Electronic Supplementary Information

Aqueous Copper-mediated Reversible Deactivation Radical Polymerization (RDRP) utilizing polyetheramine derived initiators

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Instrumentation

Nuclear Magnetic Resonance (^{1}H and ^{13}C NMR) spectra were obtained from Bruker DPX-300 and DPX-400 spectrometers. Deuterated solvents were used for NMR sample preparation and monomer conversion was calculated by comparing the vinyl protons with the polymer backbone protons.

Size exclusion chromatography (SEC) was used for determination of molecular weight (M_n and M_w) and dispersity of the polymers. The spectra were recorded on a Varian 390-LC system equipped with differential refractive index, UV and viscometry detectors, 2 x PLgel 5 mm mixed-D column (300 x 7.5 mm) using DMF (5mM NH_4BF_4) as the mobile phase at 50 ^oC. For the calibration, narrow linear poly(methyl methacrylate) standards were used in range of 200 to 1.0 x 106 g/mol. All samples were passed through 0.2 μm PTFE filter before SEC-analysis.

Matrix-assisted laser desorption/ionization-time of flight mass spectrometry (MALDI-ToF MS) was recorded in linear or reflex mode on a Bruker Daltonics Ultraflex II MALDI-ToF mass spectrometer, equipped with a nitrogen laser delivering 2 ns laser pulses at 337 nm with positive ion ToF detection performed using an accelerating voltage of 25 kV. The matrix solution was trans-2-[3-(4-tertbutylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) in THF (20 mg/mL solution). Sodium iodide (5mg/mL in THF) was added to improve the ionization. Polymer samples were dissolved to a concentration of 10 mg/mL. Calibration was performed with different linear poly (ethylene glycol) methyl ether standards.

Infrared absorption spectra (FTIR) were recorded on a Bruker VECTOR-22 FTIR spectrometer using a diamond crystal plate and a pressure tower.

UV-Vis spectra were recorded on Agilent Technologies Cary60 UV-Vis at a wavelength of 500 nm using a cuvette with 1 cm path length, which was employed for the cloud point temperature studies. The solutions (1mg/mL) were heated and cooled (temperature range: 20-80 ^{o}C) at a rate of 1 ^{o}C min^{-1} for cycles.

Dynamic light scattering (DLS) experiments were conducted at different temperatures on a MALVERN Zetasizer (backscattering angle is 173^{o}C) utilizing a quartz cuvette with 1 cm path length.

Thermogravimetric analysis (TGA) results were carried out by Mettler-Toledo TGA under nitrogen from 25 ^{o}C to 600 ^{o}C, using standard 40 μL aluminium crucibles with lids.

Differential scanning calorimetry (DSC) data was recorded on a Mettler-Toledo DSC1 under nitrogen from -100 ^{o}C to 250 ^{o}C using 40μL aluminium crucibles with lids.

Experimental Procedures

Materials

N-Isopropylacrylamide (NIPAM, 97%) was purchased from Sigma-Aldrich and purified *via* recrystallization from hexane. *N,N*-Dimethylacrylamide (DMA, 99.5%, Sigma-Aldrich), was passed through a column of basic alumina prior to use. Trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) and 2, 5-dihydroxybenzoic acid (DHB) were purchased from Sigma-Aldrich. Jeffamine (M-1000 and M-2005) were obtained from Huntsman Corporation. HPLC grade water (H_2O, VWR international, LLC) was directly used as solvent for disproportionation and polymerization reactions. *Tris*(2-(dimethylamino)ethyl)amine (Me_6TREN) was synthesized according to the literature and stored under a nitrogen atmosphere prior to use.[1] The polyetheramine-based macroinitiators were synthesized according to a general amidation reaction procedure. Copper(I) bromide (Cu(I)Br, 98%) was purchased from Sigma-Aldrich and washed with acetic acid and ethanol, and dried in *vacuo* to remove Cu(II) bromide impurities.

Macroinitiator synthesis

Jeffamine (M-1000, 38.7 g, 38.7 mmol) and triethylamine (7.16 mL, 51.5 mmol) were dissolved in anhydrous dichloromethane (100 mL) in a round-bottom flask. The flask was placed in an ice-bath to cool to 0 ^{o}C before the addition of α-bromoisobutyryl

bromide (5.25 mL, 42.6 mmol) in dichloromethane (20 mL) dropwise under nitrogen flow for 1 hour. The reaction solution was stirred at 0 °C for a further 45 min, prior warming to ambient temperature and stirred overnight. The reaction mixture was subsequently poured into ice-water (200 mL) and the organic layer was extracted with dilute $NaHCO_3$ (2 × 50 mL) followed by water (2 × 50 mL) and again with dilute $NaHCO_3$ (2 × 50 mL). The organic layer was dried over $MgSO_4$ and the volatiles removed under reduced pressure. The crude product was purified by dissolving in DCM and passed through a column of basic aluminium oxide to give a viscous off-white oil with 55% yield. The yield of the pure hydrophobic polyetheramine macroinitiator M-2005-Int was 41%. M-1000-Int: ^{1}H NMR (DMSO-d_6) δ (ppm): 1.05-1.10 (3H, (OCH_2CHCH_3)), 1.80-1.90 (6H, $COC(CH_3)_2Br$), 3.20-3.25 (3H, $CH_3(OCH_2CH_2)$), 7.51-7.54 (1H, NHCO); MALDI-TOF MS: $M_{n,Exact}[M+Na^+]$ = 1124.5555 u, $M_{n,Exp}[M+Na^+]$ = 1124.4353 u; FTIR: 1669 cm^{-1} $\nu_{C=O}$. M-2005-Int: ^{1}H NMR ($CDCl_3$) δ (ppm): 1.05-1.10 (3H, (OCH_2CHCH_3)), 1.50-2.00 (6H, $COC(CH_3)_2Br$), 3.27-3.50 (3H, $CH_3(OCH_2CH_2)$), 6.65-7.00 (1H, NHCO); MALDI-TOF MS: $M_{n,Exact}[M+Na^+]$ = 2293.4707 u, $M_{n,Exp}[M+Na^+]$ = 2293.7828 u; FTIR: 1679 cm^{-1} $\nu_{C=O}$.

General procedure for homopolymerizations by aqueous Cu-RDRP utilizing the pre-disproportionation of Cu(I)Br (target DP_n = 80)

The hydrophilic polyetheramine macroinitiator (M-1000-Int, 95.6 mg, 0.087 mmol) and NIPAM (787.6 mg, 6.96 mmol) were charged into a vial and dissolved in H_2O (3.5 mL). When the hydrophobic macroinitiator was used, instead of water, equal volume of methanol was used for its total dissolution. The solution was stirred and deoxygenated with nitrogen bubbling in an ice bath for 15 mins. Me_6TREN (9.3 µL, 0.0348 mmol) and H_2O (2 mL) were placed into a 25 mL Schlenk tube with a magnetic stirring bar and rubber septum. Cu(I)Br (10 mg, 0.0696 mmol) was then added with rapid stirring. Disproportionation happened immediately with formation of a red/purple Cu(0) precipitate and the soluble blue Cu(II) complex, and the mixture was deoxygenated by nitrogen sparging for 2 mins. Subsequently the deoxygenated monomer/macroinitiator solution was transferred into the Schlenk tube containing the copper species *via* a deoxygenated syringe and the polymerization was left to commence at 0 °C. After 15 min, samples (~0.1 mL) were taken for analysis. Samples for ^{1}H NMR analysis were directly diluted with D_2O, and catalyst residues were removed by filtration through a column of neutral alumina to DMF-SEC analysis. The ratio of monomer to macroinitiator was changed for the different targeted DP's (as shown in Table 1)

General procedure for chain extension and block copolymerization by aqueous Cu-RDRP (DP_n = 20)

Polyether amine macroinitiator (M-1000-Int, 275 mg, 0.25 mmol) and NIPAM (566 mg, 5 mmol) were charged into a vial and dissolved in H_2O (2.5 mL), and the solution was deoxygenated with nitrogen sparging for 15 mins, in an ice bath. Me_6TREN (26µL, 0.1

mmol) and H_2O (2 mL) were placed into a septum-sealed 25 mL Schlenk tube with a magnetic stirring bar. Cu(I)Br (14 mg, 0.1 mmol) was then added with rapid stirring. Disproportionation happened immediately with formation of a red/purple Cu(0) precipitate and the soluble blue Cu(II) complex, and the mixture was deoxygenated by nitrogen sparging for 2 mins. Subsequently the deoxygenated monomer/macroinitiator solution was transferred into the Schlenk tube containing the copper species *via* a deoxygenated syringe and the polymerization was left to commence at 0 ^{o}C. After 15 min, samples (~0.1 mL) were taken for analysis. Samples for ^{1}H NMR analysis were directly diluted with D_2O, and catalyst residues were removed by filtration through a column of neutral alumina to DMF-SEC analysis.
Immediately, a degassed solution of NIPAM (566 mg, 5 mmol) was transferred into the reaction Schlenk tube using a deoxygenated syringe, and the reaction solution was sampled once again after 15 min. Monomer conversion was calculated by comparison of vinyl protons with the polymer backbone protons.

Additional figures

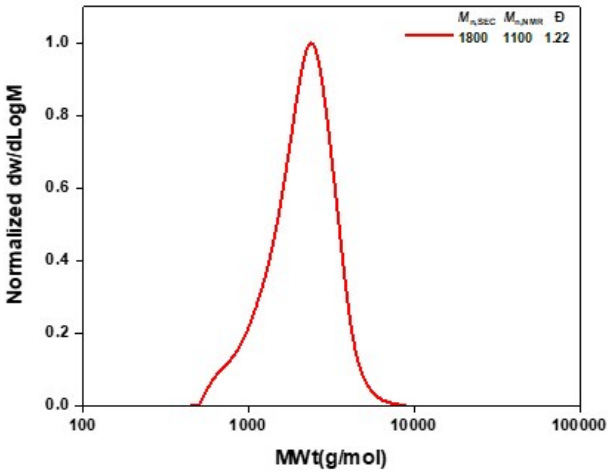

Figure S1a. SEC trace of the hydrophilic macroinitiator M-1000-Int.

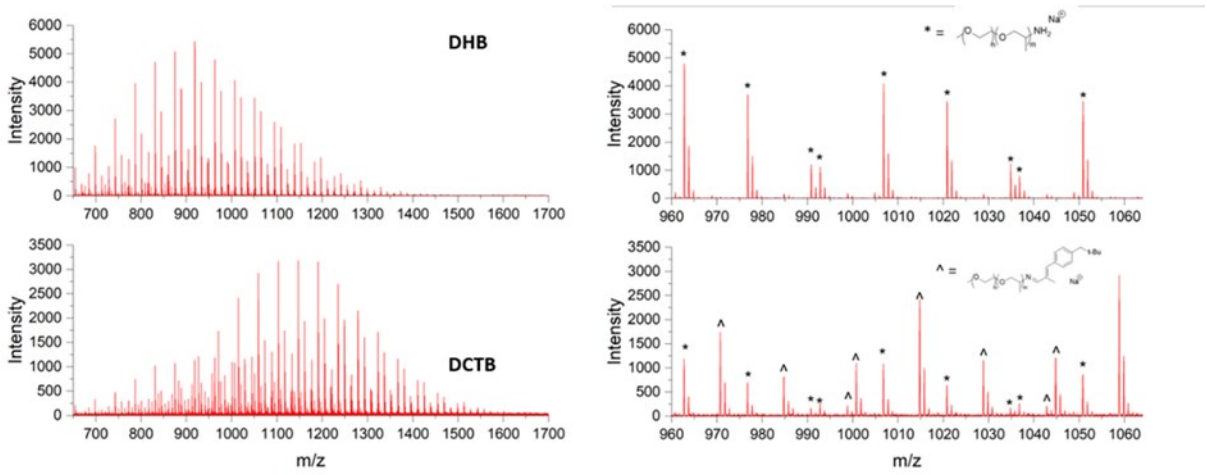

Figure S1b. MALDI-ToF spectra of M-1000 Jeffamine, both prepared using THF and NaI, and 2 different matrices (DHB and DCTB).

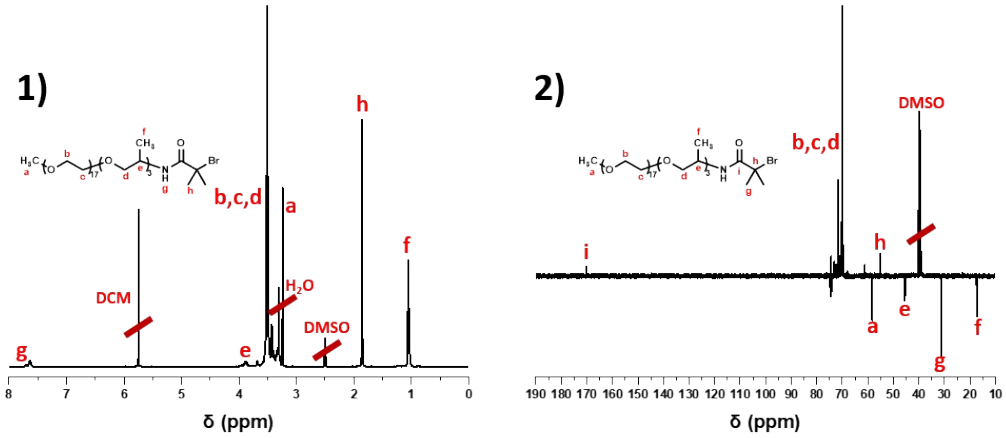

Figure S2. ^{1}H NMR (**1**) and ^{13}C NMR (**2**) spectrum of the hydrophilic Jeffamine macroinitiator M-1000-Int, using DMSO-d_6 as the solvent.

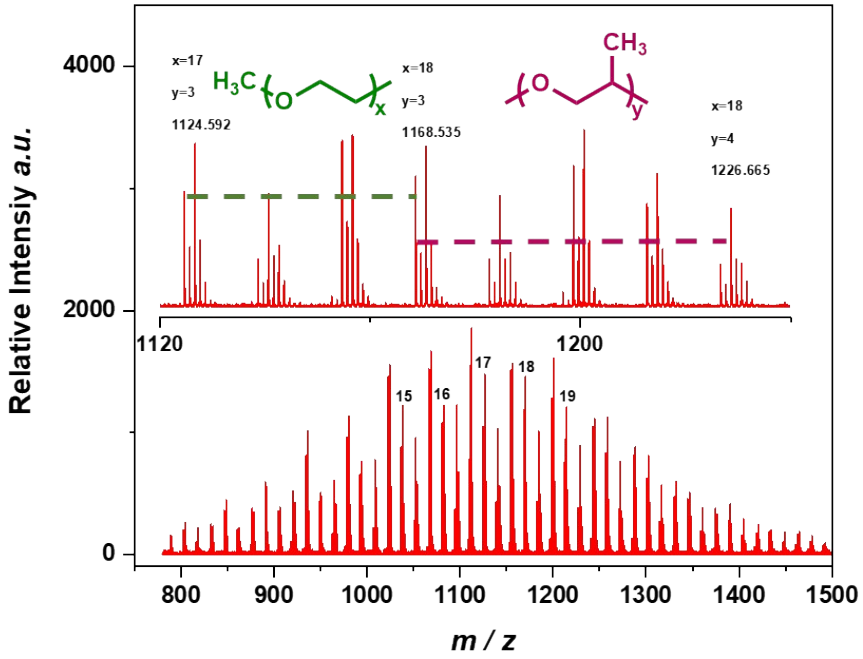

Figure S3. MALDI-TOF MS of the hydrophilic macroinitiator M-1000-Int.

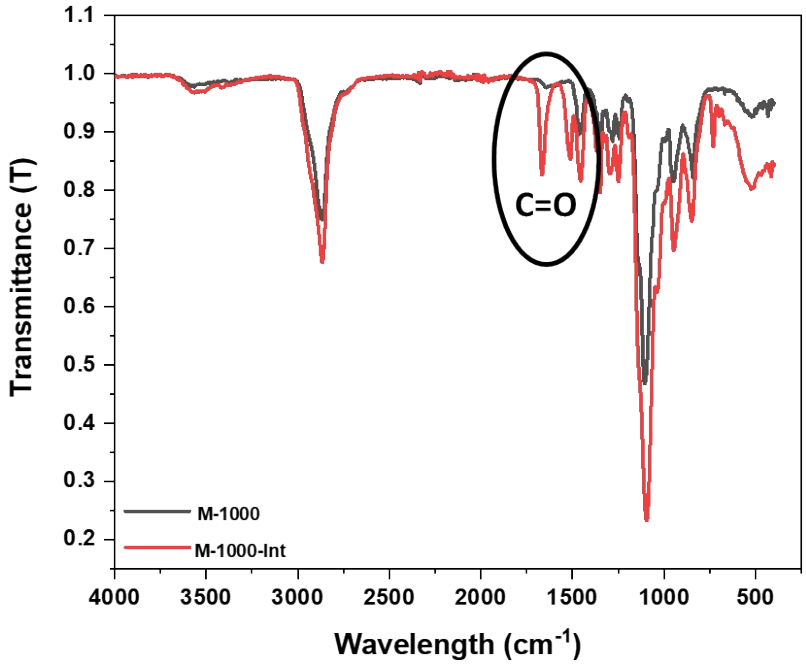

Figure S4. FTIR spectrum of Jeffamine (M-1000) and the Jeffamine macroinitiator M-1000-Int.

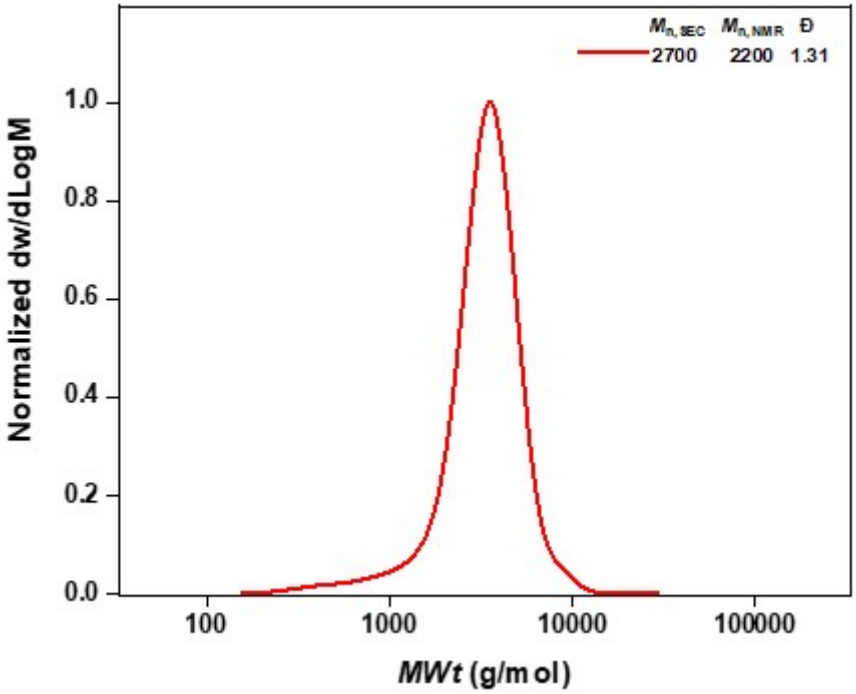

Figure S5. SEC trace of the hydrophobic Jeffamine macroinitiator M-2005-Int.

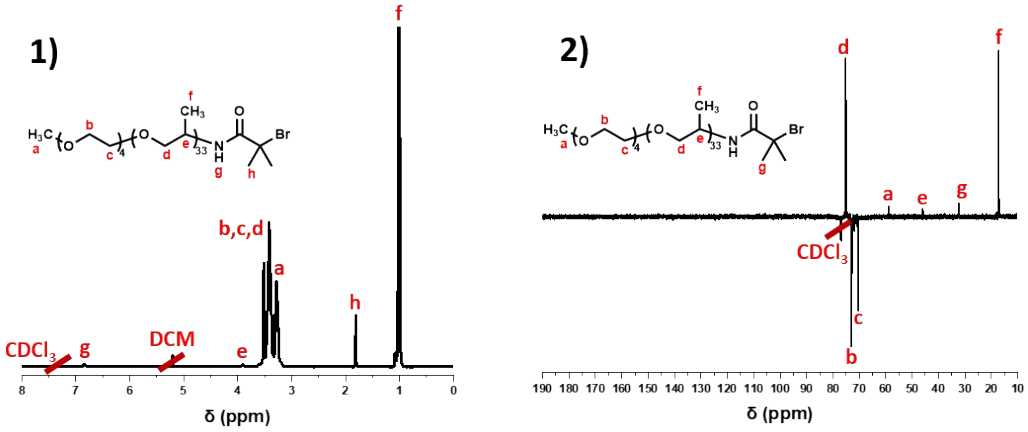

Figure S6. ^{1}H NMR (**1**) and ^{13}C NMR (**2**) spectrum of the hydrophobic Jeffamine macroinitiator M-2005-Int, using $CDCl_3$-*d* as the solvent.

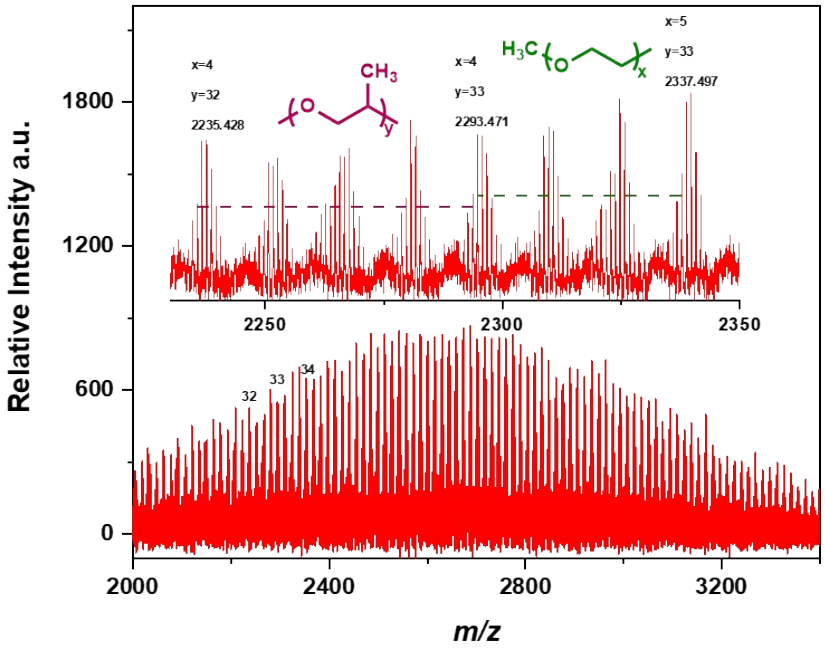

Figure S7. MALDI-TOF MS of the hydrophobic Jeffamine macroinitiator M-2005-Int.

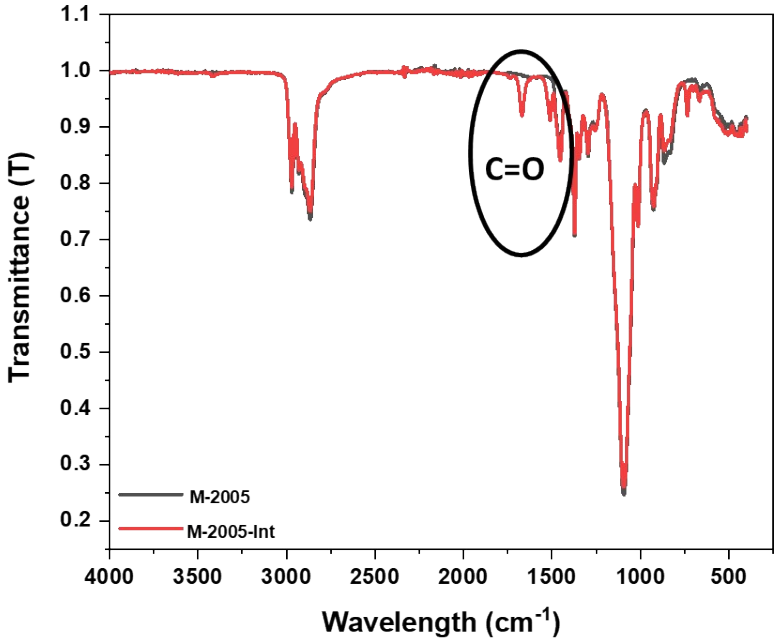

Figure S8. FTIR spectrum of Jeffamine (M-2005) and the Jeffamine macroinitiator M-2005-Int.

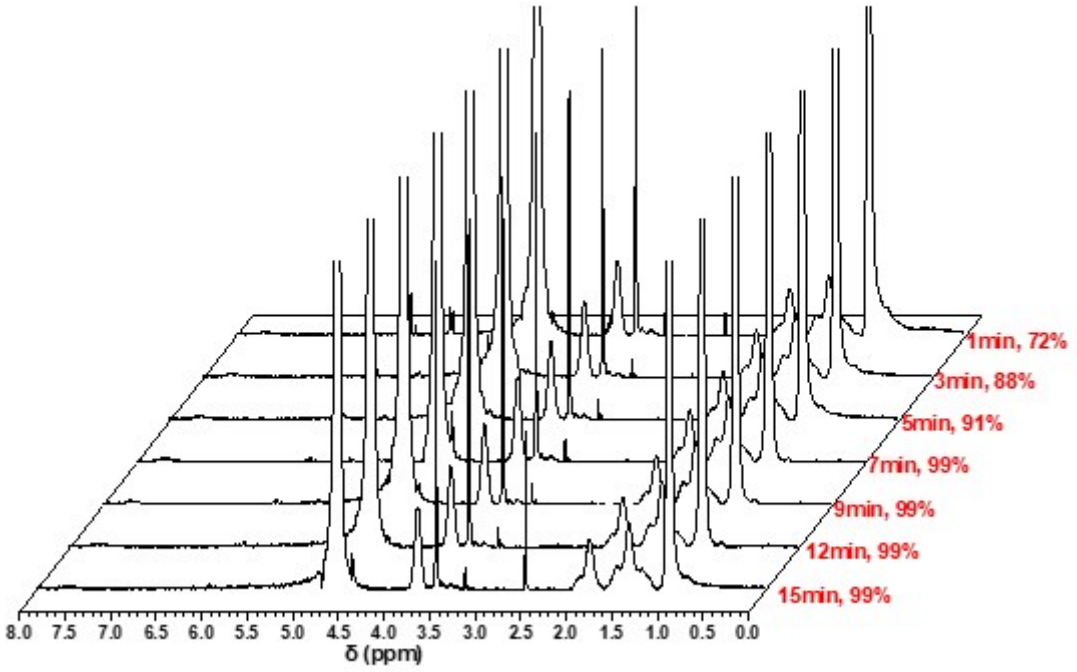

Figure S9. ^{1}H NMR kinetics (in D_2O) of the poly(N-isopropyl acrylamide)$_{80}$ homopolymer prepared by aqueous Cu-RDRP at 0^{o}C, utilizing the hydrophilic Jeffamine macroinitiator (M-1000-Int).

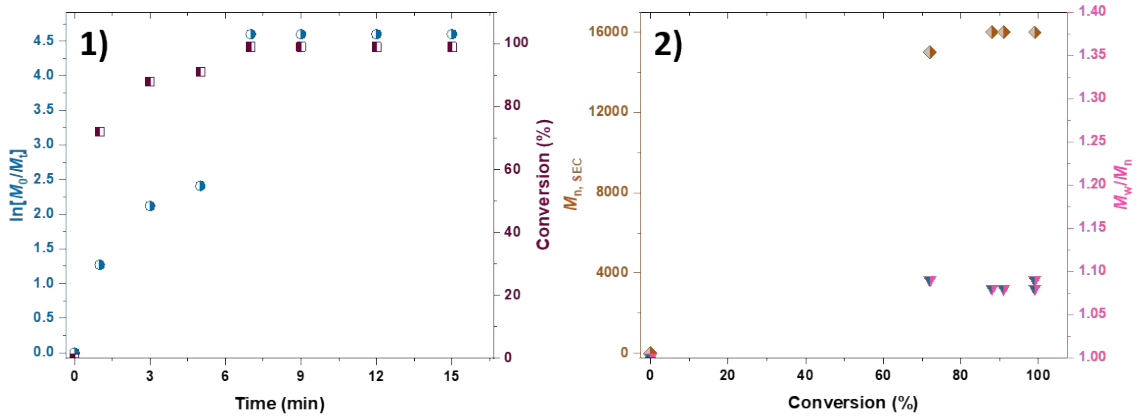

Figure S10. (**1**). Kinetic plots of ln[M_0/M_t] (left, blue) and conversion (right, dark purple) *versus* time, (**2**). Plots of M_n *versus* conversion (left, brown) and dispersity (M_w/M_n) *versus* conversion (right, pink). Conditions: [NIPAM]:[I]:[Cu(I)Br]:[Me_6TREN]=[80]:[1]:[0.8]:[0.4]. (I=hydrophilic Jeffamine macroinitiator, M-1000-Int).

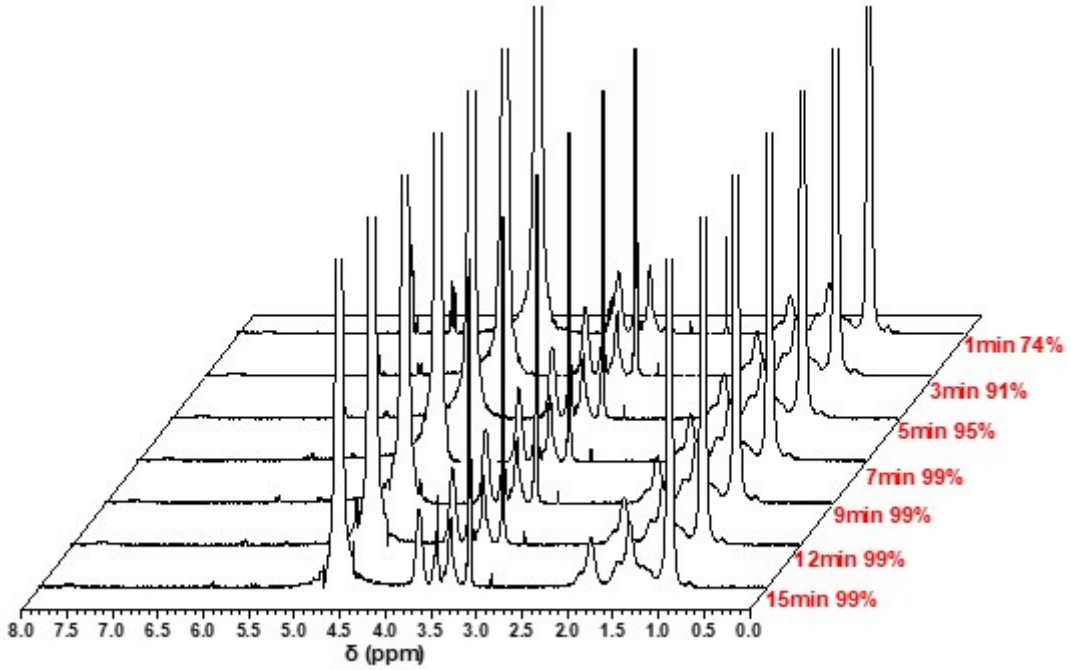

Figure S11. ^{1}H NMR kinetics (in D_2O) of poly(N-isopropyl acrylamide)$_{80}$ prepared by aqueous Cu-RDRP at 0^{o}C, utilizing the hydrophobic Jeffamine macroinitiator (M-2005-Int).

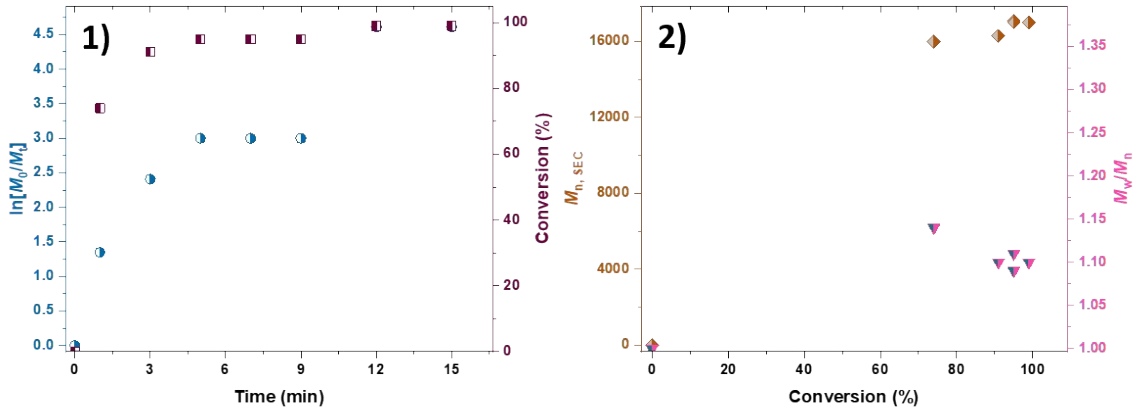

Figure S12. (**1**). Kinetic plots of ln[M_0/M_t] (left, blue) and conversion (right, dark purple) *versus* time, (**2**). Plots of M_n *versus* conversion (left, brown) and dispersity (M_w/M_n) *versus* conversion (right, pink). Conditions: [NIPAM]:[I]:[Cu(I)Br]:[Me_6TREN]=[80]:[1]:[0.8]:[0.4]. (I=hydrophobic Jeffamine macroinitiator, M-2005-Int).

Table S1. Chain extension and block copolymers prepared *via* aqueous Cu(0)-RDRP at 0°C, utilizing M-1000-Int (1-4) and M-2005-Int (5-8).

Entry	Block No.	M	$M_{n,theo}$ g mol^{-1}	$M_{n,SEC}$ g mol^{-1}	Đ	Conv. %,$_{NMR}$
1	B 1	$NIPAM_{20}$	3400	6800	1.09	>99
	B 2	$NIPAM_{20}$	5600	11200	1.08	>99
2	B 1	$NIPAM_{20}$	3400	4300	1.21	>99
	B 2	DMA_{20}	5600	10600	1.13	>99
3	B 2	$NIPAM_{20}$	3400	4600	1.21	>99
	B 2	DMA_{40}	9400	13800	1.13	>99
4	B 1	$NIPAM_{20}$	3400	4400	1.21	>99
	B 2	DMA_{80}	17000	19000	1.20	>99
5	B 1	$NIPAM_{20}$	4500	5000	1.32	>99
	B 2	$NIPAM_{20}$	6700	8000	1.15	>99
6	B 1	$NIPAM_{20}$	4500	5100	1.17	>99
	B 2	DMA_{20}	6500	11500	1.08	>99
7	B 1	$NIPAM_{20}$	4500	6500	1.19	>99
	B 2	DMA_{40}	10400	14000	1.15	>99
8	B 1	$NIPAM_{20}$	4500	4500	1.18	>99
	B 2	DMA_{80}	18000	21000	1.17	>99

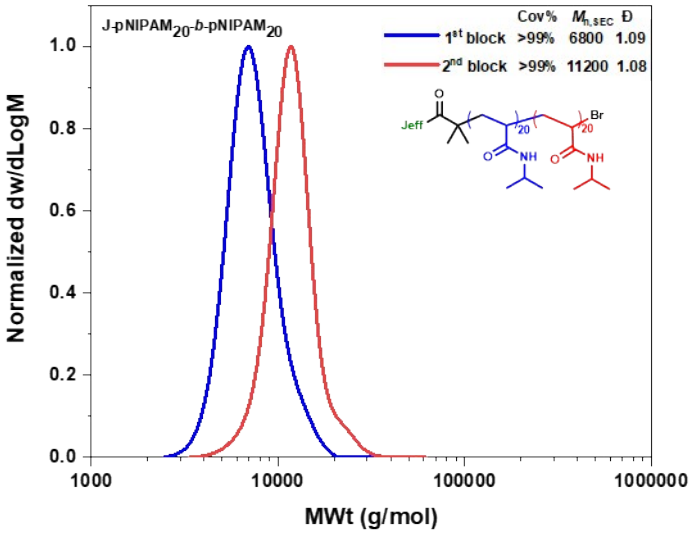

Figure S13. SEC-traces for the Jeff-pNIPAM$_{20}$-*b*-pNIPAM$_{20}$ utilizing the hydrophilic Jeffamine macroinitiator (M-1000-Int).

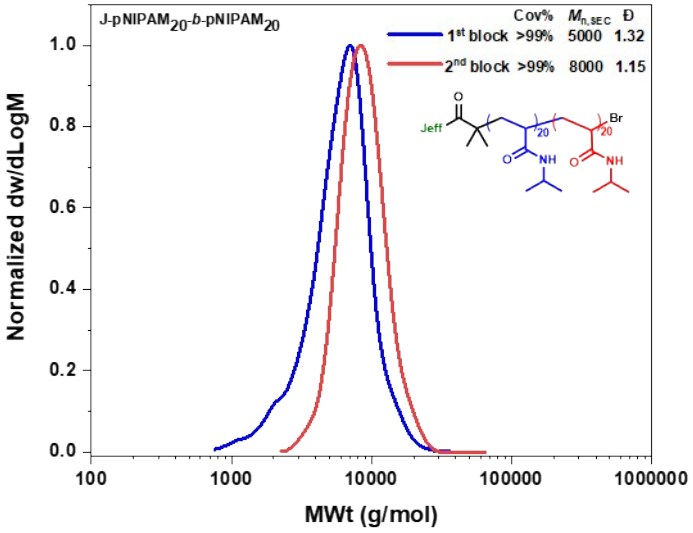

Figure S14. SEC-traces for the Jeff-pNIPAM$_{20}$-*b*-pNIPAM$_{20}$ utilizing the hydrophobic Jeffamine macroinitiator (M-2005-Int).

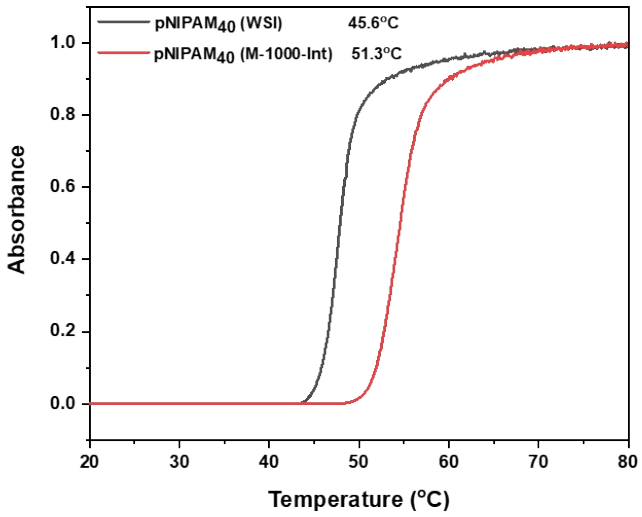

Figure S15. Cloud point measurements of poly (N-isopropyl acrylamide)$_{40}$ and M-1000-Int-pNIPAM$_{40}$.

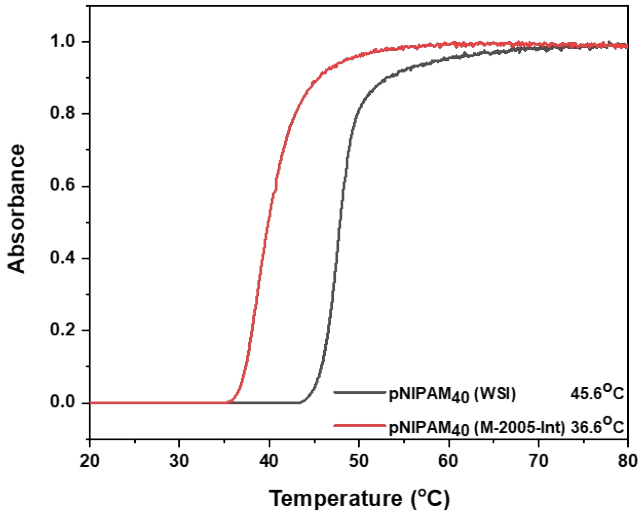

Figure S16. Cloud point measurements of poly (N-isopropyl acrylamide)$_{40}$ and M-2005-Int-pNIPAM$_{40}$.

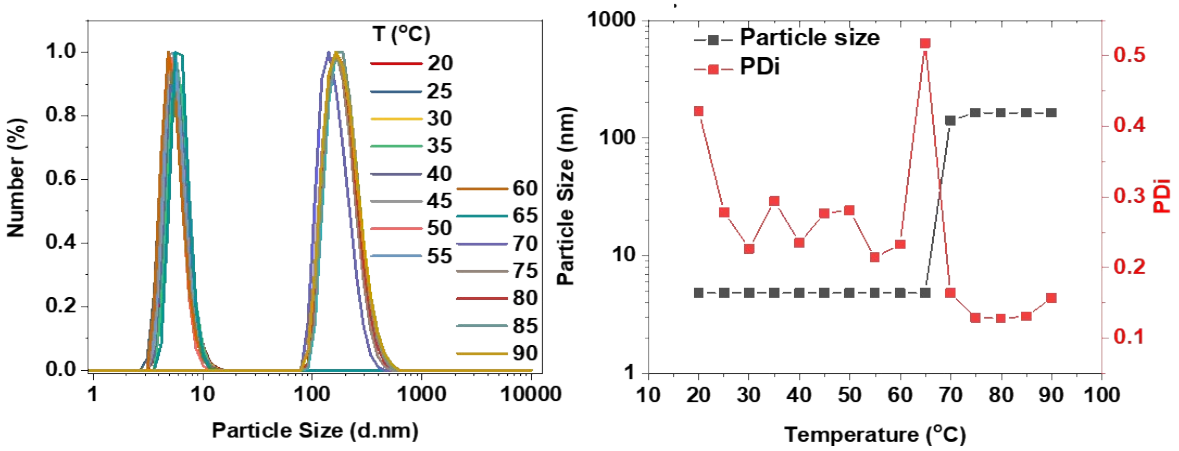

Figure S17. DLS plots for the M-1000-Int-poly(NIPAM)$_{20}$-*b*-poly(DMA)$_{80}$ at different temperatures (left) and plot of the particle size and PDi values at different temperatures (right).

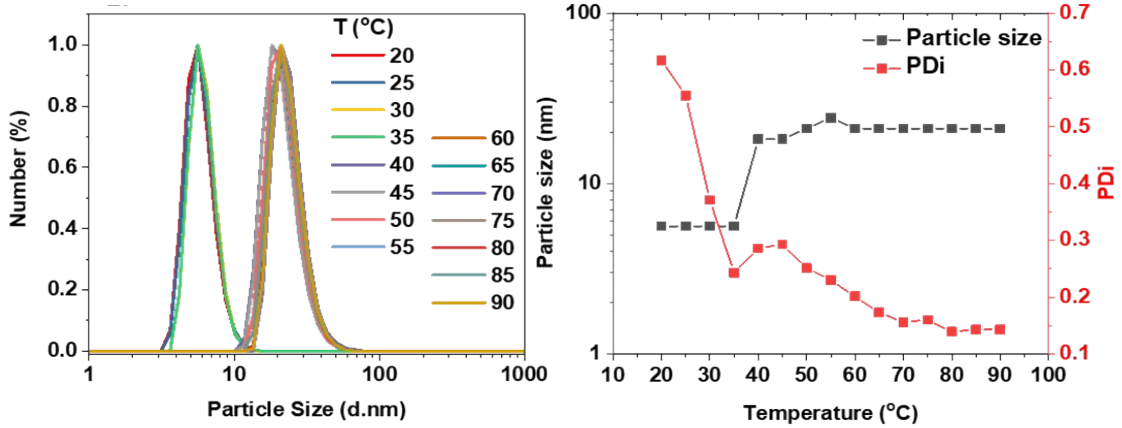

Figure S18. DLS plots for the M-2005-Int-poly(NIPAM)$_{20}$-*b*-poly(DMA)$_{80}$ at different temperatures (left) and plot of the particle size and PDi values at different temperatures (right).

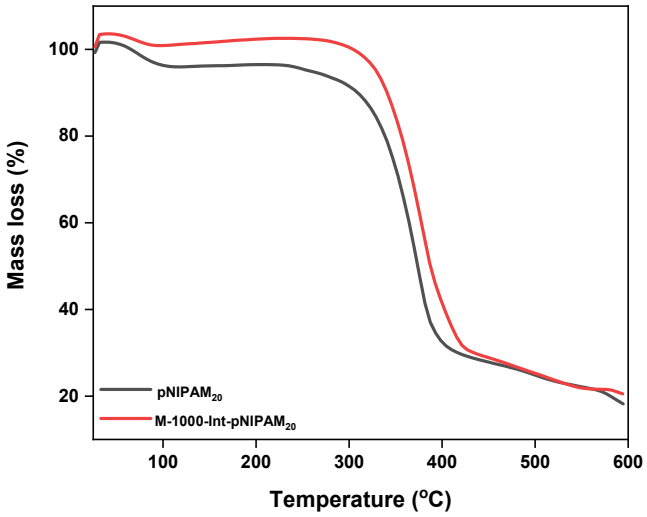

Figure S19. TGA plots of $pNIPAM_{20}$ (WSI-initiated) and M-1000-Int-$pNIPAM_{20}$.

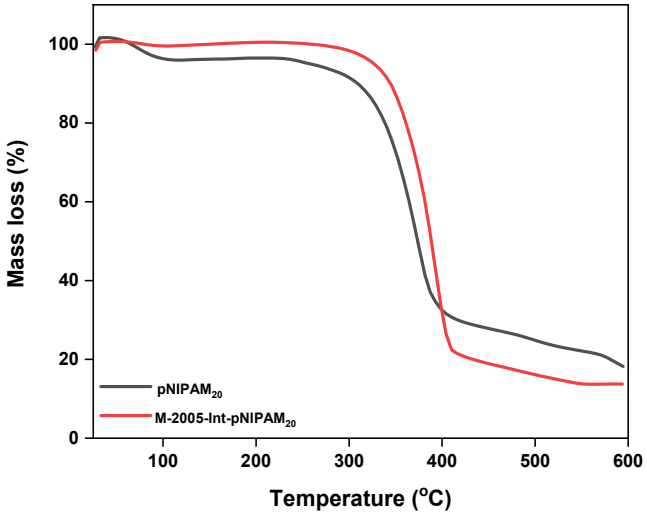

Figure S20. TGA data showing the comparison of $pNIPAM_{20}$ (WSI-initiated) and M-2005-Int-$pNIPAM_{20}$

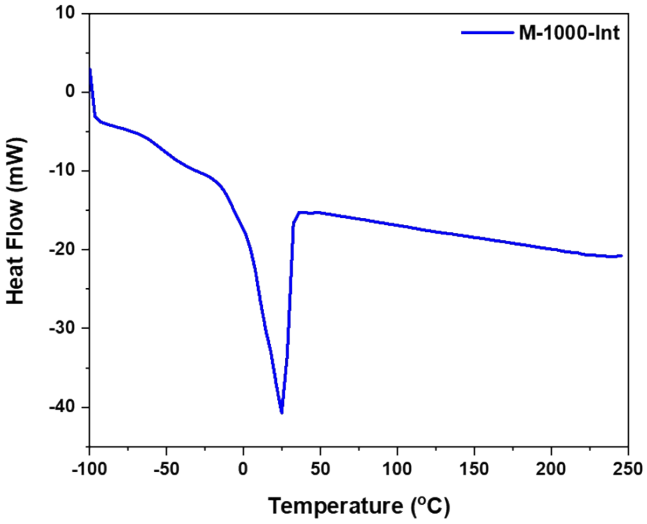

Figure S21. DSC plot of the Jeffamine M-1000-Int.

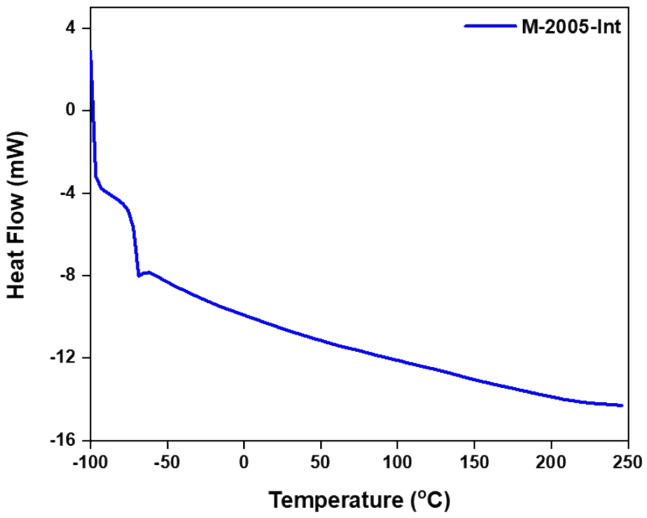

Figure S22. DSC plot of the Jeffamine M-2005-Int.

Table S2. T_g values for the WSI- & Jeffamine-initiated polymers synthesized in this work.

Entry	Polymer	T_g (°C) *
1	WSI-pNIPAM$_{20}$	136.0
2	WSI-pNIPAM$_{40}$	137.1
3	WSI-pDMA$_{40}$	120.8
4	M-1000-Int	27.7
5	M-2005-Int	-69.9
6	M-1000-Int-pNIPAM$_{40}$	104.8
7	M-2005-Int-pNIPAM$_{40}$	115.7
8	M-1000-Int-pNIPAM$_{20}$-*b*-pDMA$_{20}$	90.6
9	M-1000-Int-pNIPAM$_{20}$-*b*-pDMA$_{40}$	98.6
10	M-1000-Int-pNIPAM$_{20}$-*b*-pDMA$_{80}$	107.9
11	M-2005-Int-pNIPAM$_{20}$-*b*-pDMA$_{20}$	101.6
12	M-2005-Int-pNIPAM$_{20}$-*b*-pDMA$_{40}$	111.3
13	M-2005-Int-pNIPAM$_{20}$-*b*-pDMA$_{80}$	114.9

* T_g values reported as the midpoint of the temperature range.

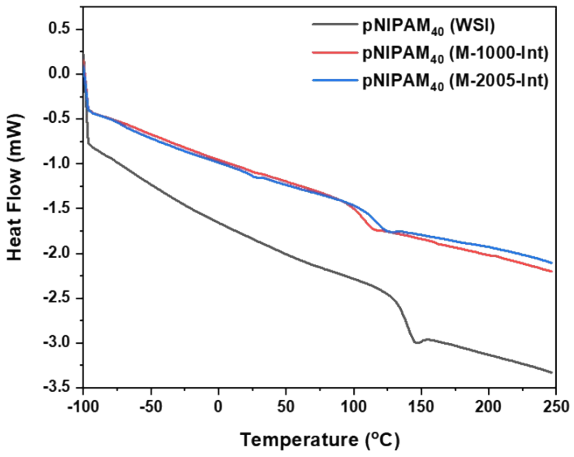

Figure S23. DCS plots of the WSI-initiated PNIPAM$_{40}$ (black), M-1000-Int-pNIPAM$_{40}$ (red) and M-2005-Int-pNIPAM$_{40}$ (blue) showing the effect of the Jeffamine-derived macroinitiators on the T_g of the synthesized polymers.

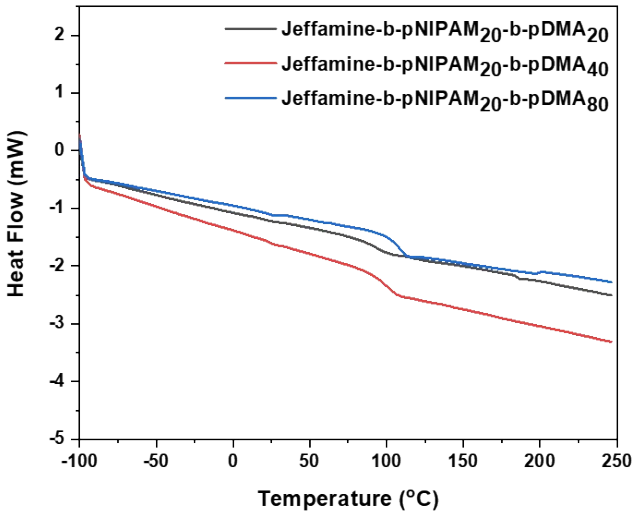

Figure S24. DSC plots of M-1000-Int-pNIPAM$_{20}$-*b*-pDMA$_x$ (DP$_n$=20, 40 and 80).

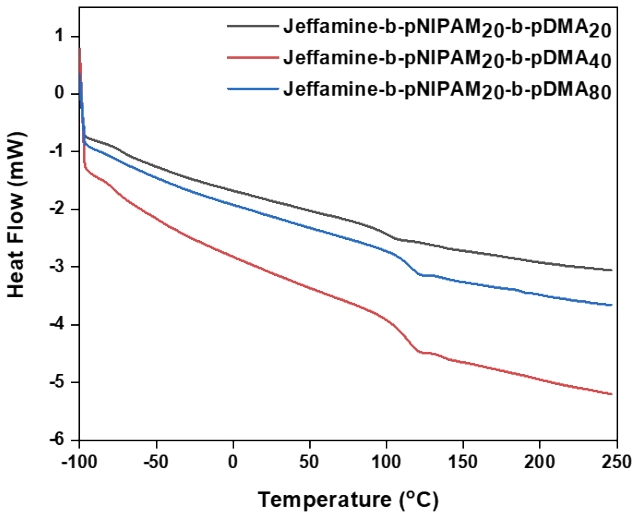

Figure S25. DSC plots of the M-2005-Int-pNIPAM$_{20}$-*b*-pDMA$_x$ (DP$_n$=20, 40 and 80).

References

1. M. Ciampolini and N. Nardi, *Inorg. Chem.*, 1966, **5**, 41-44.