Supplementary Information - figures

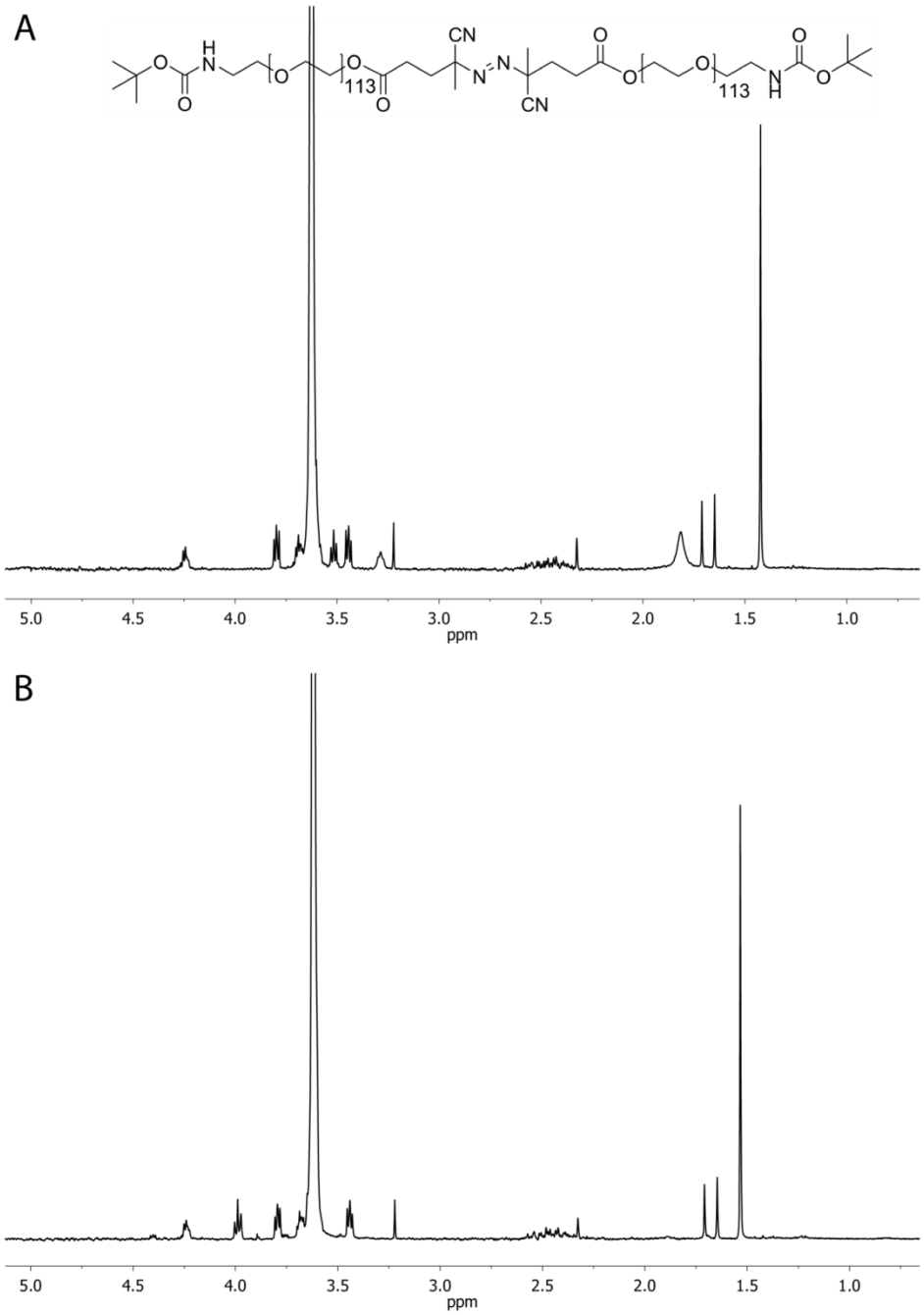

Figure S1. A) ^{1}H-NMR spectrum of (Boc-PEG$_{5000}$)$_2$-ABCPA in $CDCl_3$. δ (ppm) 4.25 (2H, PEG methylene next to ABCPA), 3.8-3.5 (910H, PEG), 2.2-2.6 (8H, ABCPA methylene), 1.71+1.64 (6H, ABCPA methyl), 1.4 (9H, Boc). B) ^{1}H-NMR spectrum of (Boc-PEG$_{5000}$)$_2$-ABCPA in $CDCl_3$ + TAIC. Reaction of TAIC with the terminal hydroxyl groups caused a shift of the CH_2 protons of PEG adjacent to the OH end to 4.4 ppm.

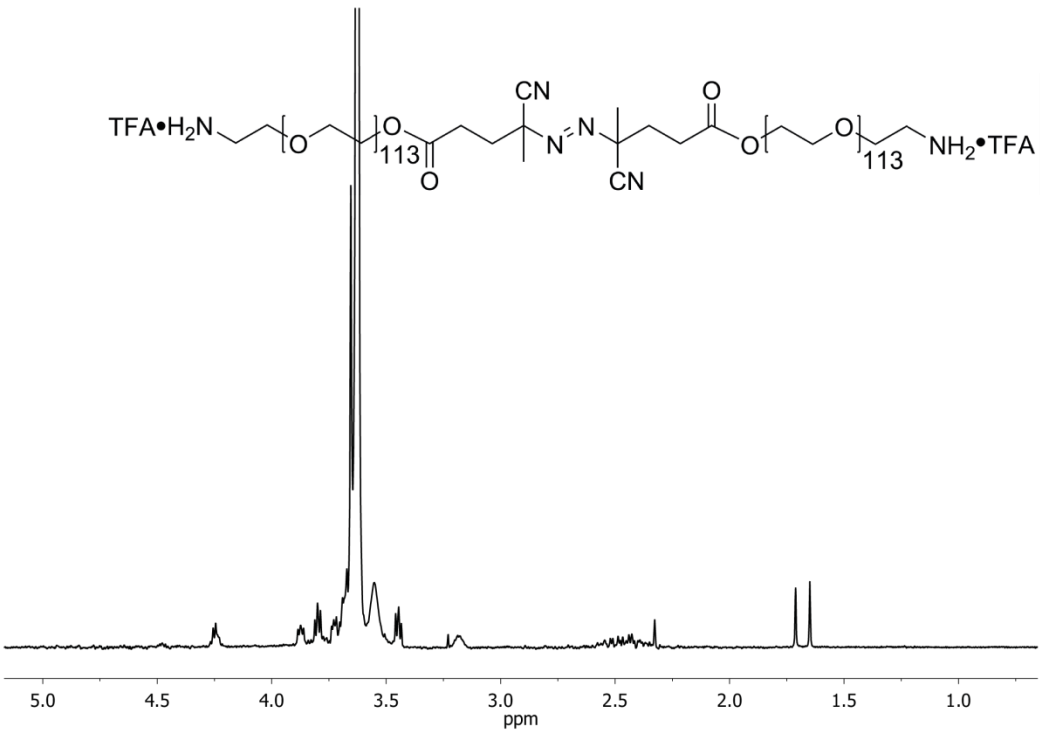

Figure S2. ^{1}H-NMR spectrum of (TFA.NH_2-PEG_{5000})$_2$-ABCPA in $CDCl_3$. Complete disappearance of the Boc signal at 1.4 ppm, showing successful removal of the Boc-group

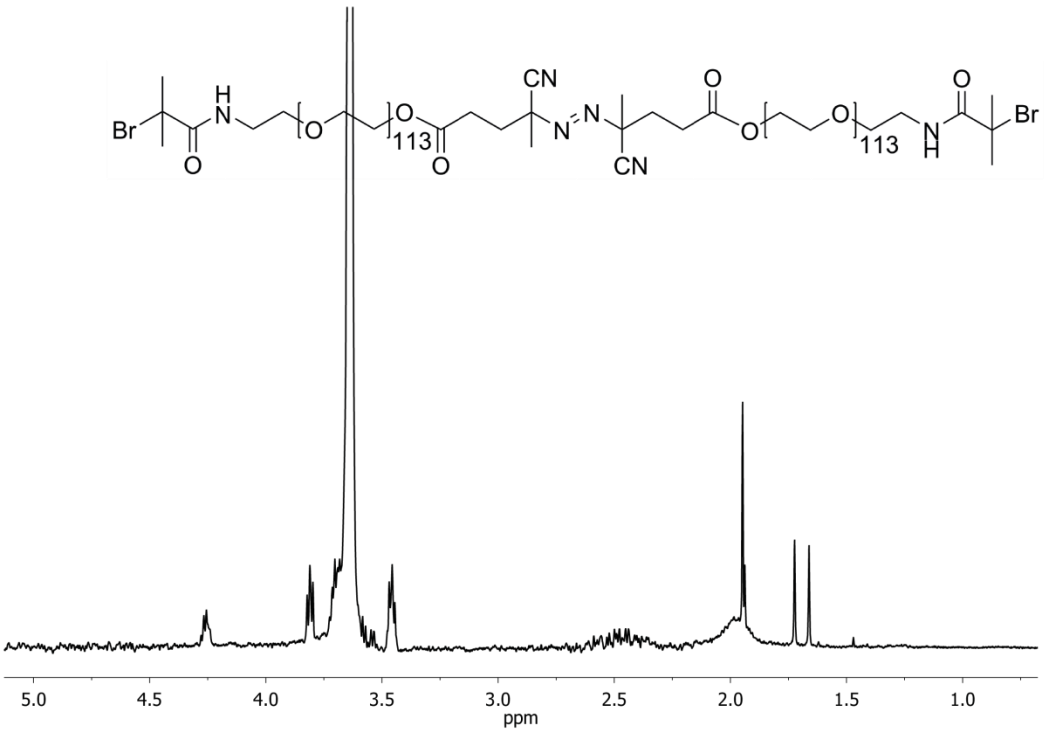

Figure S3. ^{1}H-NMR spectrum of (Br-C(CH_3)$_2$-CO-NH-PEG_{5000})$_2$-ABCPA in $CDCl_3$. The peak at δ = 1.94 shows the methyl groups of bromoisobutyryl indicating successful functionalization of the PEG macroinitiator.

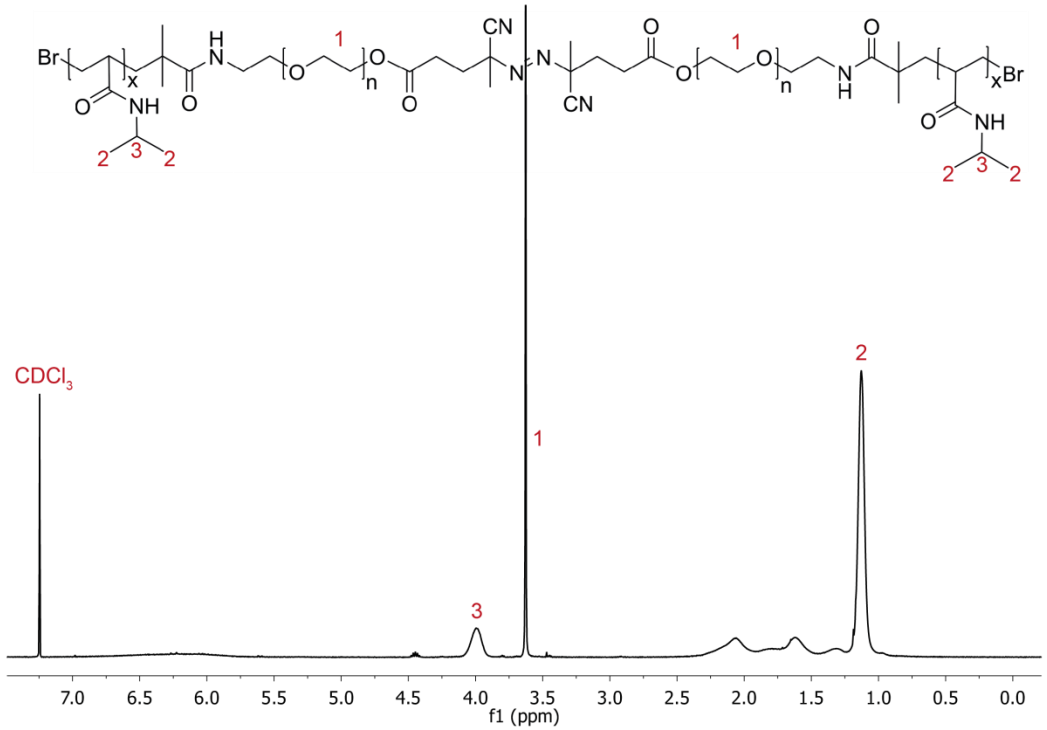

Figure S4. ^{1}H-NMR spectrum of PNIPAM-PEG-PEG-PNIPAM (NPPN) in $CDCl_3$.

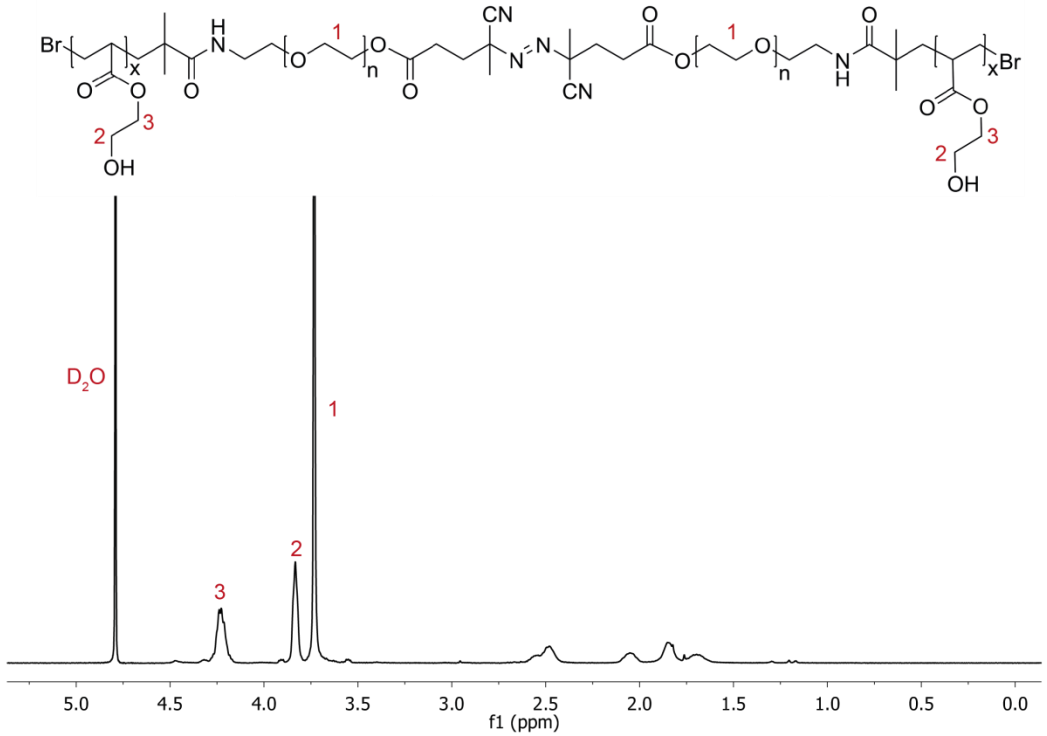

Figure S5. ^{1}H-NMR spectrum of PHEA-PEG-PEG-PHEA (HPPH) in D_2O.

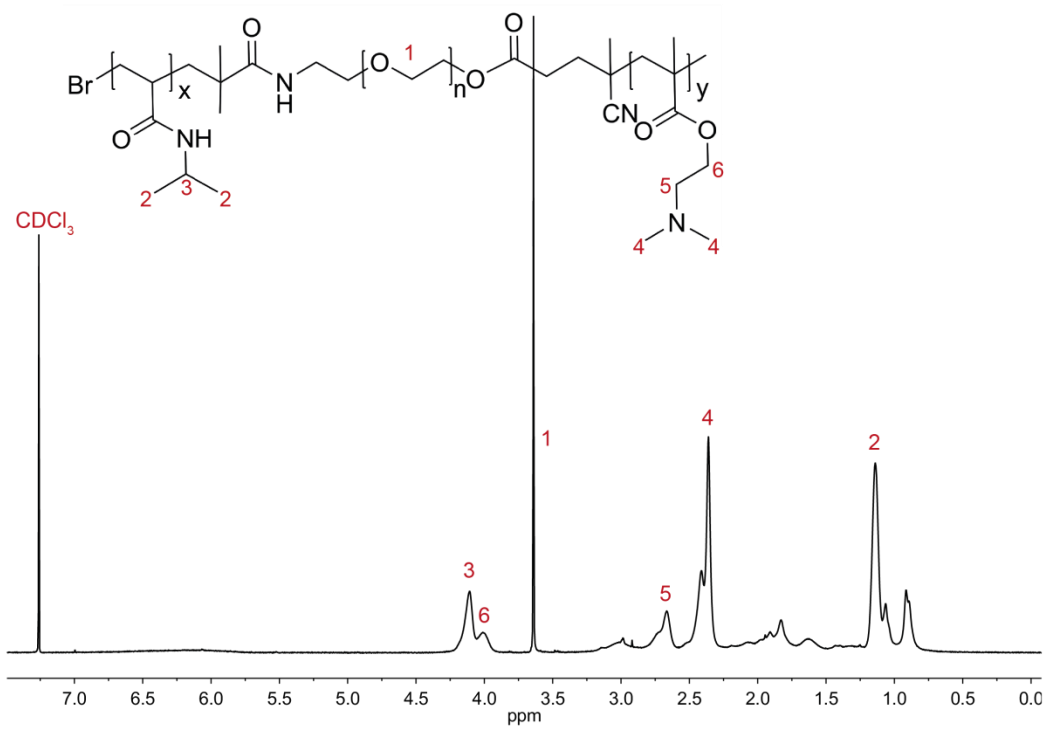

Figure S6. ^{1}H-NMR spectrum of PNIPAM-PEG-PDMAEMA (NPD) in $CDCl_3$.

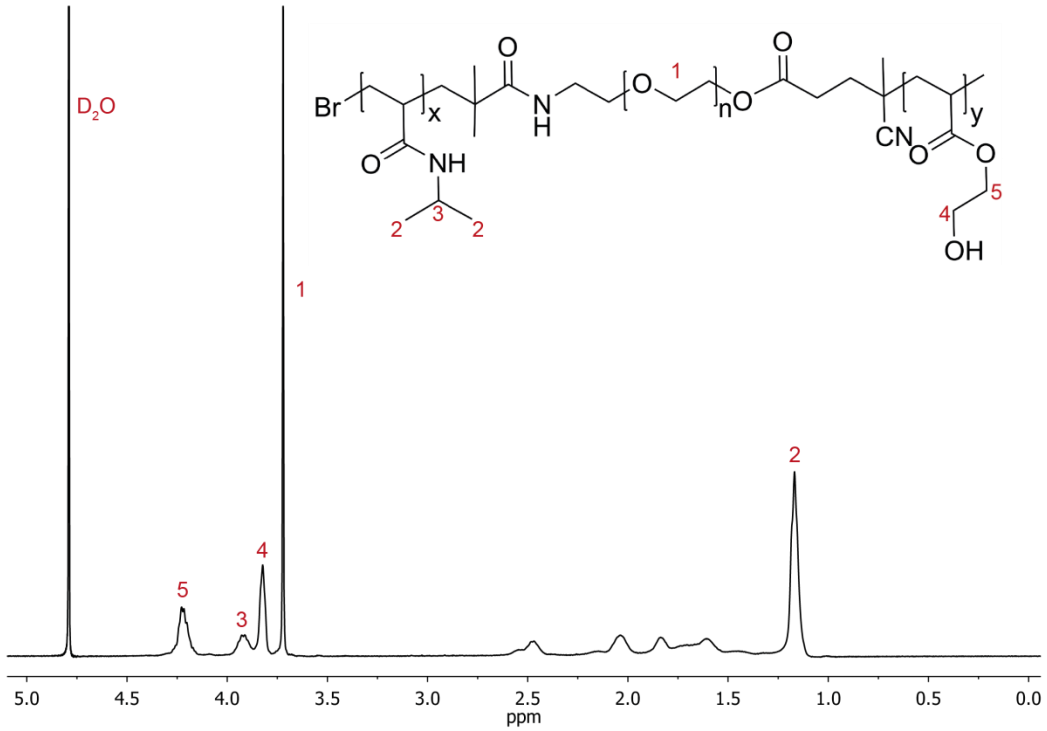

Figure S7. ^{1}H-NMR spectrum of PNIPAM-PEG-PHEA (NPH) in D_2O.

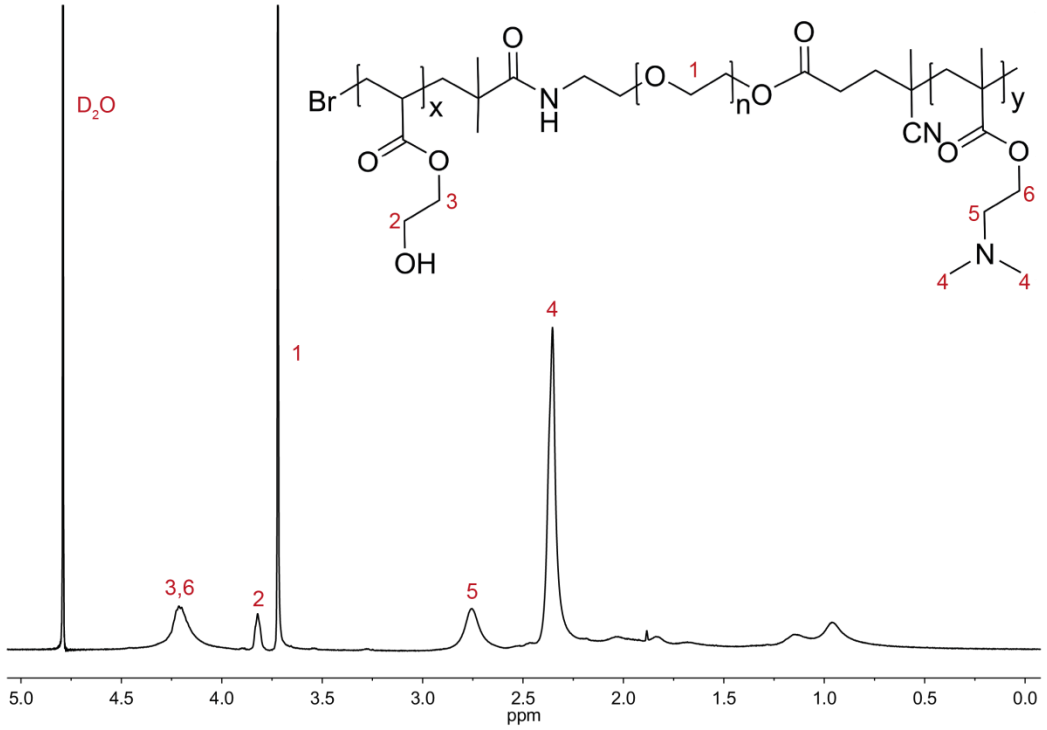

Figure S8. ^{1}H-NMR spectrum of PHEA-PEG-PDMAEMA (HPD) in D_2O.

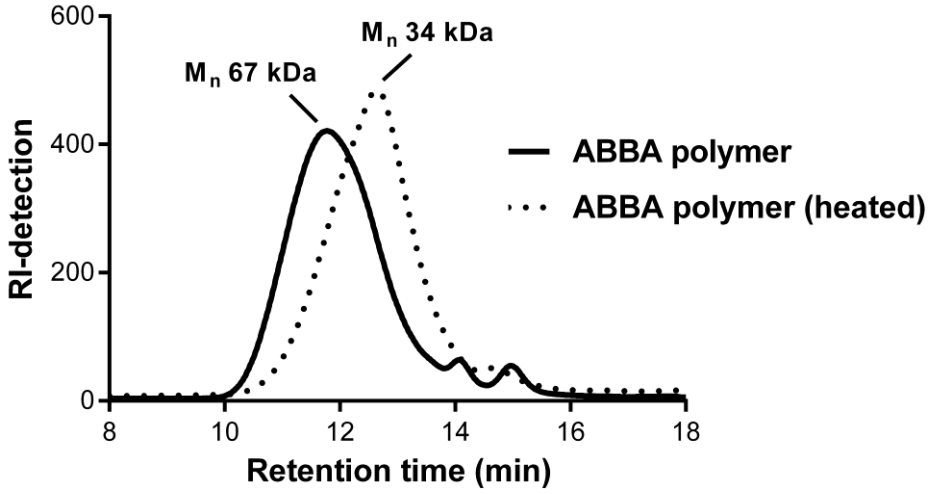

Figure S9. GPC chromatograms (RI-detection) of the ABBA polymer (PNIPAM-PEG-PEG-PNIPAM) after atom transfer radical polymerization and the same ABBA-polymer after heating at 70 °C for 24 hours in DMF, which represents similar conditions to those used during free radical polymerization.

Table S1. Characteristics of various ABC triblock copolymers synthesized by radical polymerization using the hetero-functional PEG macroinitiator. The polymer names are abbreviated according to the block composition, in which the first letter corresponds to the monomer used for the A block, the second letter to the B block and the third letter to the C block (N = NIPAM, P = PEG, D = DMAEMA).

Name	Feed PEG: monomer ratio (A block)	Feed PEG: monomer ratio (C block)	M_n A block (kDa)[a]	M_n B block (kDa)[a]	M_n C block (kDa)[a]	Total M_n (kDa)[a]	Total M_n (kDa)[b]	PDI[b]	Cloud Point (°C)[c]
NPD_1	1:566	1:789	27	5	43	75	83	1.8	34
NPD_3	1:566	1:983	27	5	56	88	62	2.1	34
NPD_2	1:283	1:1011	15	5	64	84	62	1.8	34
NPD_4	1:283	1:789	15	5	43	63	51	1.8	34
NPD_5	1:283	1:396	15	5	20	40	46	2.1	33

[a] Determined by ^{1}H-NMR. [b] Determined by GPC. [c] Determined by light scattering at 550 nm.

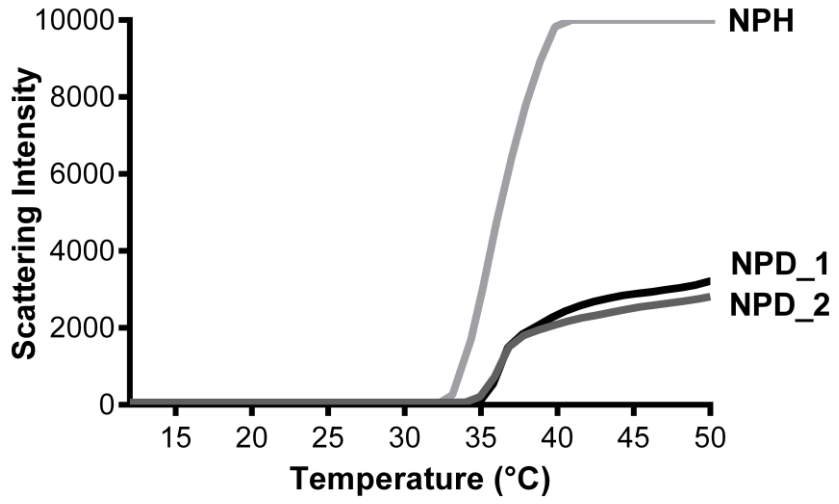

Figure S10. Light scattering intensity at 550 nm as a function of temperature for cloud point determination of thermosensitive polymers PNIPAM-PEG-PHEA (NPH) and PNIPAM-PEG-PDMAEMA (NPD_1, NPD_2) in 20 mM HEPES buffer (pH 7.4).