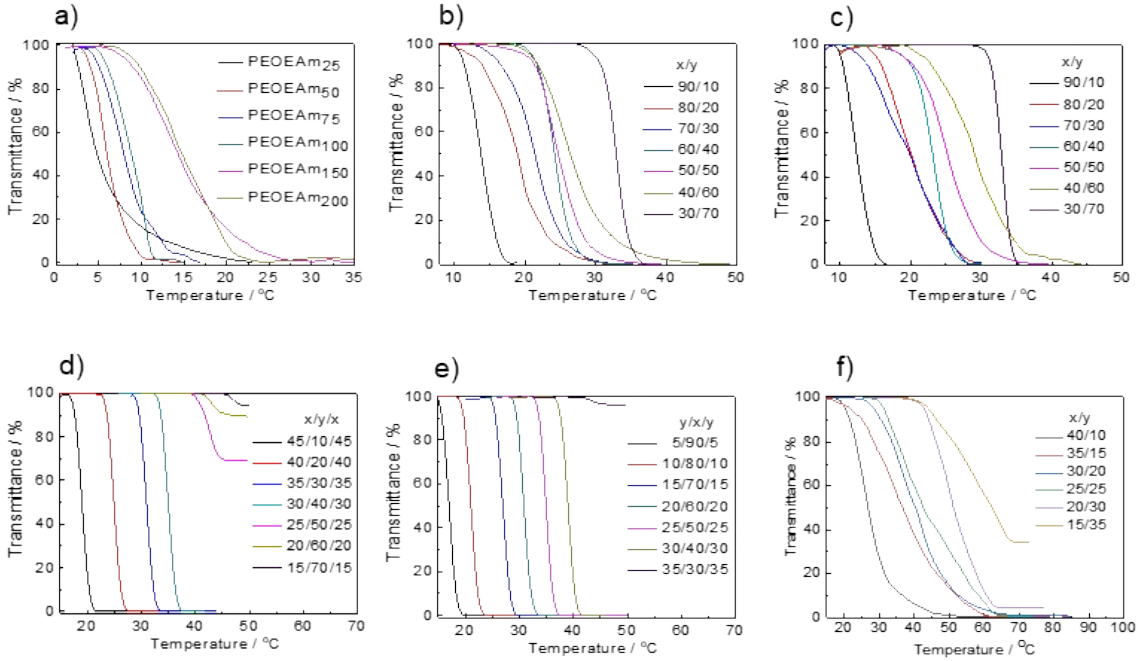

Figure S12. UV-vis absorption spectra of a) PEOEAm, b) PDMAm$_y$-*b*-PEOEAm$_x$, c) PEOEAm$_x$-*b*-PDMAm$_y$, d) PEOEAm$_x$-*b*-PDMAm$_y$-*b*-PEOEAm$_x$, e) PDMAm$_y$-*b*-PEOEAm$_x$-*b*-PDMAm$_y$, and f) (PEOEAm$_x$-*b*-PDMAm$_y$)$_2$ in water (10 g L^{-1}) at different temperatures.

6. Distribution of hydrodynamic radii.

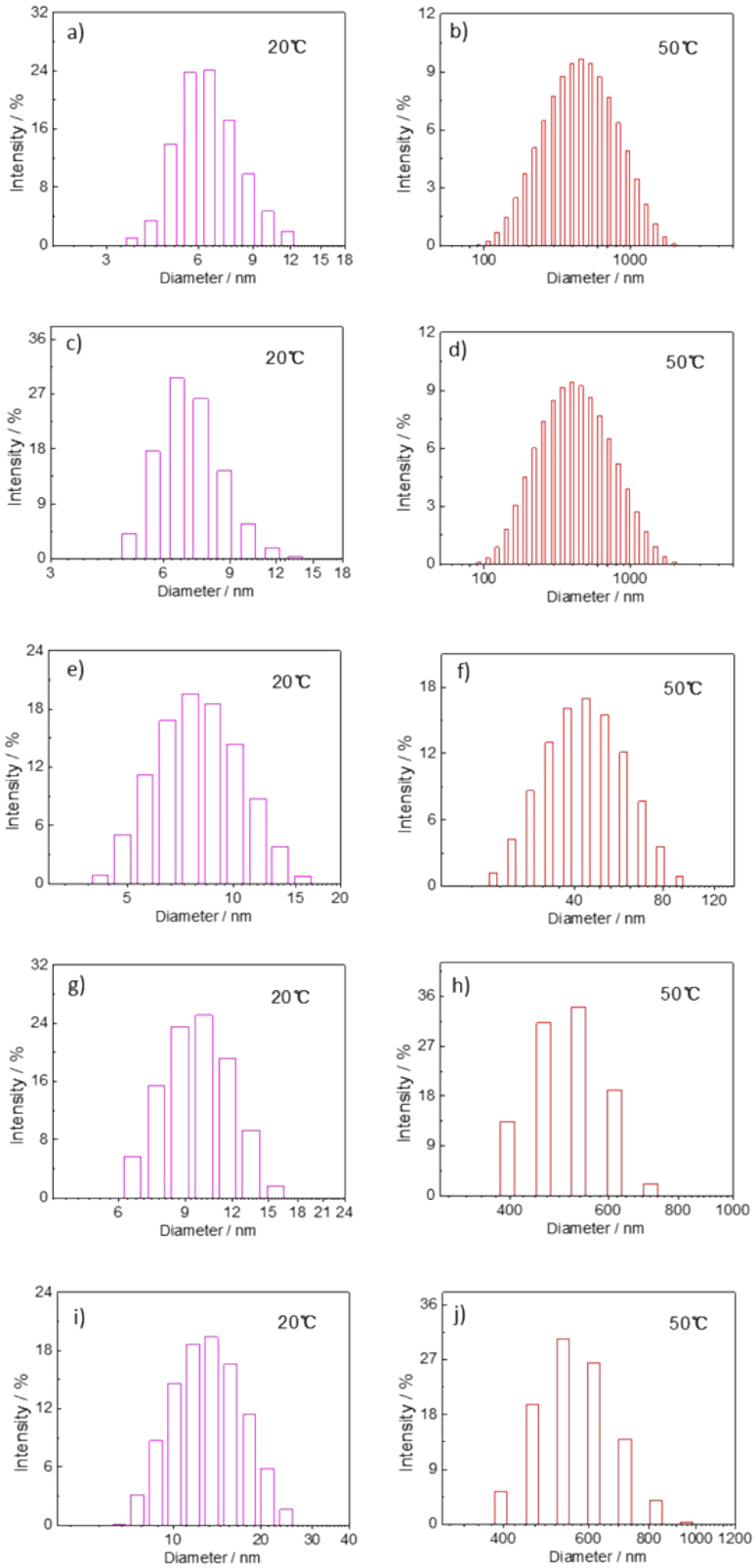

Figure S13. Distribution of hydrodynamic radii for a) and b) $PDMAm_{50}$-*b*-$PEOEAm_{50}$, c) and d) $PEOEAm_{50}$-*b*-$PDMAm_{50}$, e) and f) $PDMAm_{25}$-*b*-$PEOEAm_{50}$-*b*-$PDMAm_{25}$, g) and h) $PEOEAm_{25}$-*b*-$PDMAm_{50}$-*b*-$PEOEAm_{25}$, and i) and j) $(PEOEAm_{25}$-*b*-$PDMAm_{25})_2$.