Supporting Information for:

RAFT dispersion polymerization of *N,N*-dimethylacrylamide in a series of *n*-alkanes using a thermoresponsive poly(*tert*-octyl acrylamide) steric stabilizer

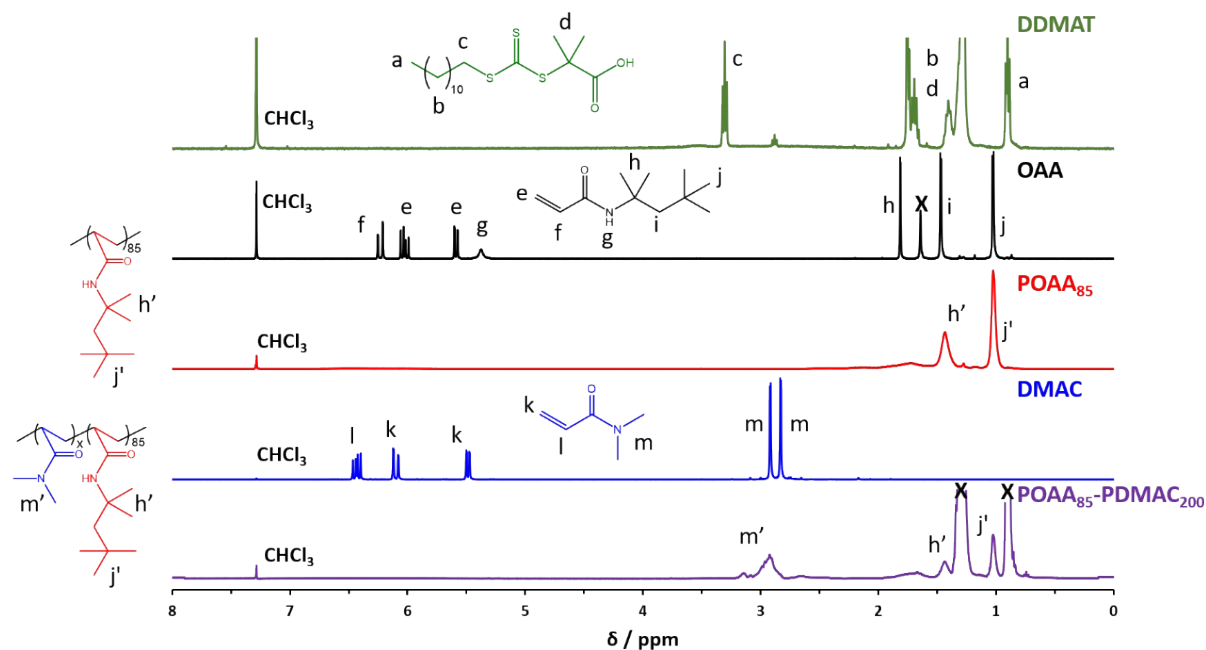R. R. Gibson, A. Fernyhough, O. M. Musa and S. P. Armes*

Figure S1. ^{1}H NMR spectra recorded in CDCl$_3$ for DDMAT RAFT agent (green), OAA monomer (black), a POAA$_{85}$ macro-CTA (red), DMAC monomer (blue) and a POAA$_{85}$-PDMAC$_{150}$ diblock copolymer (purple).
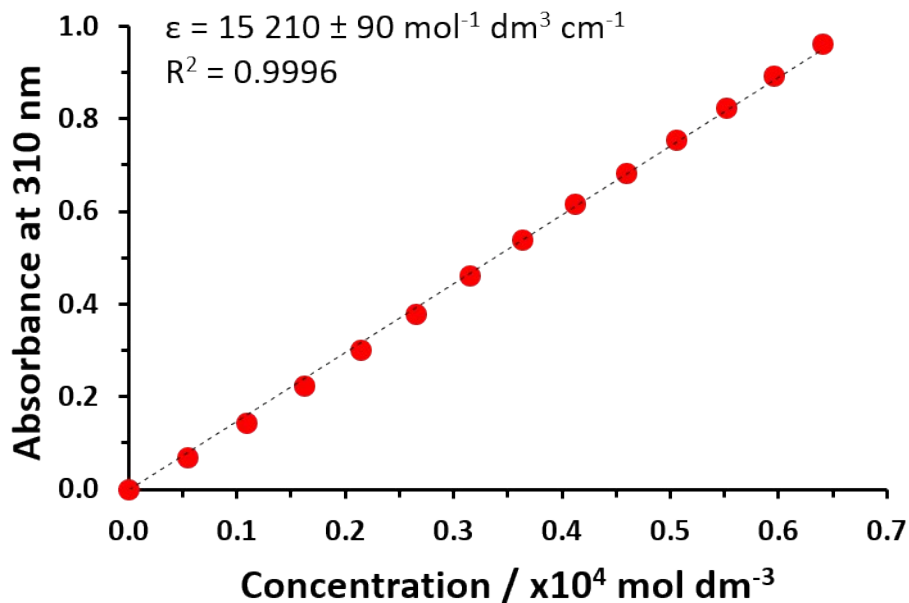
Figure S2. Beer-Lambert calibration plot constructed for the trithiocarbonate-based DDMAT RAFT agent in chloroform to calculate the molar extinction coefficient (ε) of the absorption maximum at 310 nm.

DP calculation using UV spectroscopy where c is concentration (mol dm^{-3}), A is absorbance, ε is the molar extinction coefficient (mol^{-1} dm^3 cm^{-1}), l is the path length (cm), n is the number of moles (mol), V is volume (dm^{-3}), m is mass (g) and MW is the molecular weight (g mol^{-1}).

$$c_{CTA} = \frac{A}{\varepsilon \times l} \qquad \text{(S1)}$$

$$n_{CTA} = c_{CTA} \times V \qquad \text{(S2)}$$

$$n_{CTA} = n_{poly} \qquad \text{(S3)}$$

$$MW_{poly} = \left(\frac{m_{poly}}{n_{poly}} \right) - MW_{CTA} \qquad \text{(S4)}$$

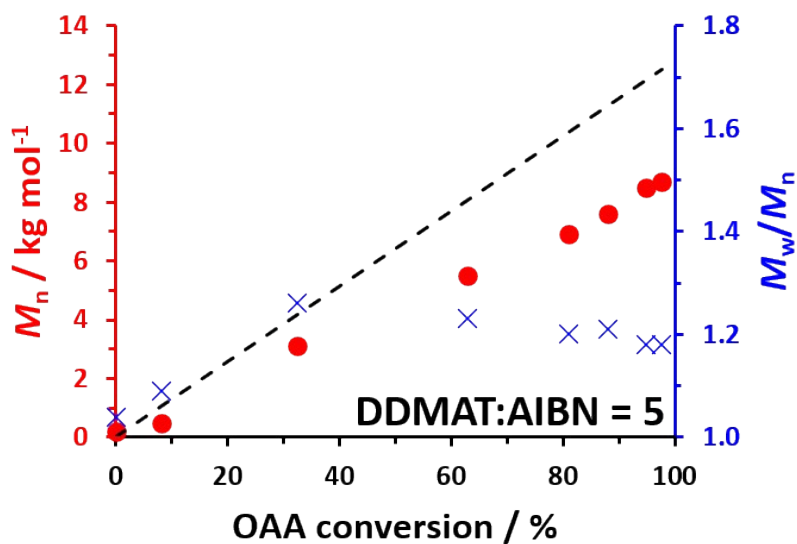$$DP = \frac{MW_{poly}}{MW_{mon}} \qquad \text{(S5)}$$

Figure S3. Evolution of M_n and M_w/M_n with conversion observed during the RAFT solution polymerization of OAA at 70 °C in 1,4-dioxane when targeting a POAA DP of 70 at 40% w/w solids using a DDMAT/AIBN molar ratio of 5. Ideal behavior (*i.e.* no GPC calibration error) is indicated by the dotted line.

Table S1. Summary of target DP, reaction time, OAA conversion and chloroform GPC data (M_n and M_w/M_n) for a series of POAA homopolymers prepared by RAFT solution polymerization in 1,4-dioxane for 60 min at 70 °C. Polymerizations were quenched prior to full OAA conversion in order to retain chain-end fidelity.

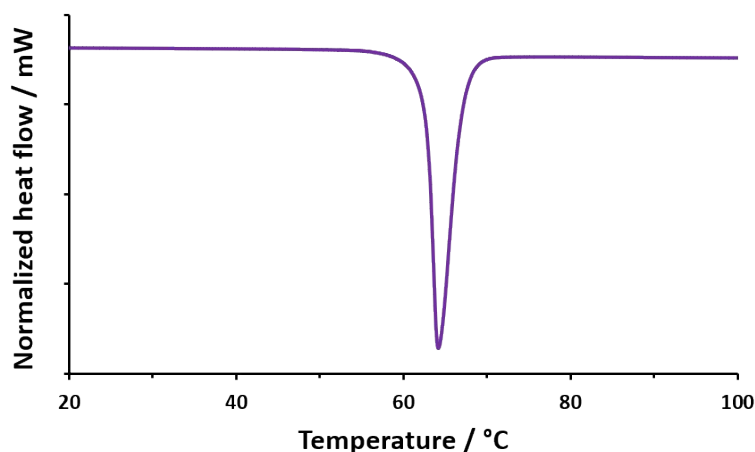| POAA DP	Target POAA DP	Conversion by ^{1}H NMR / %	M_n / g mol^{-1}	M_w/M_n	T_g / °C
22	20	83	2 800	1.13	67
39	40	79	4 900	1.17	76
72	70	79	8 100	1.19	81
85	80	85	9 900	1.18	82
99	100	77	12 200	1.22	83

Figure S4. DSC curve recorded for OAA monomer (98% purity; as received from the manufacturer) indicating a melting point of approximately 64 °C.

Table S2. Summary of DMAC monomer conversion, diblock copolymer M_n and M_w/M_n data as determined by chloroform GPC and the z-average diameters and polydispersities (PDI) determined by DLS studies for linear POAA$_{85}$-PDMAC$_x$ diblock copolymer nanoparticles prepared *via* RAFT dispersion polymerization prepared in various *n*-alkanes and a POAA$_{82}$-PDMAC$_{100}$ prepared *via* a one-pot protocol in *n*-heptane at 70 °C.

Diblock composition	Solvent	Conversion by ^{1}H NMR / %	M_n / g mol^{-1}	M_w/M_n	Z-average diameter / nm	DLS polydispersity
POAA$_{85}$-PDMAC$_{25}$	*n*-Heptane	>99	13 100	1.15	16	0.17
POAA$_{85}$-PDMAC$_{50}$	*n*-Heptane	>99	15 900	1.12	23	0.04
POAA$_{85}$-PDMAC$_{75}$	*n*-Heptane	>99	18 400	1.14	26	0.03
POAA$_{85}$-PDMAC$_{100}$	*n*-Heptane	99	19 900	1.19	32	0.03
POAA$_{85}$-PDMAC$_{125}$	*n*-Heptane	98	22 800	1.22	40	0.06
POAA$_{85}$-PDMAC$_{150}$	*n*-Heptane	98	25 100	1.26	45	0.04
POAA$_{85}$-PDMAC$_{175}$	*n*-Heptane	98	27 000	1.32	51	0.04
POAA$_{85}$-PDMAC$_{200}$	*n*-Heptane	98	29 100	1.30	62	0.07
POAA$_{85}$-PDMAC$_{225}$	*n*-Heptane	98	30 600	1.36	78	0.07
POAA$_{85}$-PDMAC$_{250}$	*n*-Heptane	98	32 900	1.42	91	0.09
POAA$_{82}$-PDMAC$_{100}$	*n*-Heptane	99	18 500	0.19	36	0.05
POAA$_{85}$-PDMAC$_{150}$	*n*-Octane	99	24 500	1.26	49	0.03
POAA$_{85}$-PDMAC$_{150}$	*n*-Decane	96	23 700	1.27	49	0.06
POAA$_{85}$-PDMAC$_{150}$	*n*-Dodecane	95	23 000	1.31	57*	0.05*
POAA$_{85}$-PDMAC$_{150}$	*n*-Tetradecane	94	23 300	1.32	60*	0.09*
POAA$_{85}$-PDMAC$_{150}$	*n*-Hexadecane	92	18 000	1.58	62*	0.07*

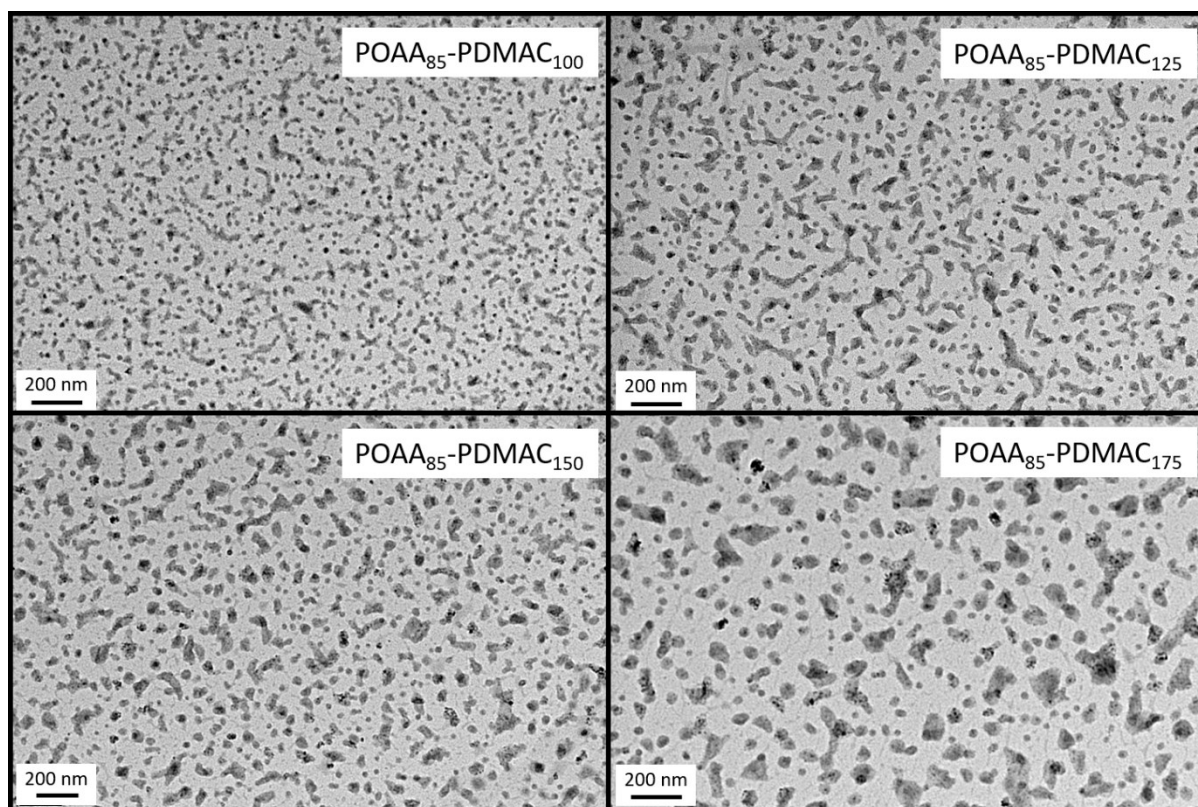*indicates DLS studies conducted above the UCST at 80 °C

Figure S5. TEM images recorded for linear $POAA_{85}$-$PDMAC_x$ nano-objects to illustrate their tendency to undergo film formation on the TEM grid during sample preparation.

Table S3. Summary of z-average diameters and polydispersities (PDI) determined by DLS studies of linear $POAA_{85}$-$PDMAC_{200}$ diblock copolymer nanoparticles and the corresponding core-crosslinked $POAA_{85}$-$PDMAC_{195}$-$PEGDA_{20}$ triblock copolymer nanoparticles in *n*-heptane (a poor solvent for PDMAC) and chloroform (a good solvent for PDMAC).

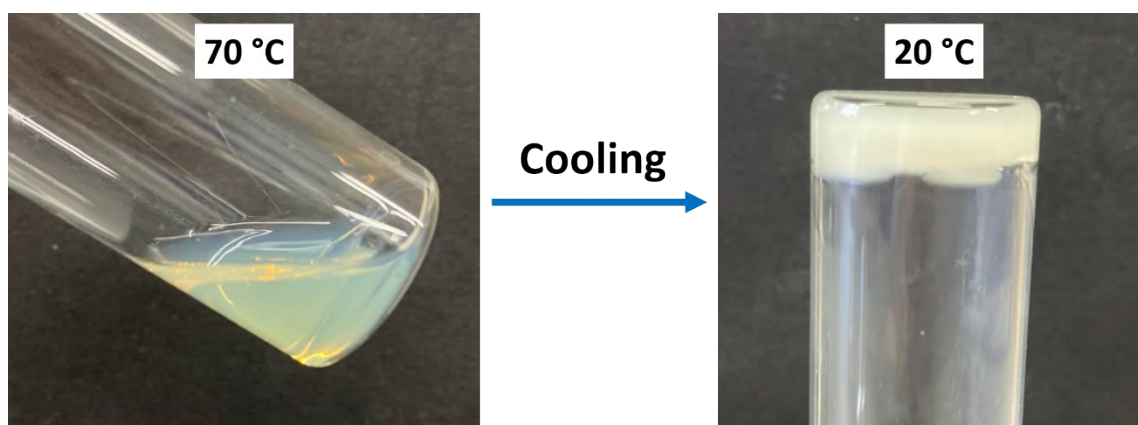| Target block copolymer composition	Z-average diameter / nm (PDI)	
	n-Heptane	Chloroform
$POAA_{85}$-$PDMAC_{200}$	62 (0.07)	/
$POAA_{85}$-$PDMAC_{195}$-$PEGDA_{20}$	65 (0.06)	90 (0.09)

Figure S6. Digital photographs recorded for POAA$_{85}$-PDMAC$_{150}$ diblock copolymer nano-objects prepared in *n*-dodecane at 70 °C (reaction temperature) and at 20 °C. The increase in turbidity suggests thermoresponsive behavior.
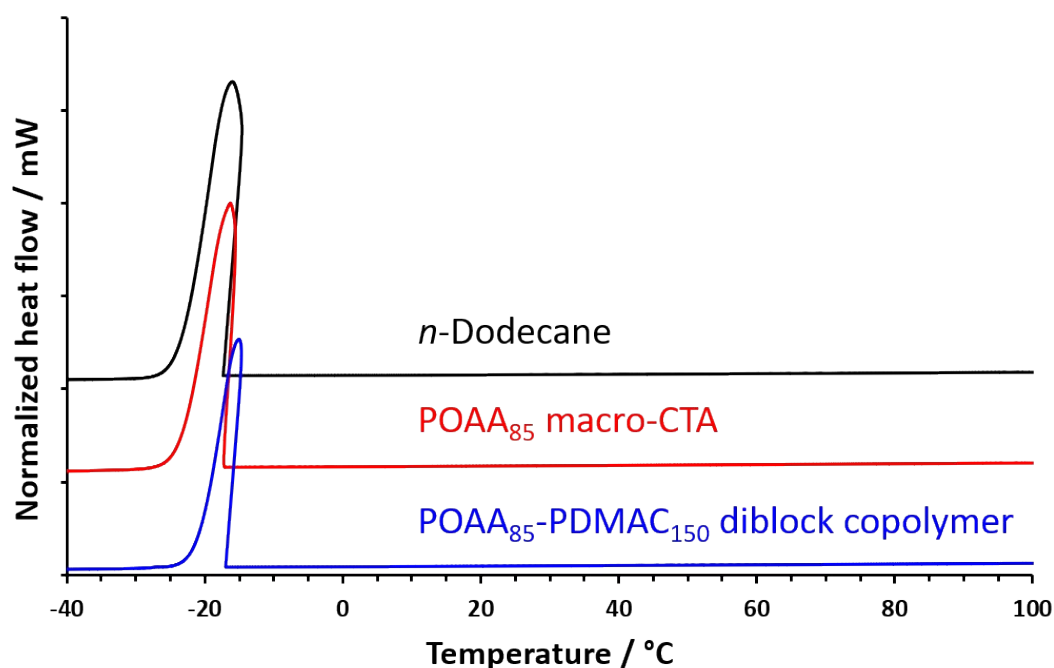

Figure S7. DSC curves recorded for *n*-dodecane (black), a 20% w/w solution of POAA$_{85}$ macro-CTA in *n*-dodecane (red) and a 20% w/w dispersion of POAA$_{85}$-PDMAC$_{150}$ nanoparticles in *n*-dodecane (blue) when cooling from 100 °C to −40 °C at 10 °C min^{-1}. The strong exotherm observed at around −20 °C is attributed to the freezing point of *n*-dodecane (usually observed at −9 °C but shifted in this data set owing to the relatively fast cooling rate). Importantly, these DSC curves do not provide any evidence for crystallization of either the POAA homopolymer or POAA-stabilized nanoparticles in *n*-dodecane.
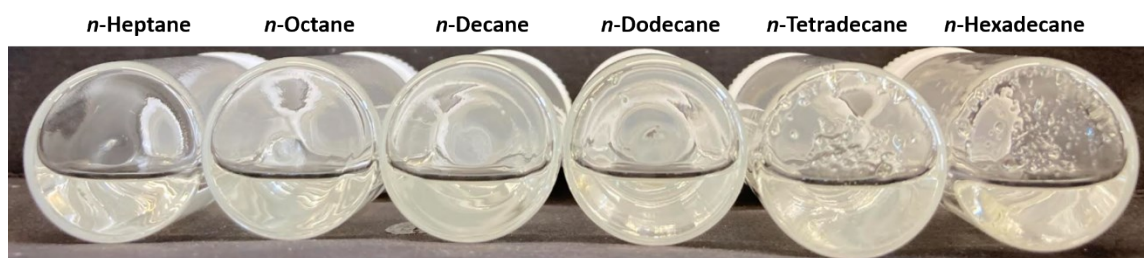
Figure S8. Digital photographs recorded for POAA$_{85}$ macro-CTA when added at 1.0% w/w concentration in turn to six different *n*-alkanes at 20 °C. This homopolymer is fully soluble in *n*-heptane, *n*-octane, *n*-decane and *n*-dodecane but it is clearly insoluble in *n*-tetradecane and *n*-hexadecane at this temperature.
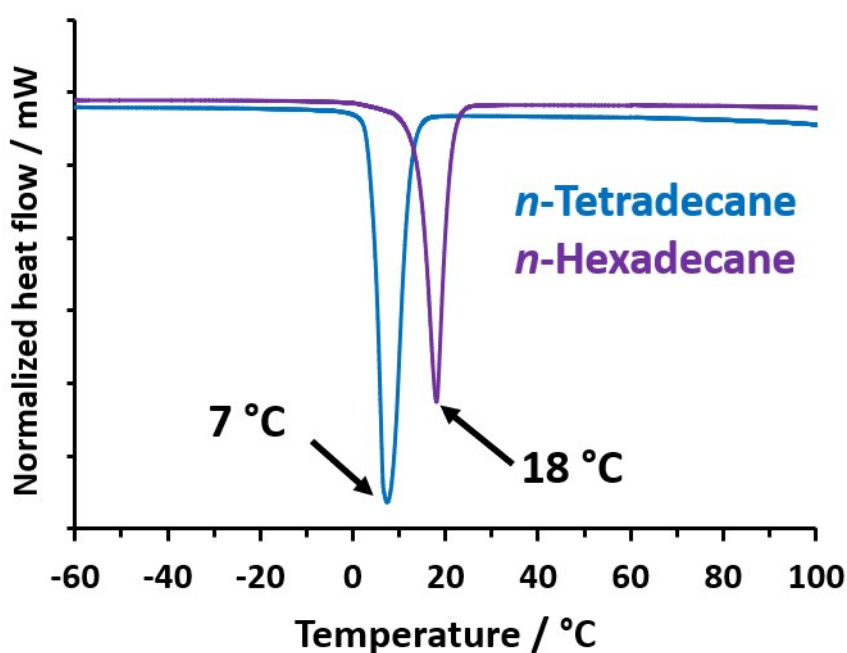

Figure S9. DSC curves recorded for a 50% w/w solution of POAA$_{85}$ macro-CTA in either *n*-tetradecane (blue) or *n*-hexadecane (purple) when heating from −60 °C to 100 °C at 10 °C min^{-1}. The strong endotherms observed at around 7 °C and 18 °C are assigned to the melting points of *n*-tetradecane and *n*-hexadecane, respectively.

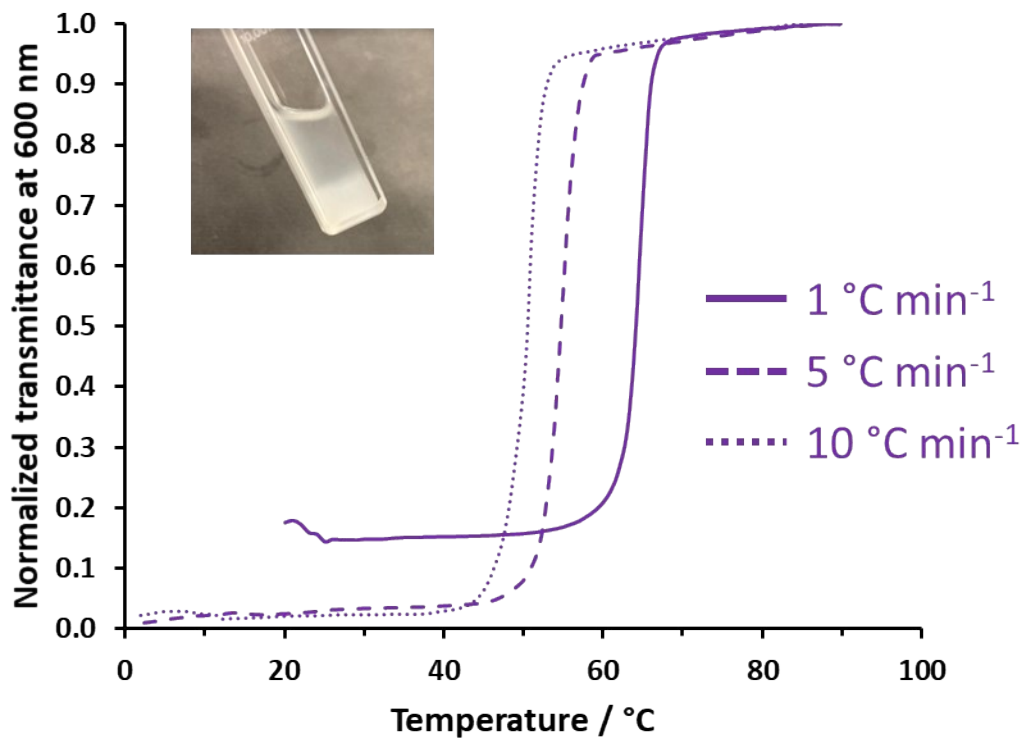**Figure S10.** Normalized transmittance (λ = 600 nm) against temperature curves recorded for 1.0% w/w dispersions of POAA$_{85}$-PDMAC$_{150}$ nanoparticles synthesized in *n*-hexadecane on cooling from 90 °C to 20 or 2 °C at cooling ramp rates of 1, 5 and 10 °C min^{-1}. The inset image is a digital photograph of the cuvette after a 1 °C min^{-1} cooling experiment indicating macroscopic sedimentation of the copolymer nanoparticle aggregates.
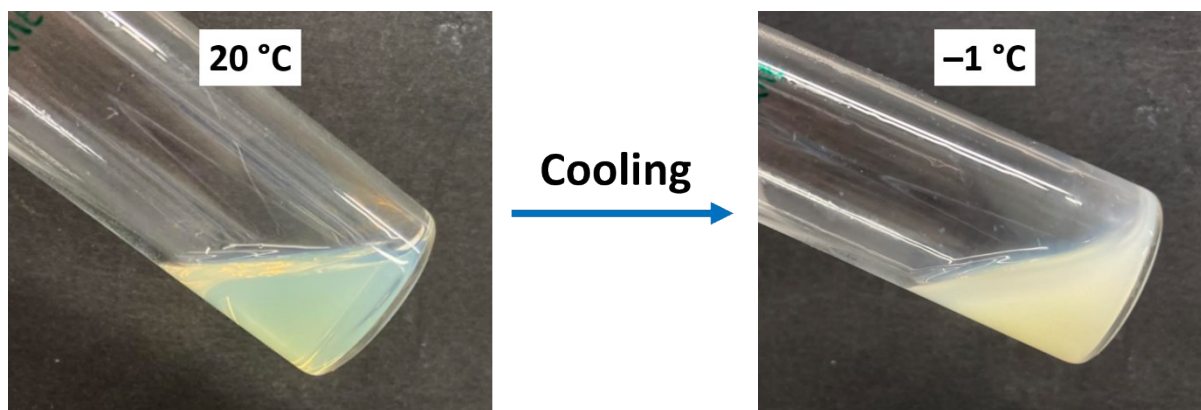

Figure S11. Digital photographs recorded for POAA$_{85}$-PDMAC$_{150}$ diblock copolymer nano-objects prepared in *n*-decane at 20 °C and −1 °C. The increase in turbidity suggests thermoresponsive behaviour for this dispersion.