Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplementary Materials for

Reversible Addition-Fragmentation Chain Transfer Step-Growth Polymerization with Commercially Available Inexpensive Bis-maleimides

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Materials and Methods

General considerations

Unless stated all reagents were purchased from commercial suppliers and used as received. Azobisisobutyronitrile (AIBN) was recrystallized with methanol. 4,4'-Bismaleimidodiphenylmethane (**M_{2A}**), Bis(3-ethyl-5-methyl-4-maleimidophenyl)methane (**M_{2B}**), 2,2-Bis[4-(4-maleimidophenoxy)phenyl]propane (**M_{2C}**), and *N*,*N*'-1,3-Phenylenedimaleimide (**M_{2D}**), were purchased from TCI chemicals. Butyl acrylate (BA) and anhydrous dioxane were passed through activated basic aluminum oxide and discarded after several uses. All NMR spectrums were recorded on a Bruker 400 MHz spectrometer in $CDCl_3$. All NMR spectrums were processed using Mestrenova.

Solvent (including initiator stock solution) is measured by weight based on the reported density to target specified volume. Initiator (AIBN) stock solution was prepared as 20 mg/ml in the solvent used for the polymerization. For simplicity, molar concentration of the reacting species here is defined by moles of the reactants divided by the total volume of the solvent (not the total volume of the solution). All experiments were carried out in 3.7 ml scintillation vials with outer dimensions of 15 mm and sealed with a 14/20 rubber septum. Thermo Scientific digital baths (Digital Dry Baths/Block Heaters – PROMO, catalog number: 88870001) equipped with heat block (holds 15 x 16 mm diameter, catalog number: 88870106) was used to maintain constant temperature. 22-gauge, 4 inch hypodermic needle (air-tite product) was used to sample the reaction mixture under argon flow. Typically, a single needle and syringe was used to take sample for both THF-SEC and ^{1}H-NMR spectroscopy, by drawing out approximately 50 to 100 µL and dropping a few drops into a vial for ^{1}H-NMR and the remaining mixture left in the needle was flushed out with THF in a separate vial for SEC analysis.

Polymer characterization

Conventional SEC analysis in THF was carried out using polystyrene calibration with a calibration range of molecular weights from 195 k to 370. These were measured using Waters 2695 separations module liquid chromatograph equipped with two Agilent ResiPore columns (linear SEC separation range up to 500 k) maintained at 35 °C, and a Waters 2412 refractive index detector. THF (with BHT as the inhibitor) was used as the mobile phase and the flow rate was set to 1 mL/min. All the samples were run with 100 µL injection volume. The dRI response was measured from the start of the peak (at low retention time) down to the high retention time corresponding to the initial species (CTA_0) at t = 0.

Intrinsic viscosity and absolute molecular weight were measured with Agilent 1260 infinity Series (Degasser, Isocratic pump, Autosampler) and Wyatt Technology Corporation detectors (Dawn Hellos – II 18 angle MALS detector, Viscostar-II viscometer, Optilab T-rEX differential refractive index detector) equipped with 3 x PLGel-Mixed-BLS (linear SEC separation range of molecular weight from 10 M to 500) and 10 µm PLgel guard column. THF (with BHT stabilizer) was used as the mobile phase and the flow rate was set to 1

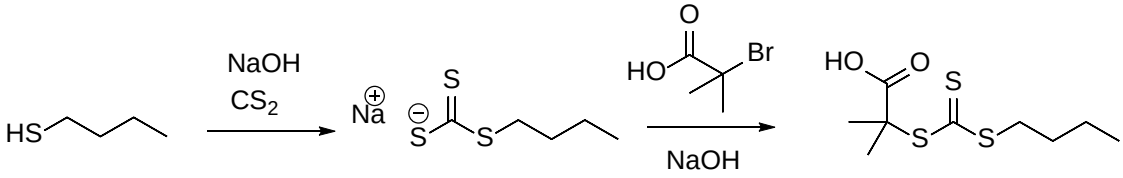
mL/min. All the samples were run with 100 µL injection volume. The dn/dC of the polymer samples in THF were determined by the instrument assuming 100 % mass recovery.

Differential scanning calorimetry (DSC) thermograms were obtained with a DSC 2500 from TA instruments. Approximately 5 mg of each sample were measured and added to a sealed pan that passed through a heat cool cycle at 10 °C/min. Reported data are from the third full cycle. The temperature ranged from -80 to 150 °C.

Thermogravimetric analyses (TGA) were measured under nitrogen with a TGA 500 from TA Instruments. About 5 mg of each sample was heated at 20 °C/min from 25 °C to 600 °C.

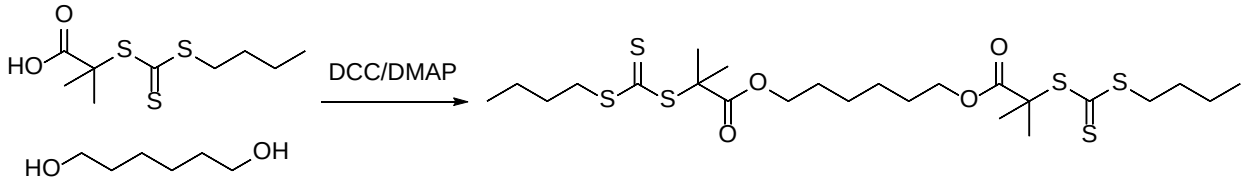
Dynamic Light Scattering measurements were carried out using Malvern Zetasizer Nano-ZS at 25 °C with a 4 mW He–Ne 633 nm laser at a scattering angle of 173° (backscattering). Samples were prepared as 10 mg/ml in deionized water and dimethylformaldehyde (DMF) filtered, which were both filtered through 0.45 µM syringe filters with nylon membrane prior to the measurement. The measurements were taken in disposable PS cuvettes (12.5 x 12.5 x 45 mm) in water and glass cuvettes (12.5 x 12.5 x 45 mm) in DMF. Samples were incubated for 1 minute at the set temperature prior to the measurement. The analysis was carried out at 25 ºC with automatic attenuation selection and measurement position.

Procedure for 2-(((butylthio)carbonothioyl)thio)-2-methylpropanoic acid synthesis:



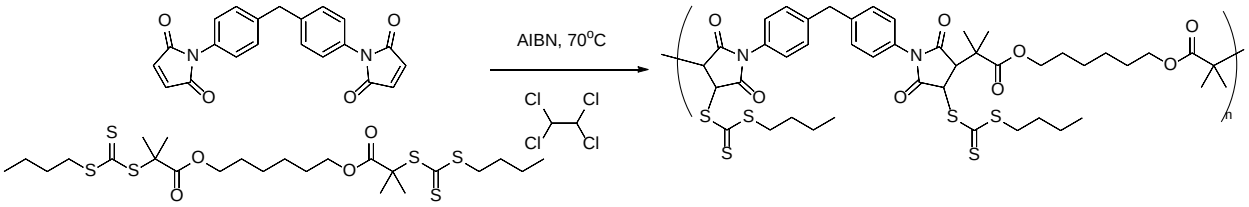
Following protocol was adapted from literature procedure[1] : 2-necked 1 liter round bottom flask equipped with stir bar was charged with NaOH (40.0 g, 1.0 mol) and deionized water (200 ml) under argon flow. After 30 minutes, butanethiol (90.0 g, 108 ml, 1.0 mol) and acetone (54 ml) was added to the solution at room temperature and left to stir for 10 minutes under argon flow. Carbon disulfide (114 g, 90.0 ml, 1.50 mol) was added and left to stir for 30 minutes at room temperature. The reaction mixture was then placed under ice bath and 2-methyl-2-bromopropanoic acid (157 g, 0.89 mol) was added under argon flow, followed by solution of NaOH (36 g, 0.90 mol) deionized water (180 ml). The solution was then left under stirring overnight at room temperature. After 16 hours, the reaction mixture was poured into a separating funnel with additional 200 ml of water and washed three times with hexane. Then 500 ml of 2 M HCl solution was added to the aqueous phase and extracted with dichloromethane (DCM). The DCM layer was then washed three times with brine and dried with sodium sulfate. The organic phase was filtered and concentrated under rotary evaporator, yielding crude orange oil. Under high vacuum the crude oil solidified, which was carefully washed with small amount of hexane and filtered, yielding 114 g of yellow crystals (50 % yield). 30 grams of the CTA was then recrystallized in 100 ml hexane, yielding 25 g of yellow needles (75 % recovered). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.29 (t, *J* = 7.5 Hz, 2H), 1.72 (s, 7H), 1.66 (m, 2H), 1.42(m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H).^{13}C NMR (400 MHz, $CDCl_3$) δ 179.21, 55.67, 36.87, 29.96, 25.32, 22.25, 13.77.

Procedure for Hexane-1,6-diyl bis(2-(((butylthio)carbonothioyl)thio)-2-methylpropanoate) synthesis:



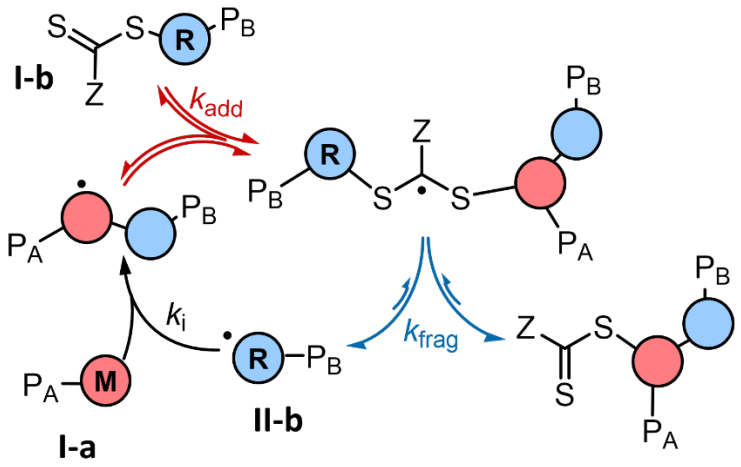
Following protocol was adapted from previously reported procedure with higher equivalence of acid precursor[2]: 2-(((butylthio)carbonothioyl)thio)-2-methylpropanoic acid (15 g, 0.060 mol), hexane diol (2.7 g, 0.023 mol) and anhydrous DCM (100 ml) was charged into dry 250 ml round bottom flask equipped with stir bar. DMAP (279 mg, 2.29 mmol) then was added, followed by DCC (11.3 g, 0.055 mol) and left to stir overnight. The mixture was directly passed through Silica gel (500 g SiO_2) eluting with DCM. The collected yellow solution was concentrated under rotary evaporator and further concentrated under high vacuum, yielding orange oil (9 g, 67 % yield). ^{1}H-NMR ($CDCl_3$, 400 MHz, ppm): δ 4.07 (t, *J* = 6.5 Hz, 4H), 3.27 (t, *J* = 7.5 Hz, 4H), 1.68 (s, 12H) 1.62(m, 8H), 1.41 (m, 4H), 1.33(m, 4H) 0.92 (t, *J* = 7.3 Hz, 6H). ^{13}C-NMR ($CDCl_3$, 400 MHz, ppm): δ 173.16, 66.08, 56.10, 36.69, 30.07, 28.41, 25.72, 25.51, 22.23, 13.79

Procedure for Poly(M_{2A}-*alt*-CTA_2) synthesis:

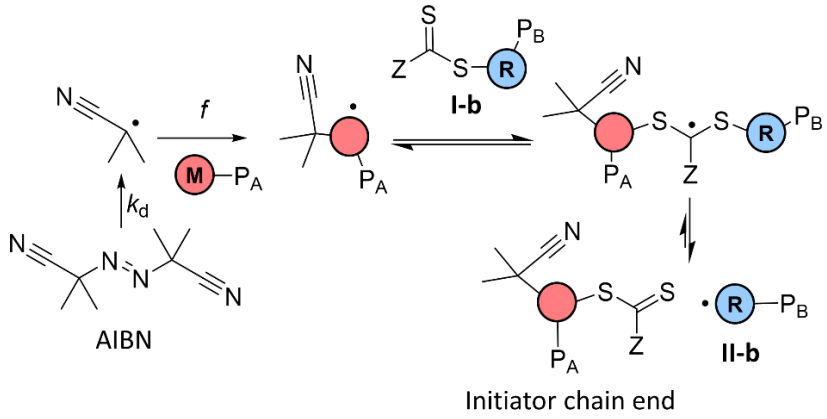


Bifunctional monomer, **M_{2A}** (175.5 mg, 0.490 mmol) was first charged into the vial, followed by bifunctional CTA, **CTA_2** (287 mg, 0.490 mmol) was carefully added via 1 ml syringe with a 21 g needle. Next, 0.577 ml tetrachloroethane (TCE) and 0.402 ml AIBN stock solution (20 mg/ml in TCE) were added to target molar concentration of [**M_{2A}**]$_0$:[**CTA_2**]$_0$:[AIBN]$_0$ = 0.5 : 0.5 : 0.05 M. The vial was then equipped with a stir bar and rubber septum, which was left to stir at 40 °C until **M_{2A}** was completely solubilized. The solution was then purged with argon for 10 minutes and then heated at 70 °C for 4 hours. Monomer conversion (*p*) was determined by ^{1}H-NMR spectroscopy by integrating C*H*=C*H* maleimide ring proton(s) relative to CH_3 at 0.96 ppm on the Z-group of the CTA. For purification, the reaction mixture was diluted in approximately equal volume of chloroform and precipitated directly into 50 ml centrifuge tube with diethyl ether and collected with centrifugation. After discarding the supernatant, the polymers were redissolved in chloroform and then reprecipitated again in diethyl ether twice. Typical yields of 60 % are obtained.

Procedure for Poly(M_{2A}-*alt*-CTA_2) synthesis with stoichiometric CTA excess:
Stoichiometric imbalance is introduced using excess of **CTA_2**, by keeping the combined concentration of the two bifunctional reagents and initiator concentration constant to the procedure above ([**M_{2A}**]$_0$ + [**CTA_2**]$_0$ = 1 M). For example, to target *r* = 0.98: **M_{2A}** (250 mg, 69.8 mmol), **CTA_2** (417 mg, 71.2 mmol), 0.831 ml TCE and 0.579 ml AIBN stock solution (20 mg/ml in TCE) was used to target initial molar concentration of [**M_{2A}**]$_0$:[**CTA_2**]$_0$:[AIBN]$_0$ = 0.495 : 0.505 : 0.05 M.



Scheme S1: RAFT Step-growth mechanism. In the proposed RAFT step-growth mechanism, the growth of polymeric chains is mediated by addition of the monomer functionality (**I-a**) with the R• species (**II-b**) of the initial bifunctional reagents or polymer end groups, which forms the polymer backbone as a radical intermediate. This backbone radical intermediate then proceeds to chain transfer with the end group CTA (**I-b**) of the initial bifunctional reagents or polymer end groups, which upon fragmentation regenerates R• species (**II-b**) and forms stable polymer backbone.



Scheme S2: Initiation mechanism of RAFT step-growth through thermal decomposition of AIBN. The AIBN decomposes with rate constant k_d and the initiator derived radical specifies then adds to monomer functional group (on initial bifunctional reagents or polymer end groups) with initiator efficiency, *f*. The resulting monomer-centered radical species which proceeds to chain transfer with end group CTA (**I-b**) (of the initial bifunctional reagents or polymer end groups), which upon fragmentation generates R• species (**II-b**) and initiator chain end species.

Table S1. Characterization of Poly(**M_{2A}**-*alt*-**CTA_2**) molecular weight evolution

Entry	$[M_{2A}]_0/[CTA_2]_0$	Time (hr)	p	$r_{th,AIBN}$	$M_{w,th}$	$M_{w,th}(r_{th,AIBN})$	M_w[a]	M_w/M_n[a]	M_z/M_w[a]
1	1.00	0	0	1.000	472	472	527	1.00	1.00
		0.5	0.833	0.992	5.2k	5.1k	4.3k	1.89	1.62
		1.0	0.943	0.984	16.1k	14.2k	10.2k	2.56	1.68
		2.0	0.983	0.970	55.1k	29.4k	18.3k	3.53	1.79
		4.0	0.993	0.949	134k	28.4k	24.9k	3.52	1.83
							28.6k*	2.05*	1.76*
2	0.980	0	0	0.980	472	472	532	1.00	1.00
		0.5	0.81	0.972	4.3k	4.2k	3.7k	1.82	1.60
		1.0	0.943	0.964	13.8k	12.4k	9.0k	2.33	1.64
		2.0	0.983	0.951	34.8k	22.5k	16.2k	2.90	1.73
		4.0	0.994	0.930	58.7k	22.4k	20.2k	3.08	1.74
							22.9k*	1.86*	1.63*
3	0.935	0	0	0.935	472	472	523	1.00	1.00
		0.5	0.822	0.927	4.2k	4.1k	3.6k	1.81	1.60
		1.0	0.951	0.920	11.4k	10.4k	7.6k	2.26	1.65
		2.0	0.988	0.908	20.8k	15.8k	11.7k	2.60	1.67
		4.0	0.996	0.889	25.2k	15.0k	13.7k	2.88	1.71
							15.7k*	1.69*	1.55*
4	0.818	0	0	0.820	472	472	522	1.00	1.00
		0.5	0.831	0.814	3.4k	3.4k	3.1k	1.77	1.57
		1.0	0.968	0.808	7.3k	6.9k	5.6k	2.07	1.64
		2.0	0.981	0.798	8.1k	7.2k	7.3k	2.23	1.63
		4.0	0.998	0.782	9.4k	7.6k	8.0k	2.32	1.65
							9.9k*	1.50*	1.44*

[a.] Molecular weight analysis by SEC with PS calibration
*Analysis after purification

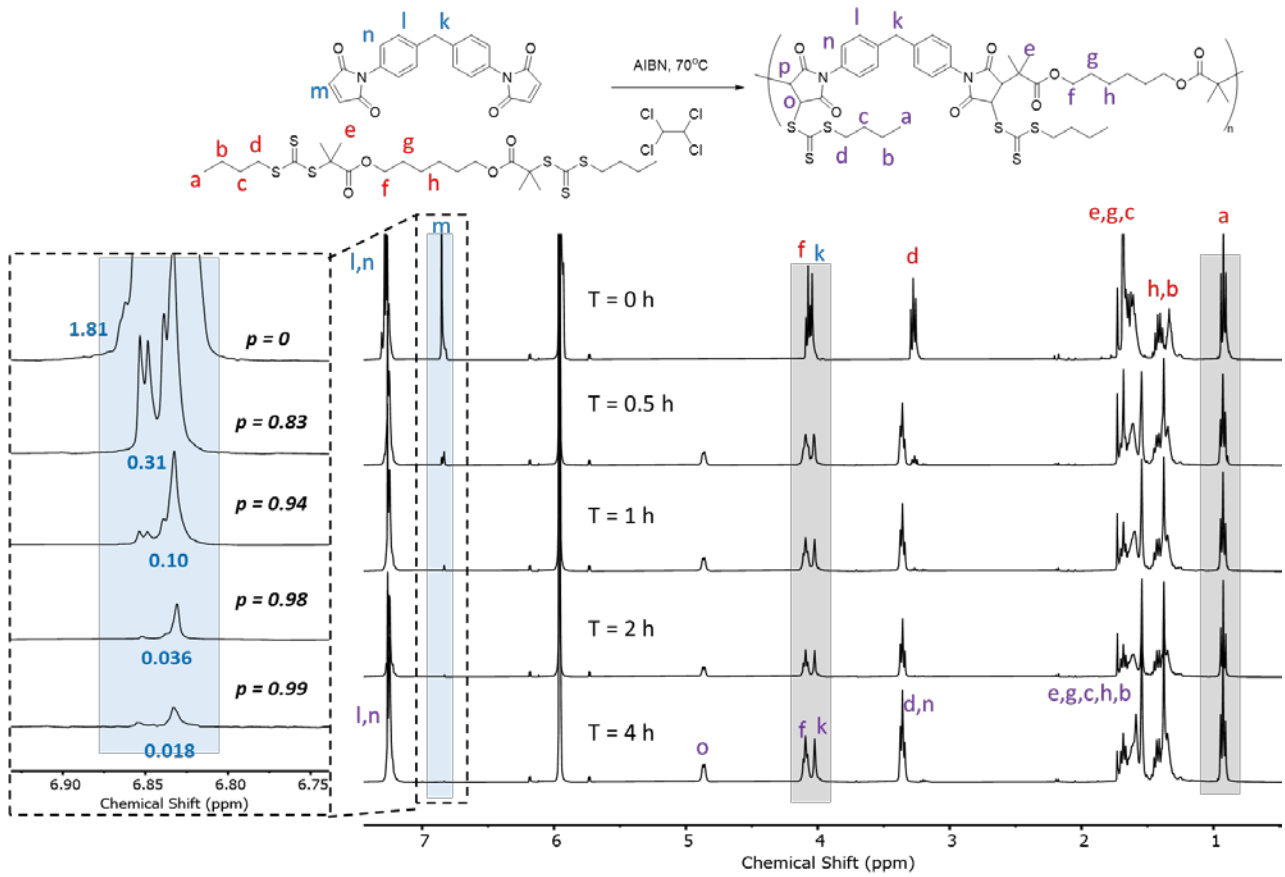


Figure S1: ^{1}H-NMR ($CDCl_3$, 400 MHz) profile of RAFT step-growth polymerization of M_{2A} and CTA_2 in TCE. Z -group C*H*$_3$(H_a, grey region) corresponding to 3 protons was used as an internal reference. Alternatively, overlapping C*H*$_2$ region of the backbone can be used as an internal reference (H_f and H_k, grey region).

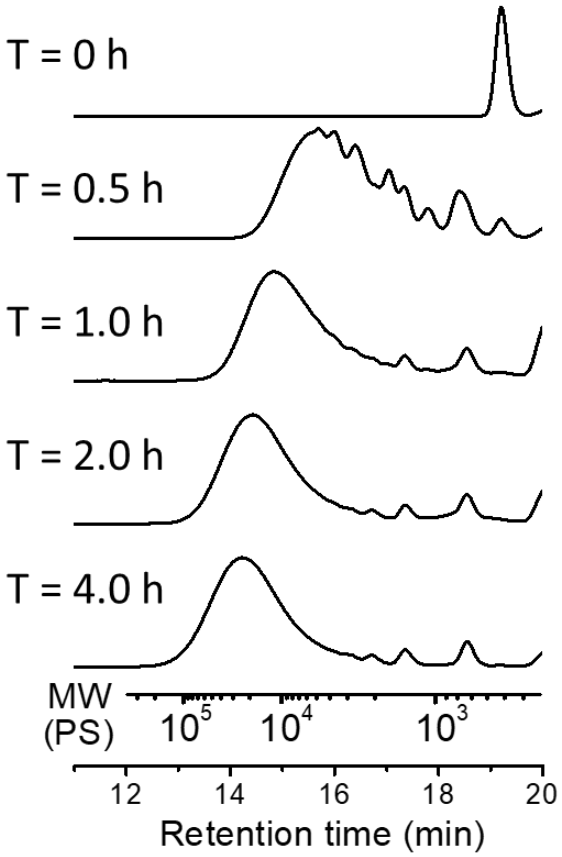


Figure S2: SEC analysis (dRI, THF) of RAFT step-growth polymerization using balanced stochiometric ratio of **M_{2A}** and **CTA_2**.

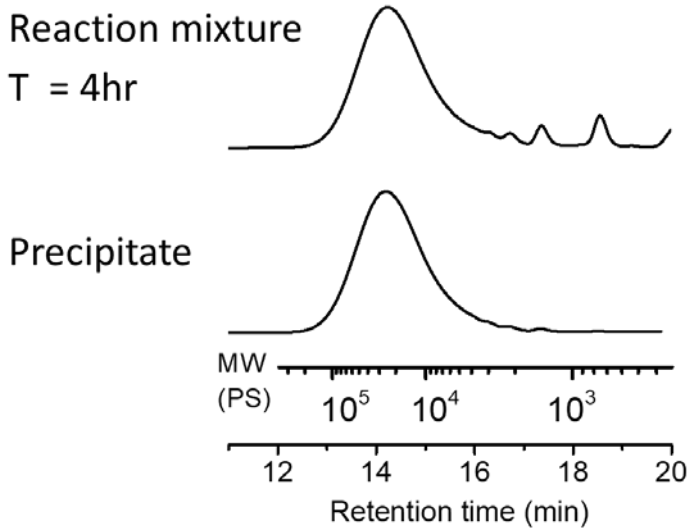


Figure S3: SEC analysis (dRI, THF) before and after precipitation of P(**M_{2A}**-alt-**CTA_2**) using balanced stochiometric ratio of **M_{2A}** and **CTA_2**.

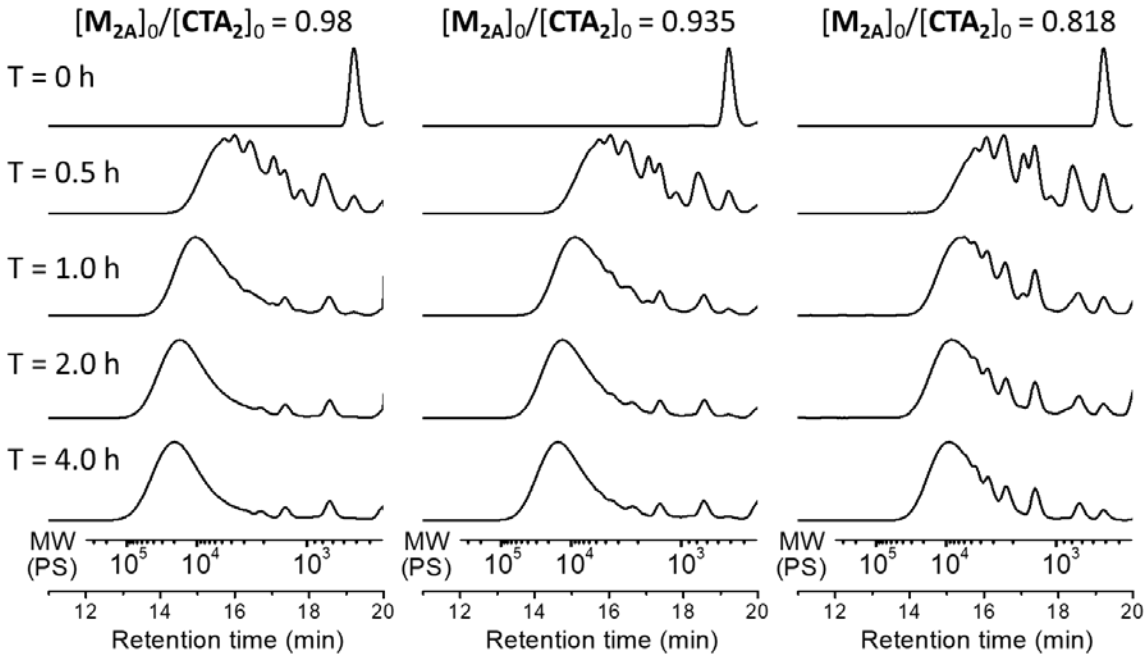


Figure S4: SEC analysis (dRI, THF) of RAFT step-growth polymerization using imbalanced stochiometric ratio of **M2A** and **CTA2** (r = $[M]_0/[CTA]_0$ = 0.98, 0.935, 0.818).

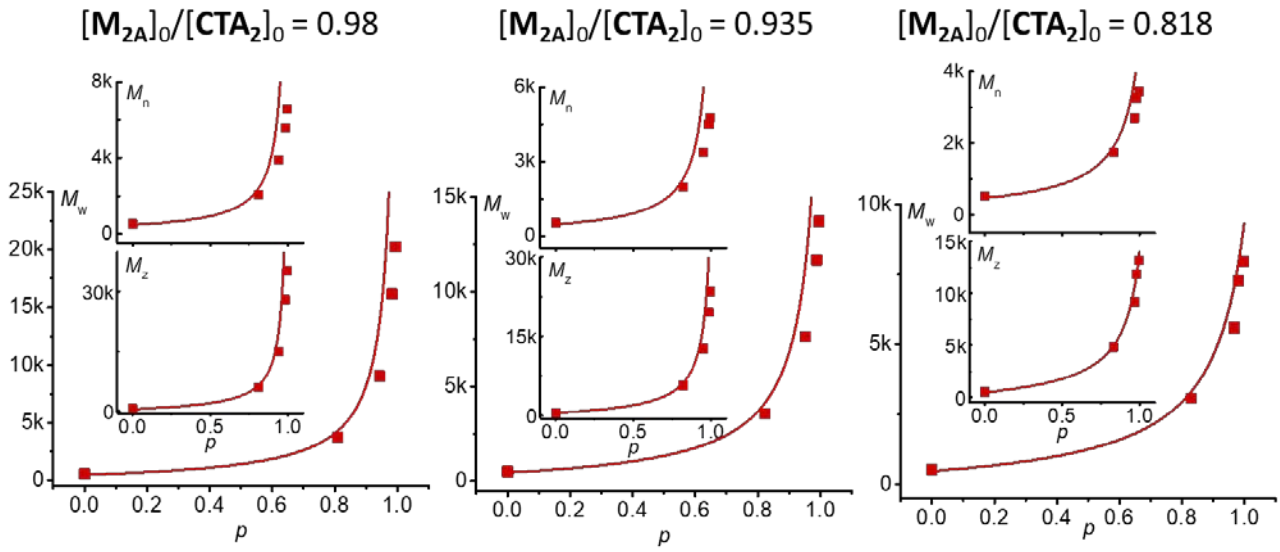


Figure S5: Evolution of molecular weight averages with conversion of P(**M2A**-alt-**CTA2**) using stochiometric excess of **CTA2** (r = $[M]_0/[CTA]_0$ = 0.98, 0.935, 0.818).

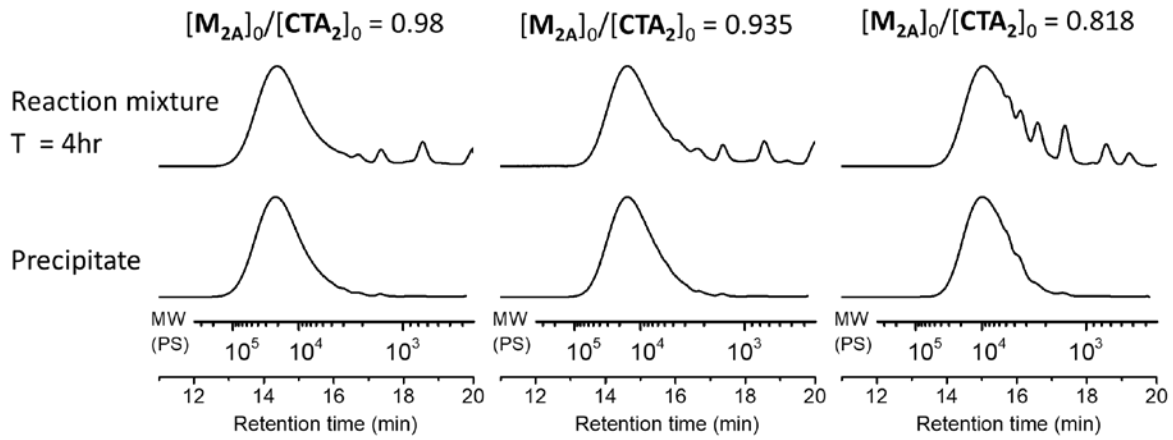
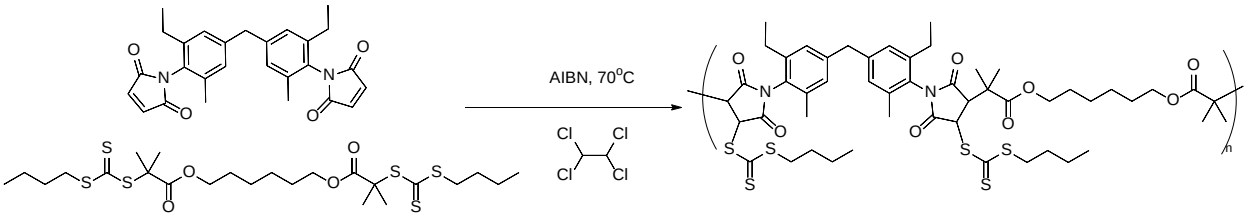


Figure S6: SEC analysis (dRI, THF) Before and after precipitation of P(**M$_{2A}$**-alt-**CTA$_2$**) using stochiometric excess of **CTA$_2$** (r = $[M]_0/[CTA]_0$ = 0.98, 0.935, 0.818).

Procedure for Poly(M_{2B}-*alt*-CTA_2) synthesis:



Bifunctional monomer, **M_{2B}** (187.5 mg, 0.424 mmol) was first charged into the vial, followed by bifunctional CTA, **CTA_2** (248.3 mg, 0.424 mmol) was carefully added via 1 ml syringe with a 21 g needle. Next, 0.500 ml TCE and 0.348 ml AIBN stock solution (20 mg/ml in TCE) were added to target molar concentration of [**M_{2B}**]$_0$:[**CTA_2**]$_0$:[AIBN]$_0$ = 0.5 : 0.5 : 0.05 M. The vial was then equipped with a stir bar and rubber septum; the solution was then purged with argon for 10 minutes and then heated at 70 °C for 21 hours. Monomer conversion was determined by ^{1}H-NMR spectroscopy by integrating C*H*=C*H* maleimide ring proton(s) relative to CH_3 at 0.96 ppm on the Z-group of the CTA. For purification, the reaction mixture was diluted in approximately equal volume of chloroform and precipitated directly into 50 ml centrifuge tube with methanol and collected by centrifugation. After discarding the supernatant, the polymers were redissolved in chloroform and then reprecipitated again in methanol. Typical yields of 67 % are obtained.

Table S2. Characterization of Poly(**M_{2B}**-*alt*-**CTA_2**) in TCE

Entry	Time (hr)	*p*	$r_{th,AIBN}$	$M_{w,th}$	$M_{w,th}(r_{th,AIBN})$	M_w[a]	M_w/M_n[a]	M_z/M_w[a]
1	0	0.000	1.000	535	535	461	1.03	1.04
	0.5	0.303	0.992	1.0k	1.0k	830	1.33	1.39
	1.0	0.477	0.984	1.5k	1.5k	1.2k	1.52	1.50
	2.0	0.626	0.970	2.3k	2.3k	2.1k	1.77	1.60
	4.0	0.831	0.949	5.8k	5.1k	4.2k	1.94	1.60
	21	0.955	0.891	23.2k	10.4k	16.8k	2.22	1.67
2*	21	0.942	0.891	17.9k	9.3k	13.1k	2.16	1.73
						13.1k**	1.79**	1.57**

[a] Molecular weight analysis by SEC with PS calibration

*Repeated

**Analysis after purification

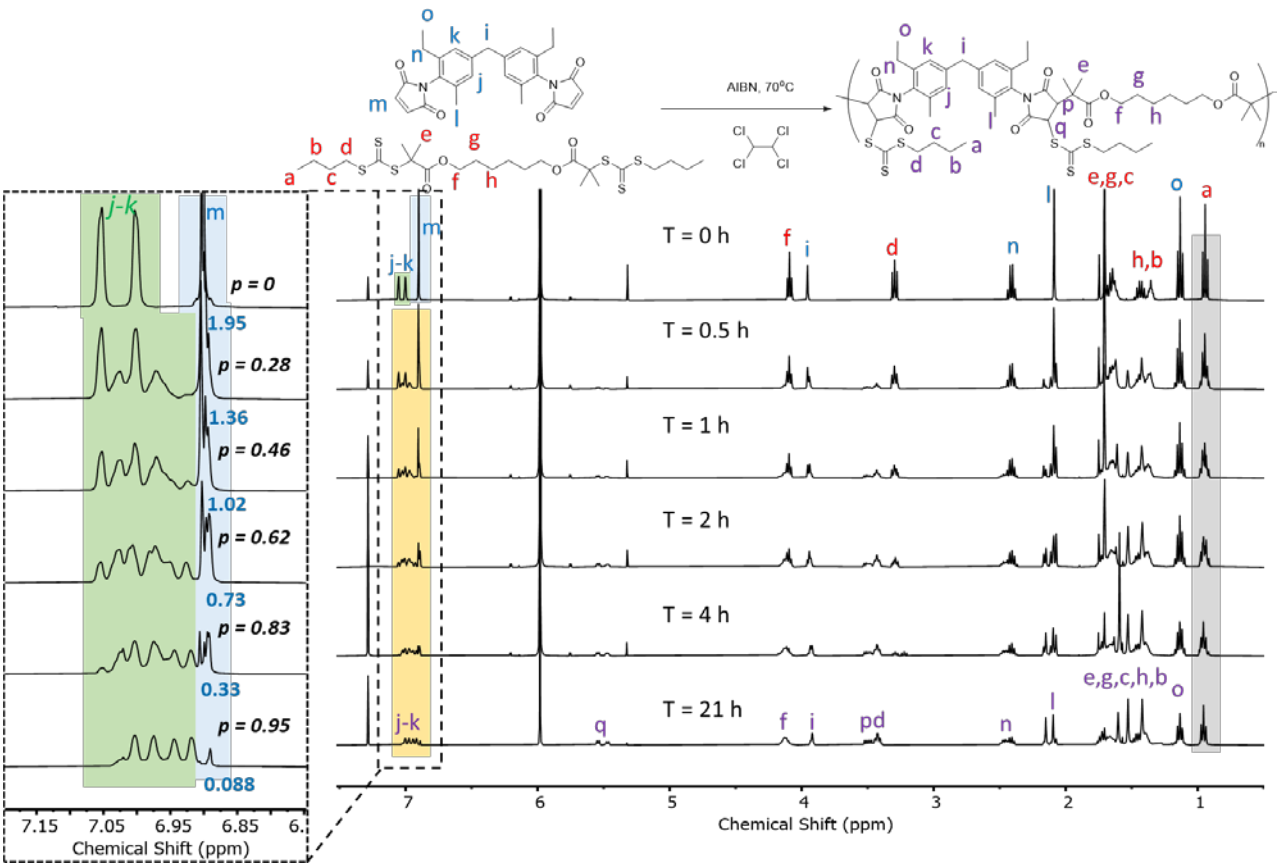


Figure S7: ^{1}H-NMR ($CDCl_3$, 400 MHz) profile of RAFT step-growth polymerization of M_{2B} and CTA_2 in TCE. Z -group C*H*$_3$(H_a, grey region) corresponding to 3 protons was used as an internal reference. Alternatively, C*H*$_2$ next to the ester-oxygen (H_f, grey region) can be used as internal reference. Note the monomer peak (H_m, blue region) overlaps slightly with aromatic peaks (H_{j-k}, green region) during the polymerization.

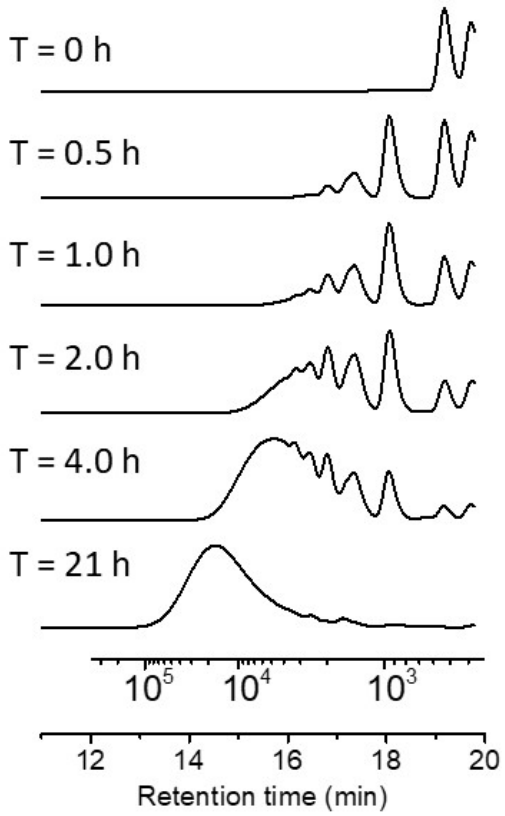


Figure S8: SEC analysis (dRI, THF) of RAFT step-growth polymerization using balanced stochiometric ratio of **M_{2B}** and **CTA_2**.

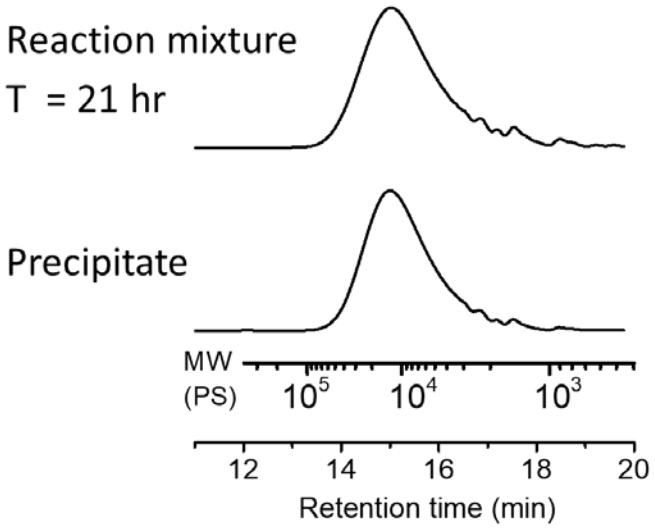
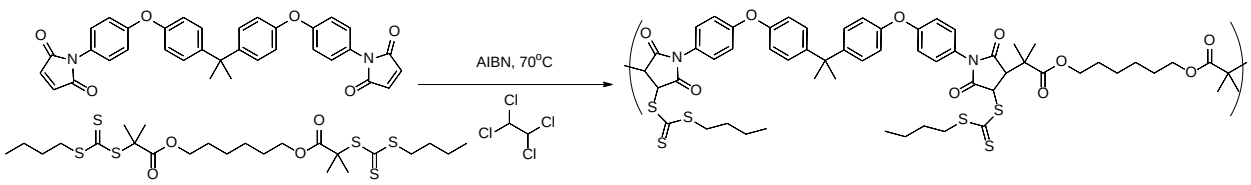


Figure S9: SEC analysis (dRI, THF) before and after precipitation of P(**M_{2B}**-alt-**CTA_2**)

Procedure for Poly(M_{2C}-*alt*-CTA_2) synthesis:



Bifunctional monomer, **M_{2C}** (143.1 mg, 0.250 mmol) was first charged into the vial, followed by bifunctional CTA, **CTA_2** (147 mg, 0.250 mmol) was carefully added via 1 ml syringe with a 21 g needle. Next, 0.296 ml TCE and 0.206 ml AIBN stock solution (20 mg/ml in TCE) to target molar concentration of $[\mathbf{M_2}]_0$:$[\mathbf{CTA_2}]_0$:$[AIBN]_0$ = 0.5 : 0.5 : 0.05 M. The vial was then equipped with a stir bar and rubber septum; the solution was then purged with argon for 10 minutes and then heated at 70 °C for 4 hours. Monomer conversion was determined from ^{1}H-NMR spectroscopy by integrating C*H*=C*H* maleimide ring proton(s) relative to CH_3 at 0.96 ppm on the Z-group. For purification, the reaction mixture was diluted in approximately equal volume of chloroform and precipitated directly into 50 ml centrifuge tube with diethyl ether and collected by centrifugation. After discarding the supernatant, the polymers were redissolved in chloroform and then reprecipitated again in diethyl ether. Typical yields of 71 % are obtained.

Table S3. Characterization of Poly(**M_{2C}**-*alt*-**CTA_2**) in TCE

Entry	Time (hr)	*p*	$r_{th,AIBN}$	$M_{w,th}$	$M_{w,th}(r_{th,AIBN})$	M_w[a]	M_w/M_n[a]	M_z/M_w[a]
1	0	0	1.000	578	578	419	1.01	1.01
	0.5	0.869	0.992	8.2k	8.0k	7.0k	1.97	1.61
	1.0	0.956	0.984	25.7k	21.9k	22.8k	3.29	1.92
	2.0	0.993	0.970	162k	52.4k	67.6k	7.08	2.56
2*	2.0	0.992	0.970	144k	50.1k	55.6k	5.11	2.12
						52.7k**	2.98**	2.14**

[a.] Molecular weight analysis by SEC with PS calibration
*Repeated
**Analysis after purification

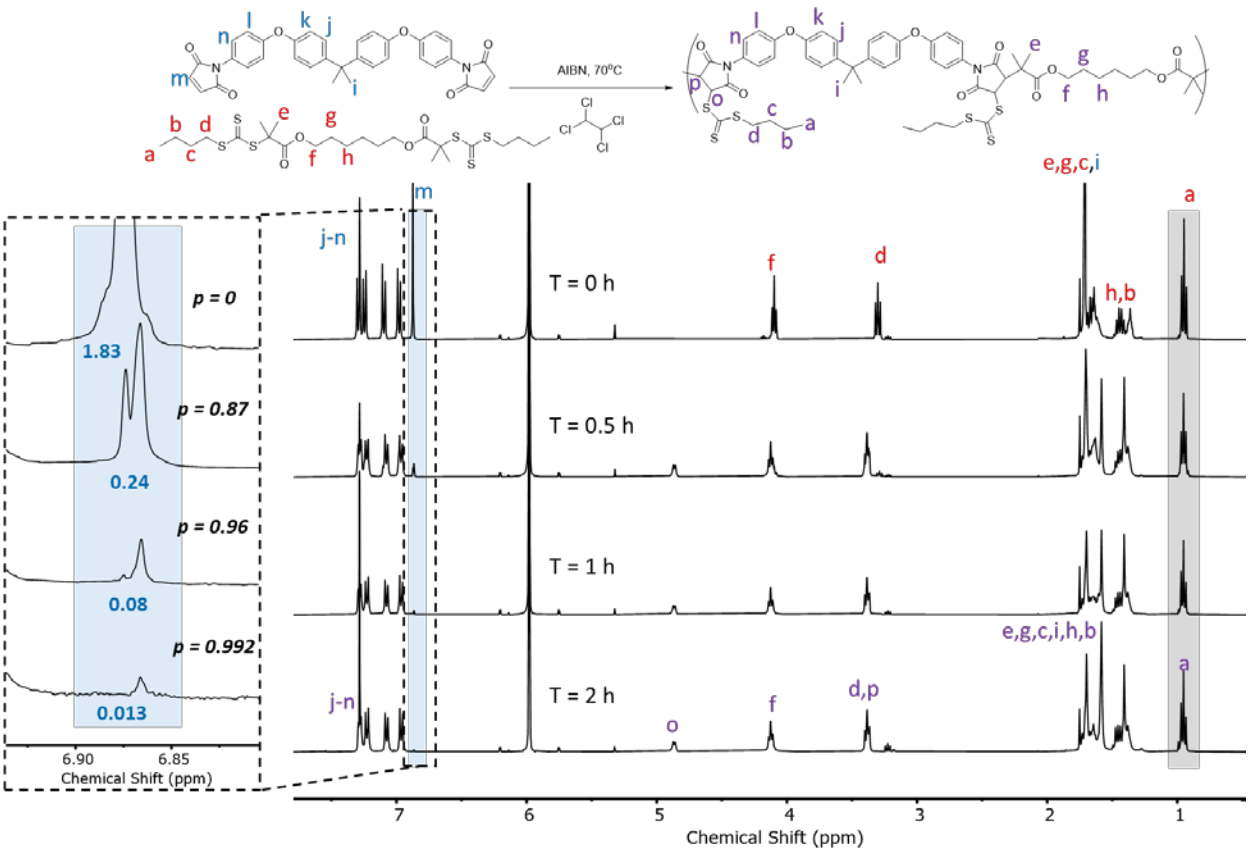


Figure S10: ^{1}H-NMR ($CDCl_3$, 400 MHz) profile of RAFT step-growth polymerization of **M2c** and **CTA2** in TCE. Z-group C*H*$_3$(grey region) corresponding to 3 protons was used as an internal reference.

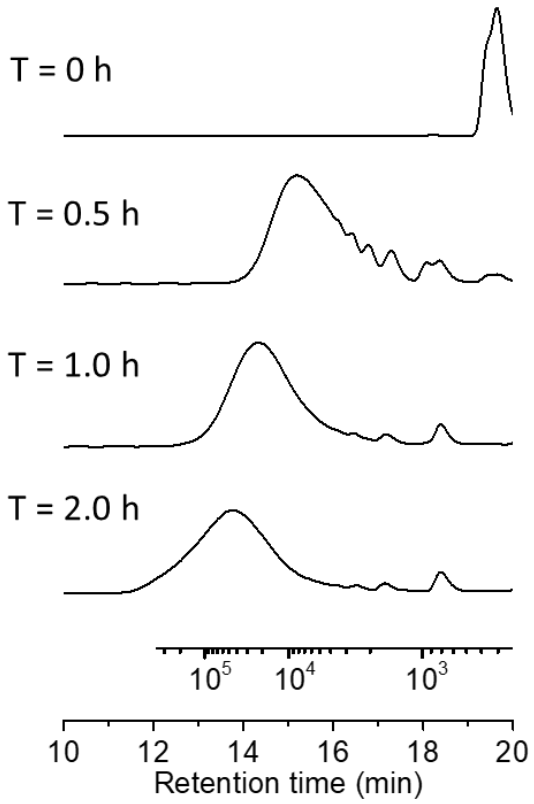


Figure S11: SEC analysis (dRI, THF) of RAFT step-growth polymerization using balanced stochiometric ratio of **M_{2C}** and **CTA_2**.

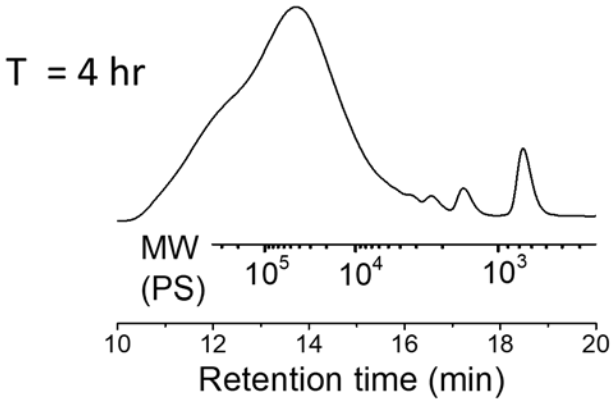


Figure S12: SEC analysis (dRI, THF) of RAFT step-growth polymerization of **M_{2C}** and **CTA_2** after 4 hours.

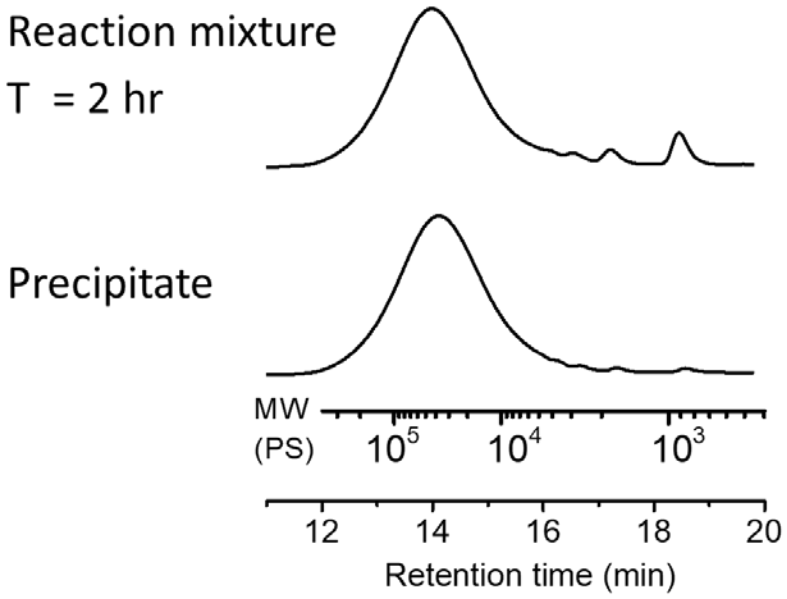
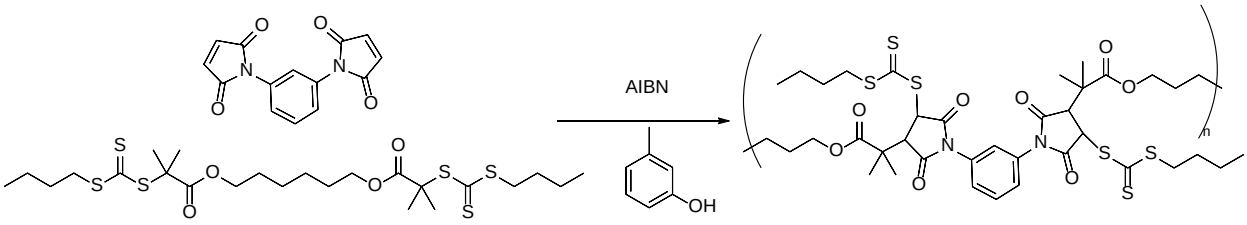


Figure S13: SEC analysis (dRI, THF) before and after precipitation of P(**M$_{2C}$**-alt-**CTA$_2$**)

Procedure for Poly(M_{2D}-*alt*-CTA_2) synthesis:



Bifunctional monomer, **M_{2D}** (200 mg, 0.746 mmol) was first charged into the vial, followed by bifunctional CTA, **CTA_2** (437 mg, 0.746 mmol) was carefully added via 1 ml syringe with a 21 g needle. Next, 0.879ml *m*-cresol and 0.612 ml AIBN stock solution (20 mg/ml in *m*-cresol) to target molar concentration of [**M_{2D}**]$_0$:[**CTA_2**]$_0$:[AIBN]$_0$ = 0.5 : 0.5 : 0.05 M. The vial was then equipped with a stir bar and rubber septum; the solution was then purged with argon for 10 minutes and then heated at 70 °C for 4 hours. As the solvent signals overlapped with the C*H*=C*H* maleimide ring proton(s) by ^{1}H-NMR, the relative integrals at 6.54-6.91 ppm corresponding to the monomer and the solvent was measured with respect to the solvent signal at 7.07-7.27 ppm. This was compared with ^{1}H-NMR of *m*-cresol to determine monomer conversion. For purification, RAFT step-growth polymers were precipitated directly into 50 ml centrifuge tube with diethyl ether and collected by centrifugation. After discarding the supernatant, the polymers were redissolved in acetone and then reprecipitated again in diethyl ether.

Table S4. Characterization of Poly(**M_{2D}**-*alt*-**CTA_2**) in *m*-cresol

Entry	Time (hr)	*p*	$r_{th,AIBN}$	$M_{w,th}$	$M_{w,th}(r_{th,AIBN})$*	M_w[a]	M_w/M_n[a]	M_z/M_w[a]
1	0	0	1.000	427	427	500	1.01	1.00
	0.5	0.537	0.992	1.8k	1.4k	1.3k	1.38	1.43
	1.0	0.811	0.984	10.2k	4.0k	2.9k	1.92	1.69
	2.0	0.947	0.970	17.7k	12.4k	7.1k	3.27	1.86
	4.0	0.967	0.949	184k	14.4k	13.0k	4.85	1.95
						17.5k*	1.59*	1.49*

[a.] Molecular weight analysis by SEC with PS calibration
*Analysis after purification

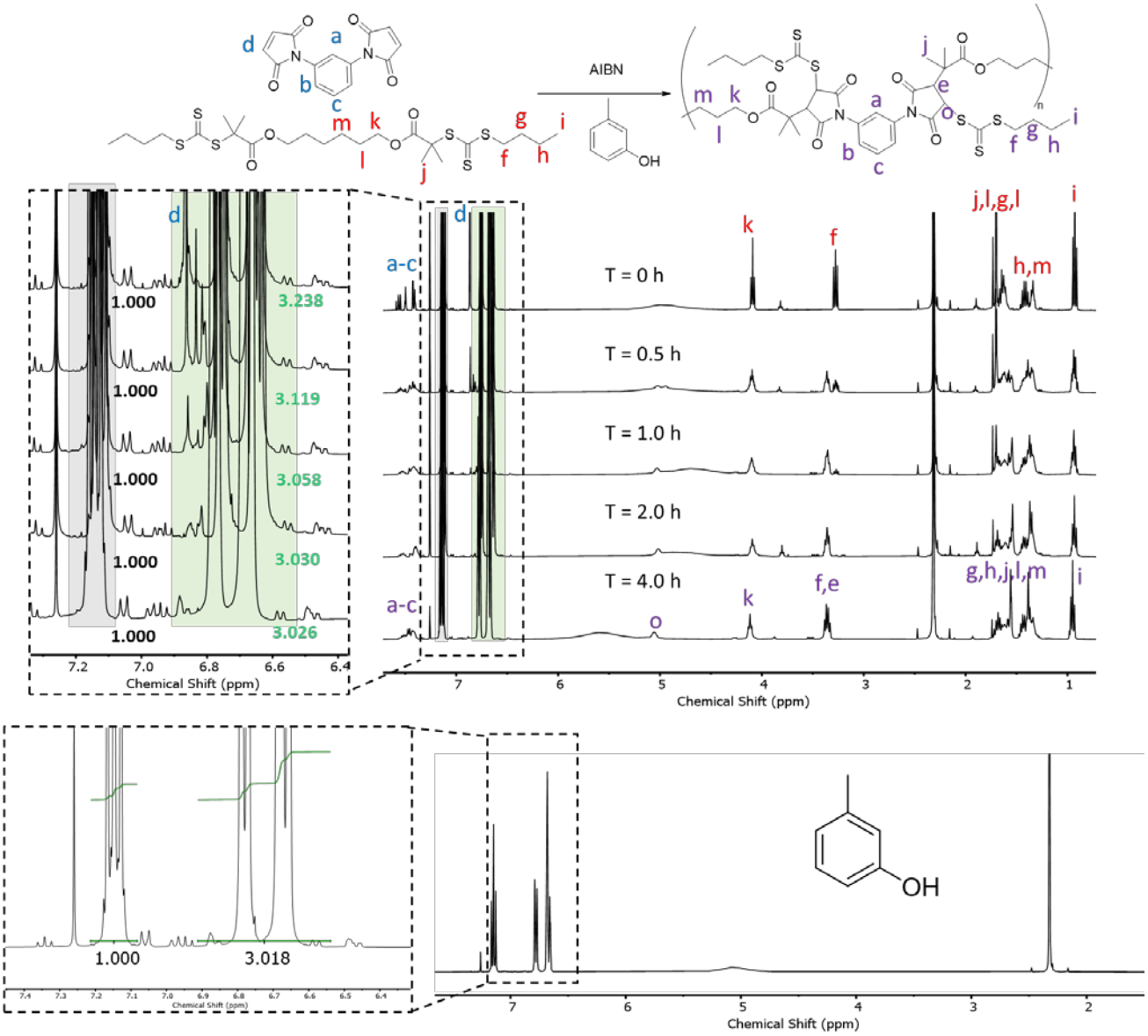


Figure S14: ^{1}H-NMR ($CDCl_3$, 400 MHz) profile of step-growth polymerization with **M_{2D}** and **CTA_2** in m-cresol. Due to the monomer peak (H_d, blue) overlapping with peaks present in *m*-cresol, the monomer conversion was determined from relative integrals at 6.54 ppm to 6.91 ppm (green region) corresponding to the monomer and the solvent, with respect to the solvent signal at 7.07 to 7.27 (grey region). The ^{1}H-NMR of *m*-cresol and corresponding integrals shown at the bottom.

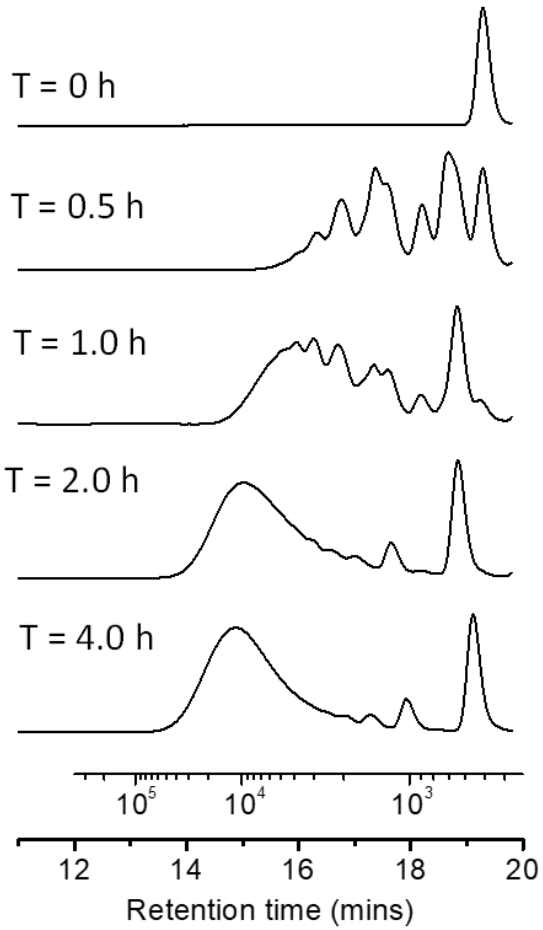


Figure S15: SEC analysis (dRI, THF) of RAFT step-growth polymerization using balanced stochiometric ratio of **M_{2D}** and **CTA_2**.

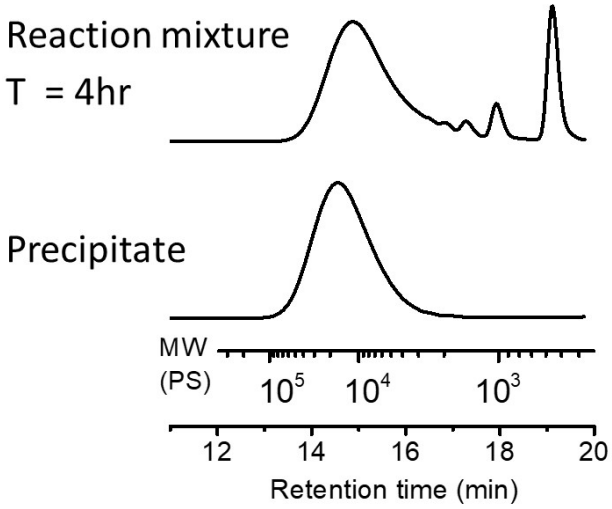


Figure S16: SEC analysis (dRI, THF) before and after precipitation of P(**M_{2D}**-alt-**CTA_2**)

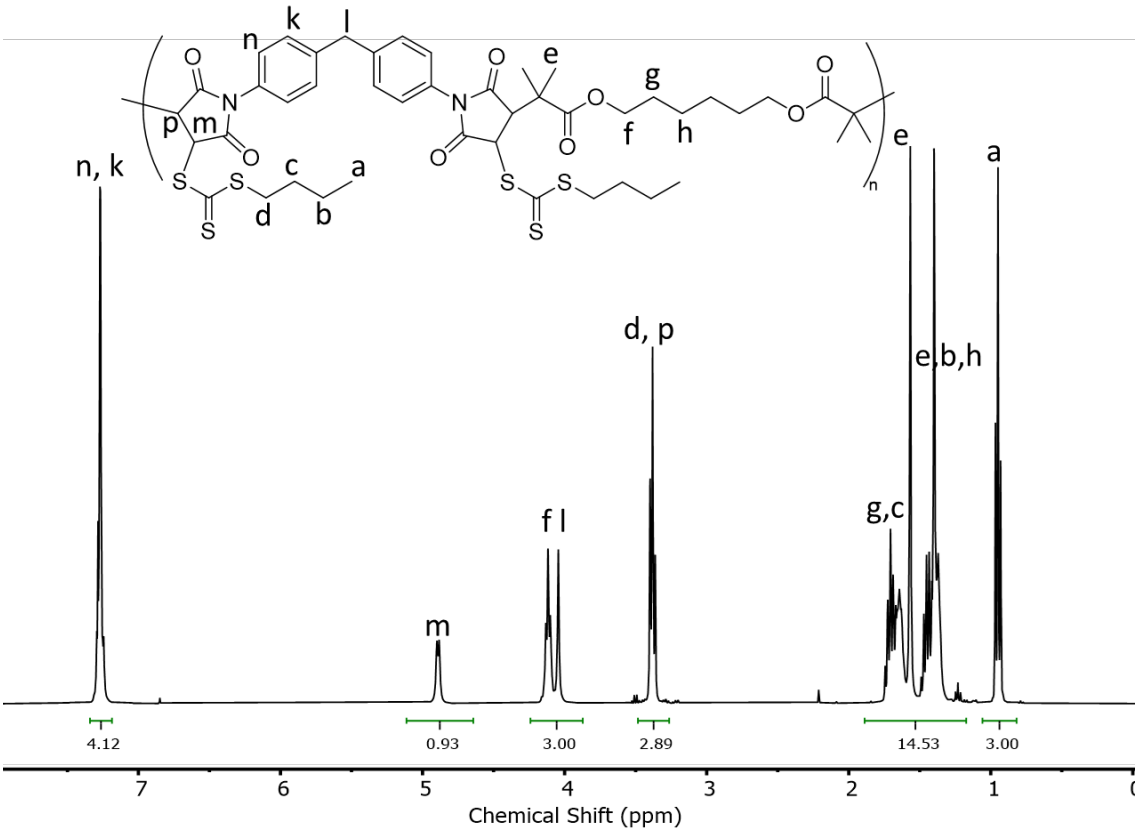


Figure S17: ^{1}H-NMR ($CDCl_3$, 400 MHz) of P(**M_{2A}**-*alt*-**CTA_2**)

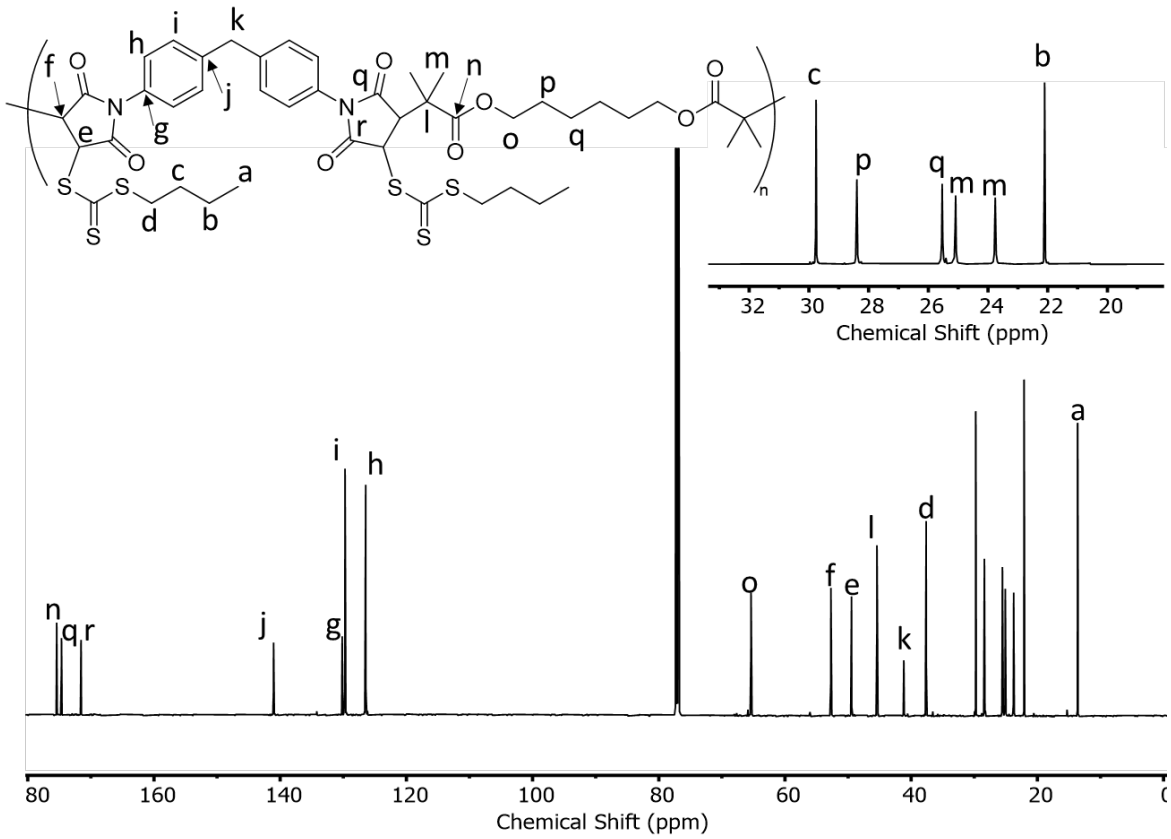


Figure S18: ^{13}C-NMR ($CDCl_3$, 400 MHz) of P(**M_{2A}**-*alt*-**CTA_2**)

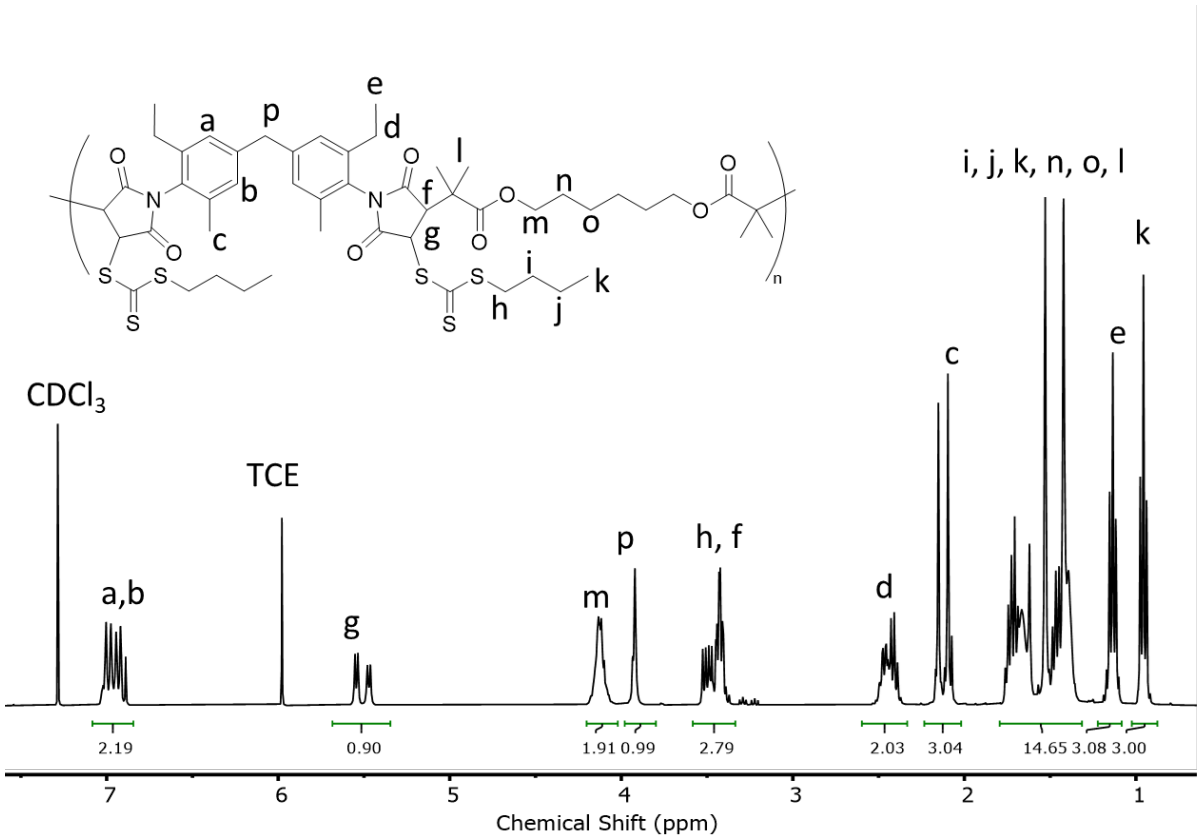


Figure S19: ^{1}H-NMR ($CDCl_3$, 400 MHz) of P(**M_{2B}**-*alt*-**CTA_2**)

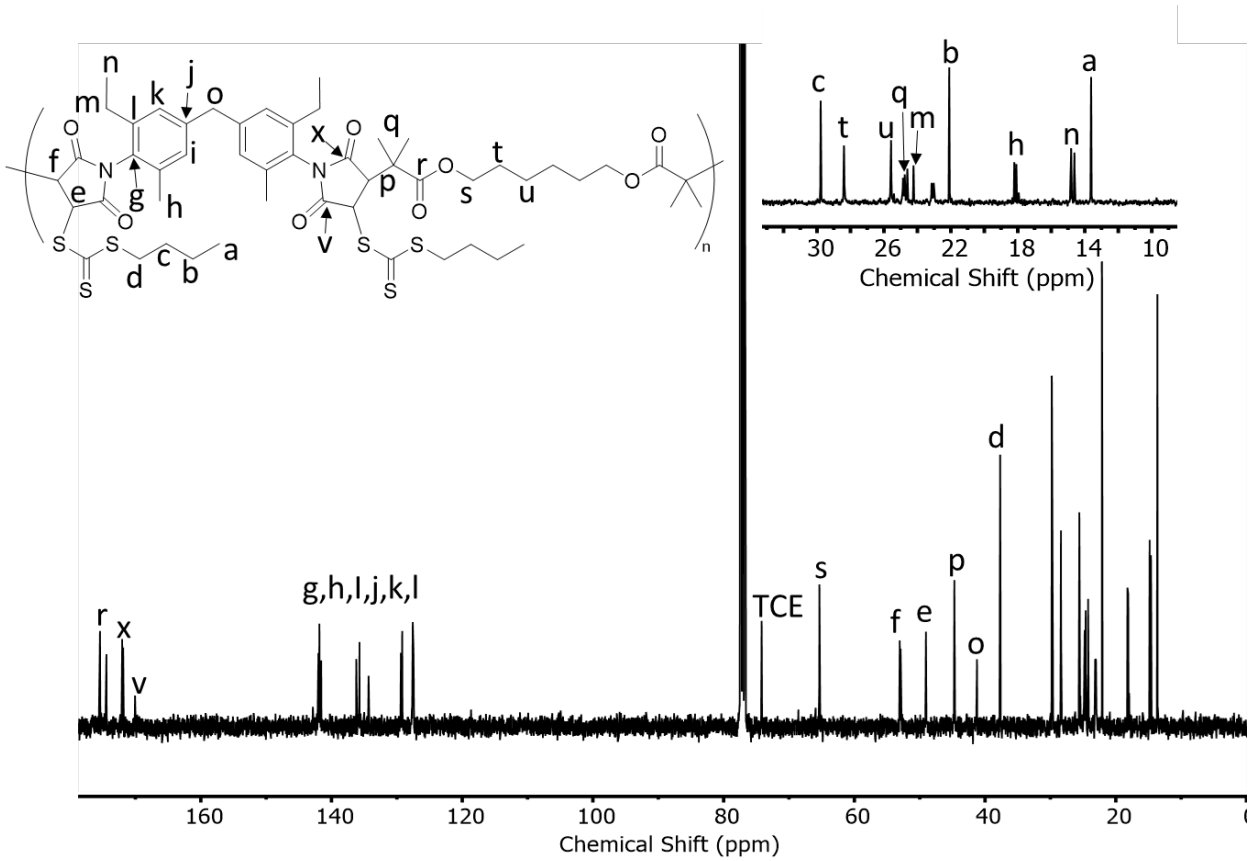


Figure S20: ^{13}C-NMR ($CDCl_3$, 400 MHz) of P(**M_{2B}**-*alt*-**CTA_2**)

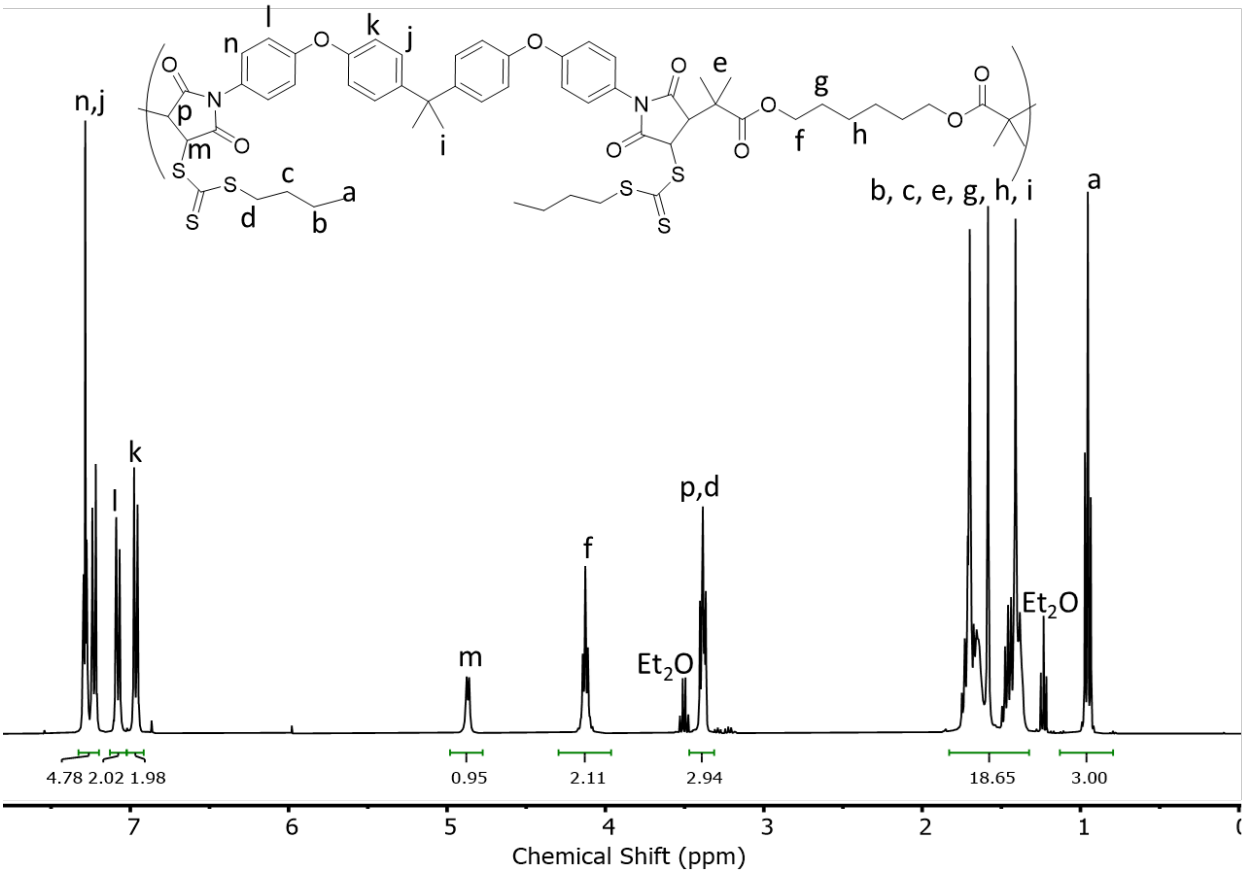


Figure S21: ^{1}H-NMR ($CDCl_3$, 400 MHz) of P(**M_{2C}**-*alt*-**CTA_2**)

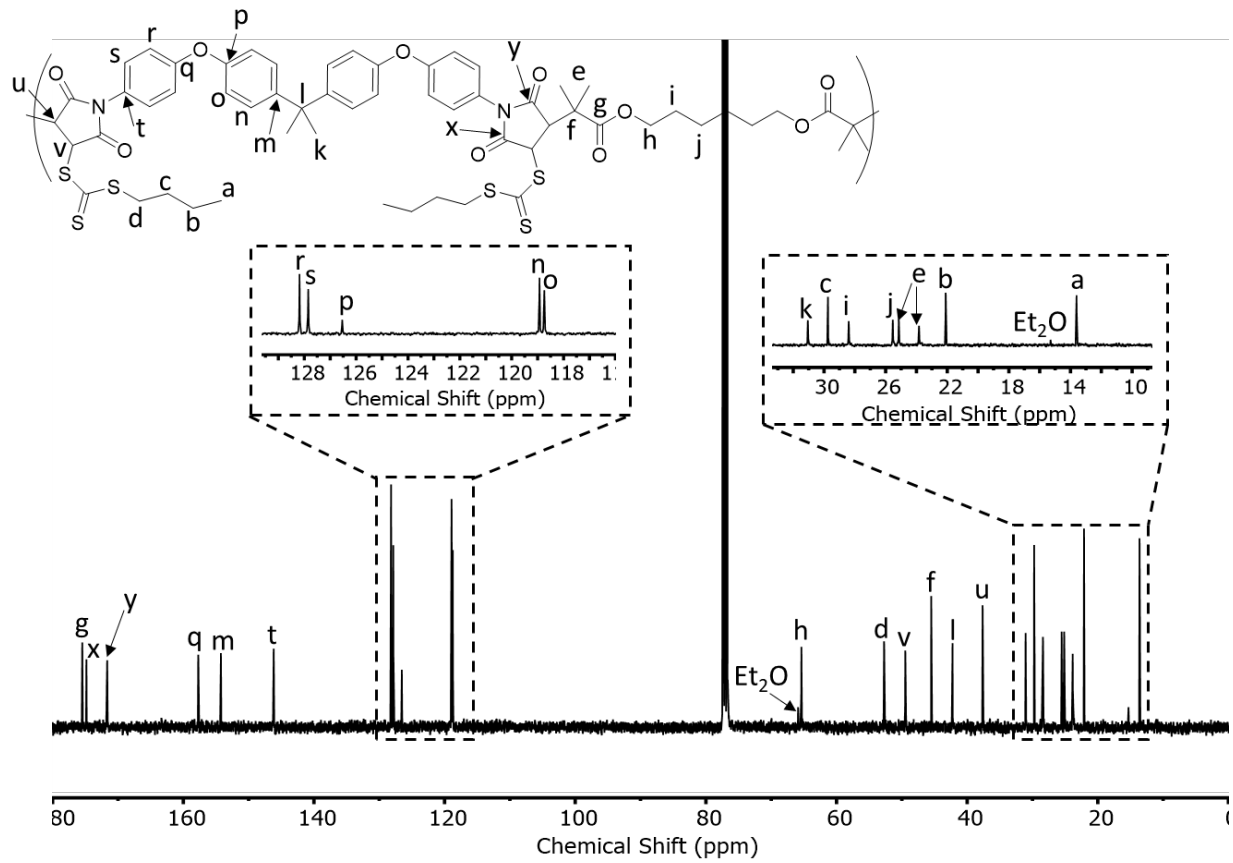


Figure S22: ^{13}C-NMR ($CDCl_3$, 400 MHz) of P(**M_{2C}**-*alt*-**CTA_2**)

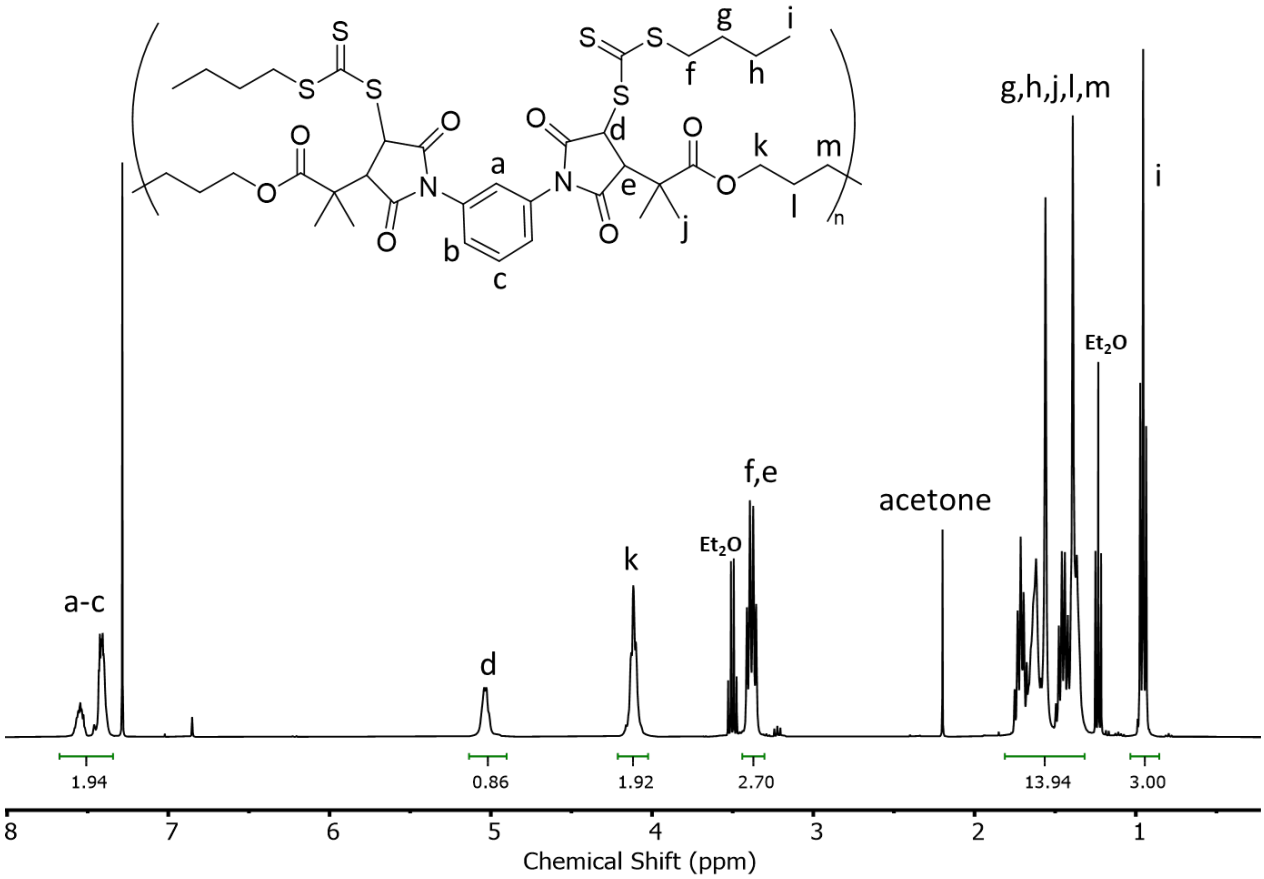


Figure S23: ^{1}H-NMR ($CDCl_3$, 400 MHz) of P(**M_{2D}**-*alt*-**CTA_2**)

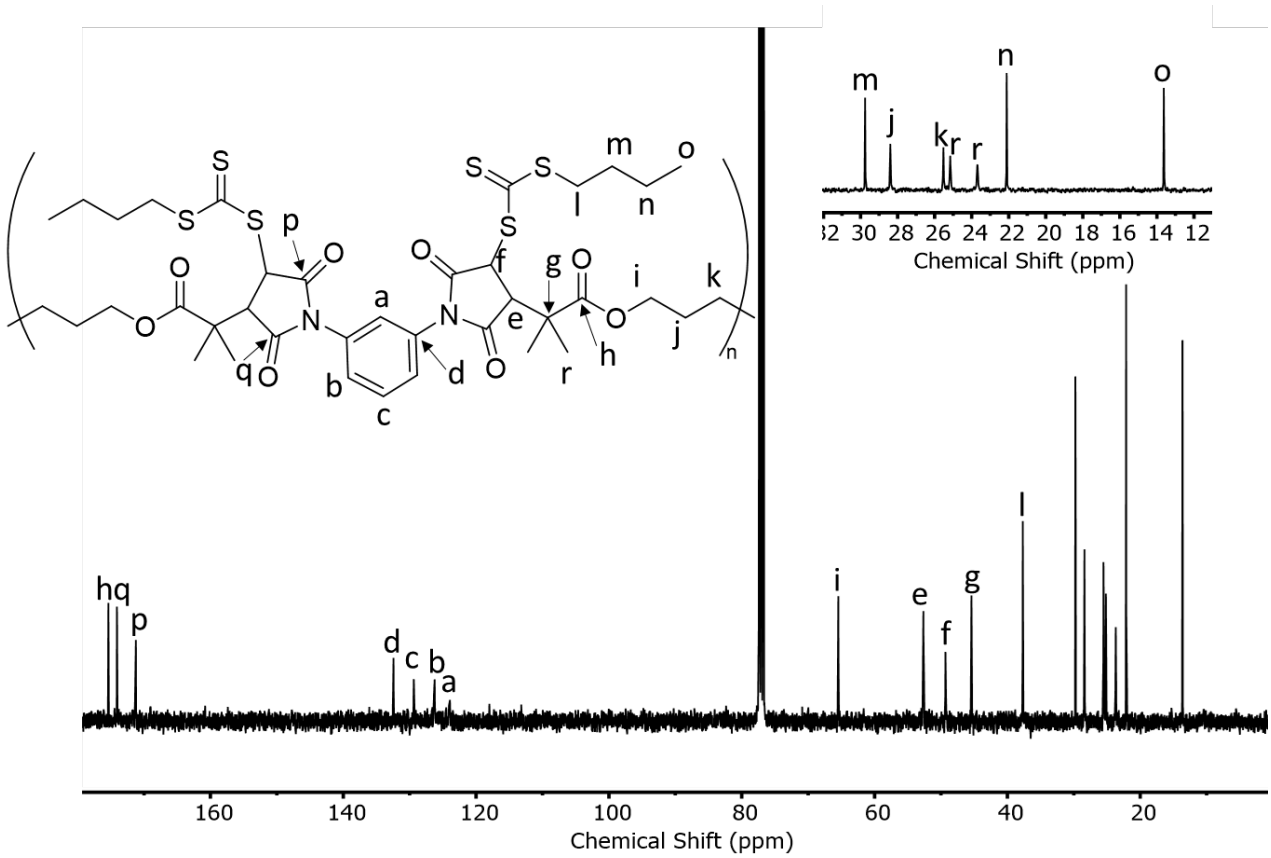


Figure S24: ^{13}C-NMR ($CDCl_3$, 400 MHz) of P(**M_{2D}**-*alt*-**CTA_2**)

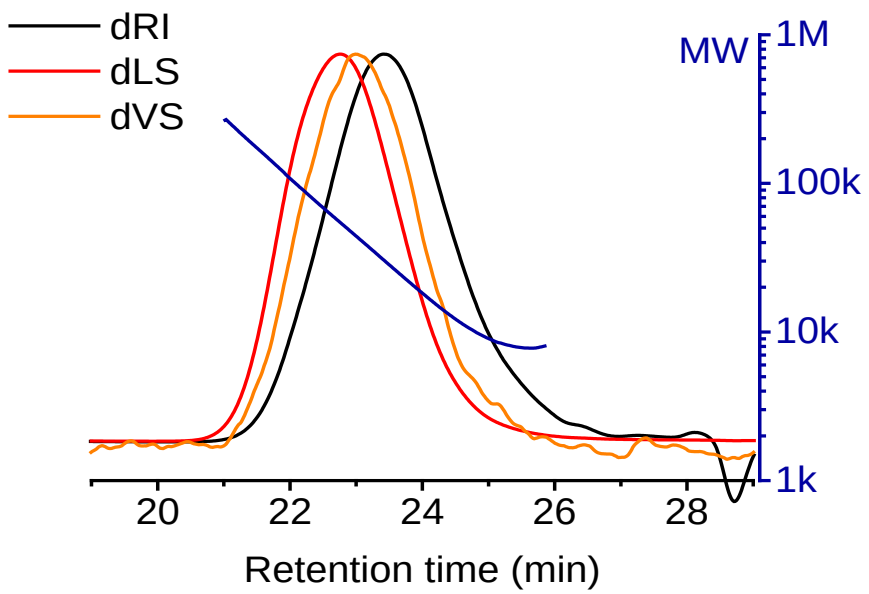


Figure S25: Normalized response from multidetector SEC analysis (dRI, dLS, dVS) of purified P(**M$_{2A}$**-*alt*-**CTA$_2$**) (Table S1, entry 1) in THF. The molecular weight was determined from the LS-detector with dn/dc value of 0.151 from 100 % mass recovery. M_n = 22.3k, M_w = 37.9k, M_z = 63.2k.

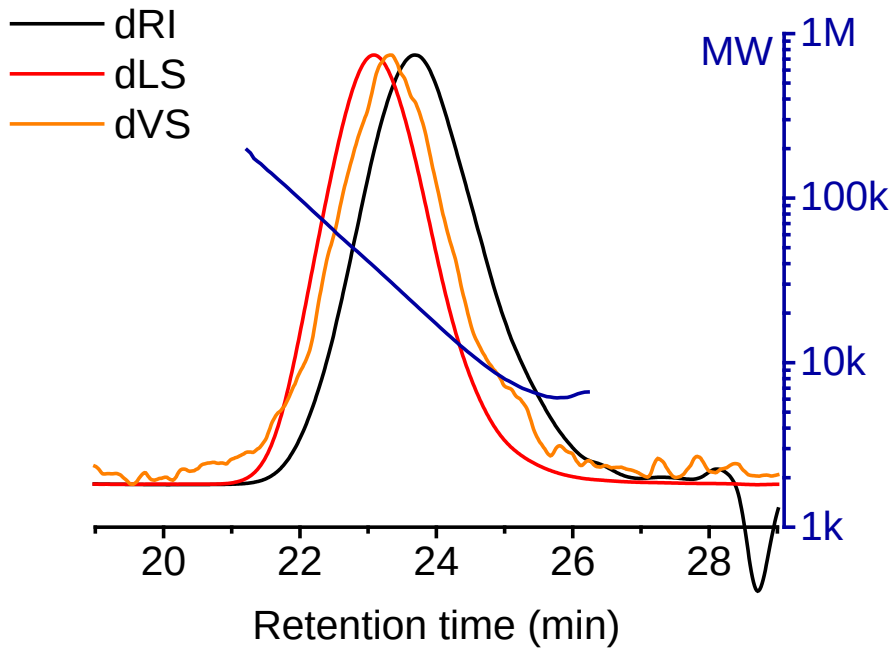


Figure S26: Normalized response from multidetector SEC analysis (dRI, dLS, dVS) of purified P(**M$_{2A}$**-*alt*-**CTA$_2$**) (Table S1, entry 2) in THF. The molecular weight was determined from the LS-detector with dn/dc value of 0.153 from 100 % mass recovery. M_n = 16.6k, M_w = 26.8k, M_z = 42.6k.

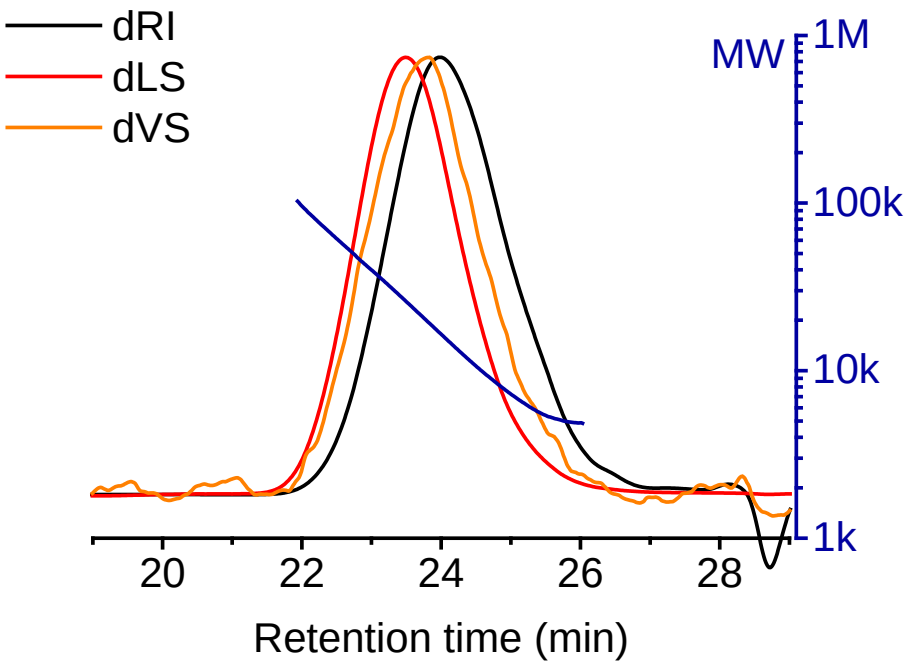


Figure S27: Normalized response from multidetector SEC analysis (dRI, dLS, dVS) of purified P(**M$_{2A}$**-*alt*-**CTA$_2$**) (Table S1, entry 3) in THF. The molecular weight was determined from the LS-detector with dn/dc value of 0.152 from 100 % mass recovery. M_n = 12.6k, M_w = 19.0k, M_z = 28.3k.

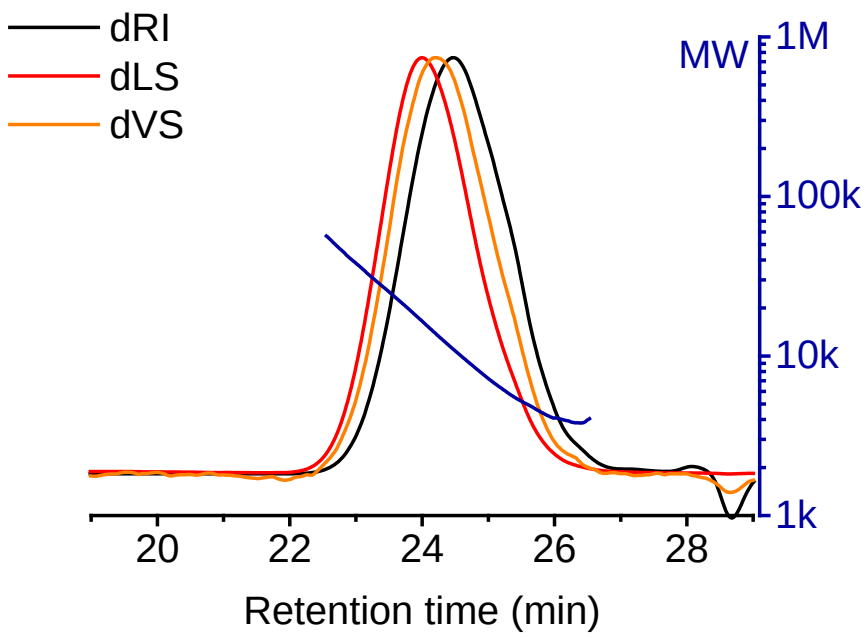


Figure S28: Normalized response from multidetector SEC analysis (dRI, dLS, dVS) of purified P(**M$_{2A}$**-*alt*-**CTA$_2$**) (Table S1, entry 4) in THF. The molecular weight was determined from the LS-detector with dn/dc value of 0.148 from 100 % mass recovery. M_n = 9.2k, M_w = 12.5k, M_z = 17.0k.

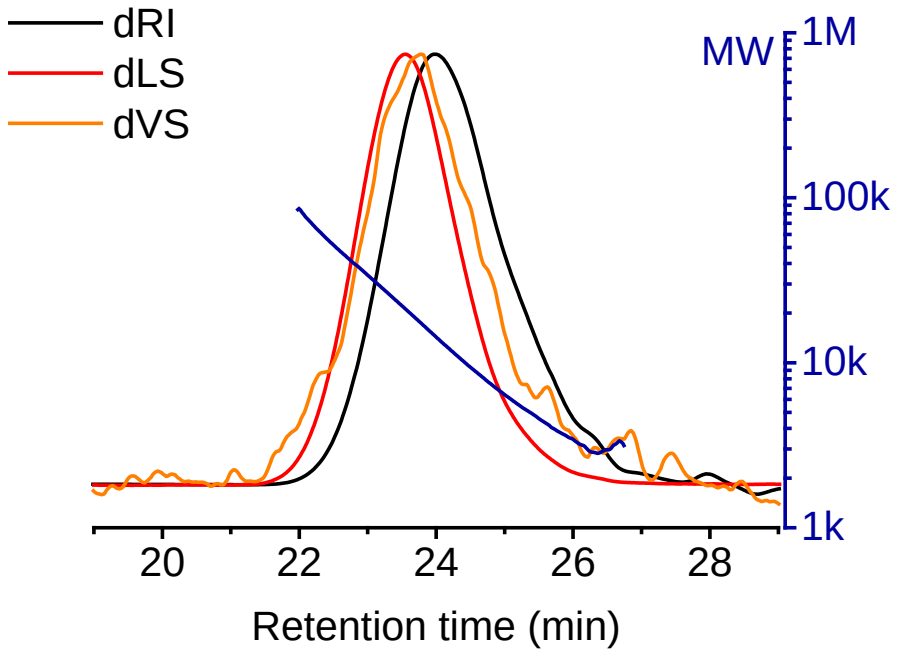


Figure S29: Normalized response from multidetector SEC analysis (dRI, dLS, dVS) of purified P(**M$_{2B}$**-*alt*-**CTA$_2$**) (**Table S2**, entry 2) in THF. The molecular weight was determined from the LS-detector with dn/dc value of 0.157 from 100 % mass recovery. M_n = 9.8k, M_w = 15.4k, M_z = 23.0k.

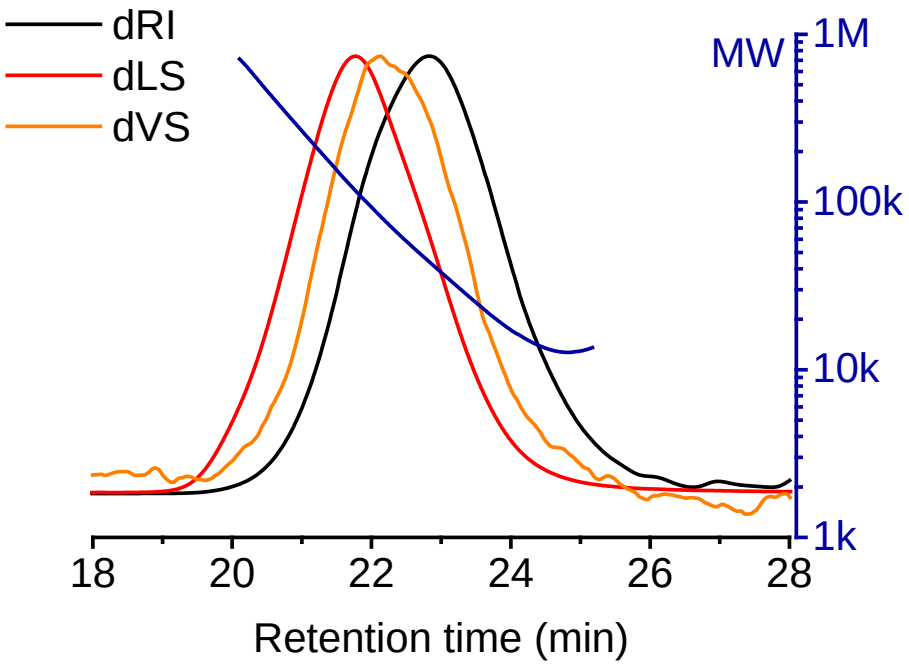


Figure S30: Normalized response from multidetector SEC analysis (dRI, dLS, dVS) of purified P(**M$_{2C}$**-*alt*-**CTA$_2$**) (**Table S3**, entry 2) in THF. The molecular weight was determined from the LS-detector with dn/dc value of 0.165 from 100 % mass recovery. M_n = 34.8k, M_w =68.8k, M_z = 150.8k.

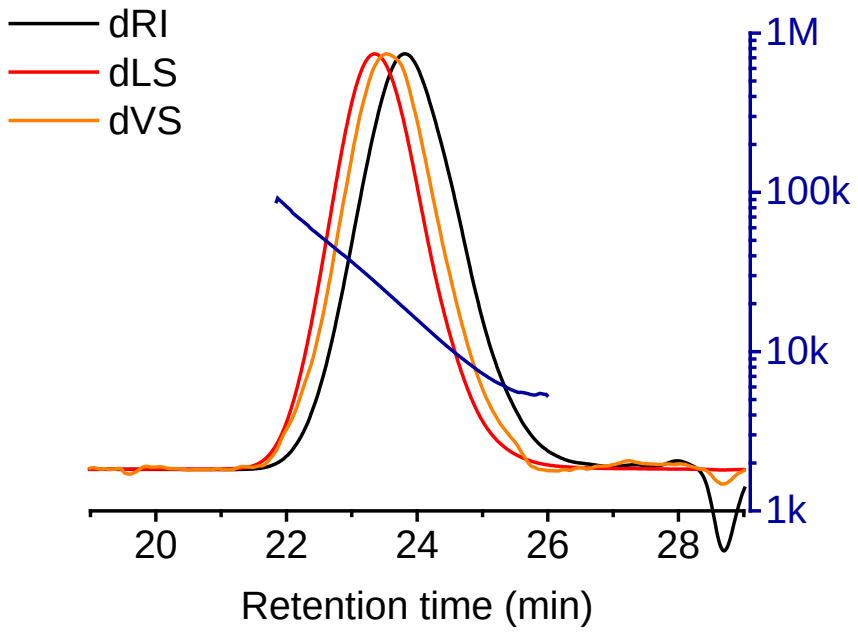


Figure S31: Normalized response from multidetector SEC analysis (dRI, dLS, dVS) of purified P(**M$_{2D}$**-*alt*-**CTA$_2$**) (**Table S4**, entry 1)) in THF. The molecular weight was determined from the LS-detector with dn/dc value of 0.170 from 100 % mass recovery. M_n = 14.7k, M_w = 20.9k, M_z = 29.0k.

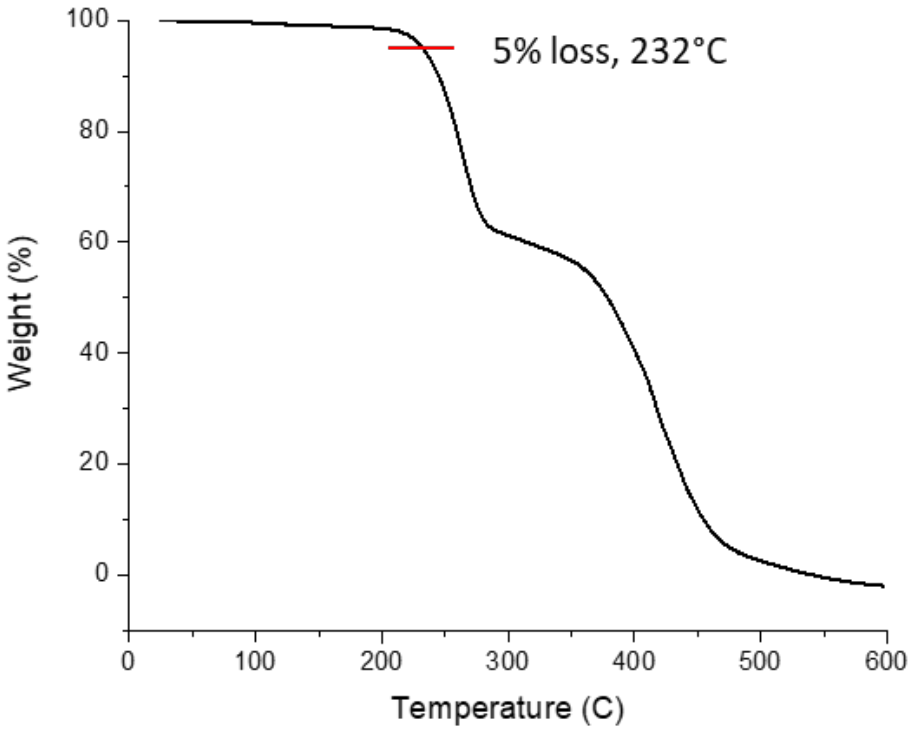


Figure S32: TGA Thermogram of P(**M$_{2A}$**-*alt*-**CTA$_2$**)

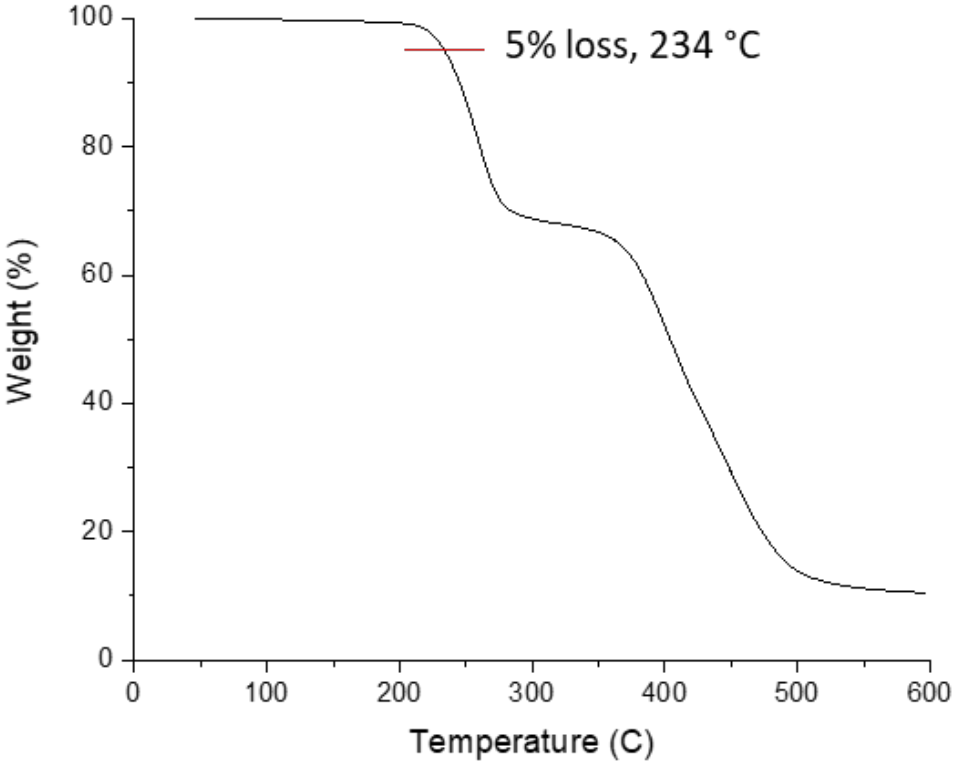


Figure S33: TGA Thermogram of P(**M_{2B}**-*alt*-**CTA_2**)

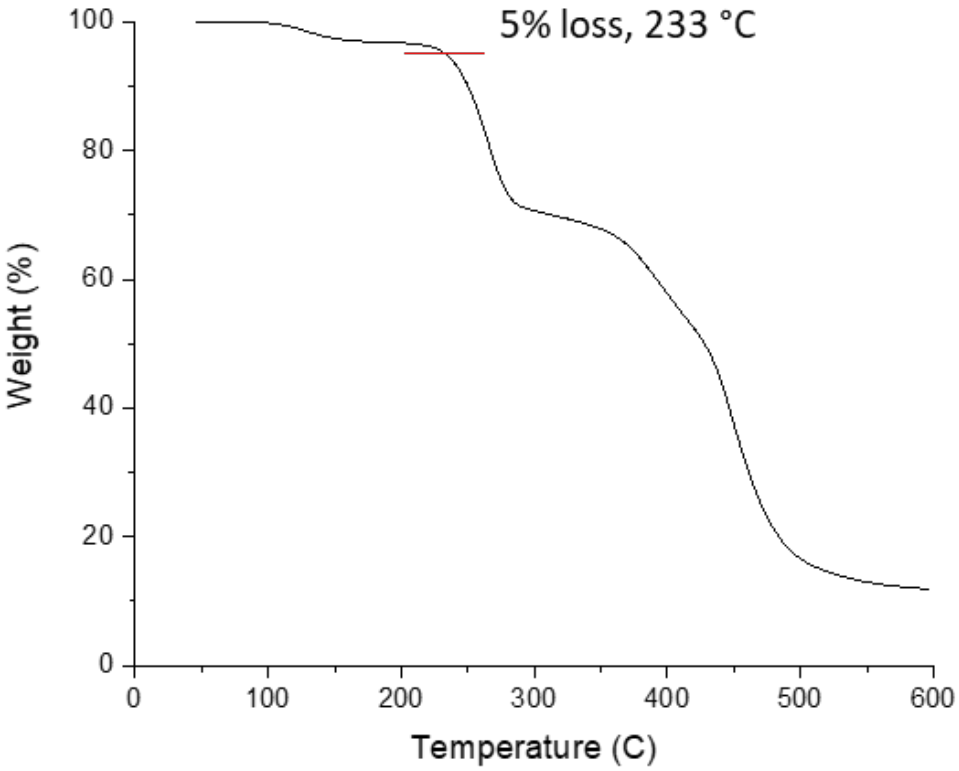


Figure S34: TGA Thermogram of P(**M$_{2C}$**-*alt*-**CTA$_2$**)

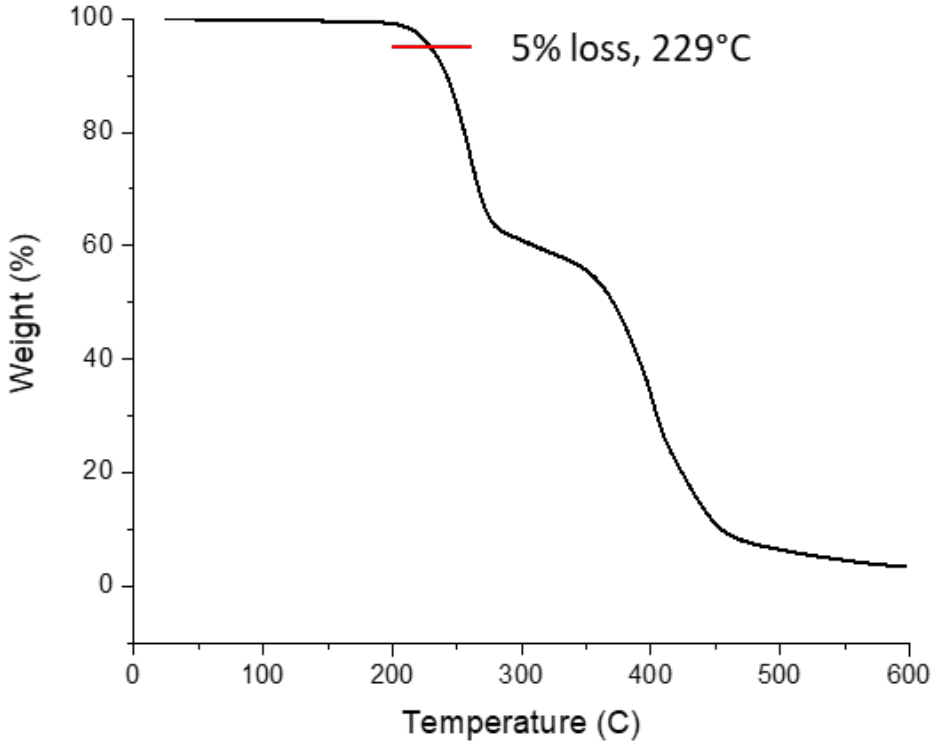


Figure S35: TGA Thermogram of P(**M_{2D}**-*alt*-**CTA_2**)

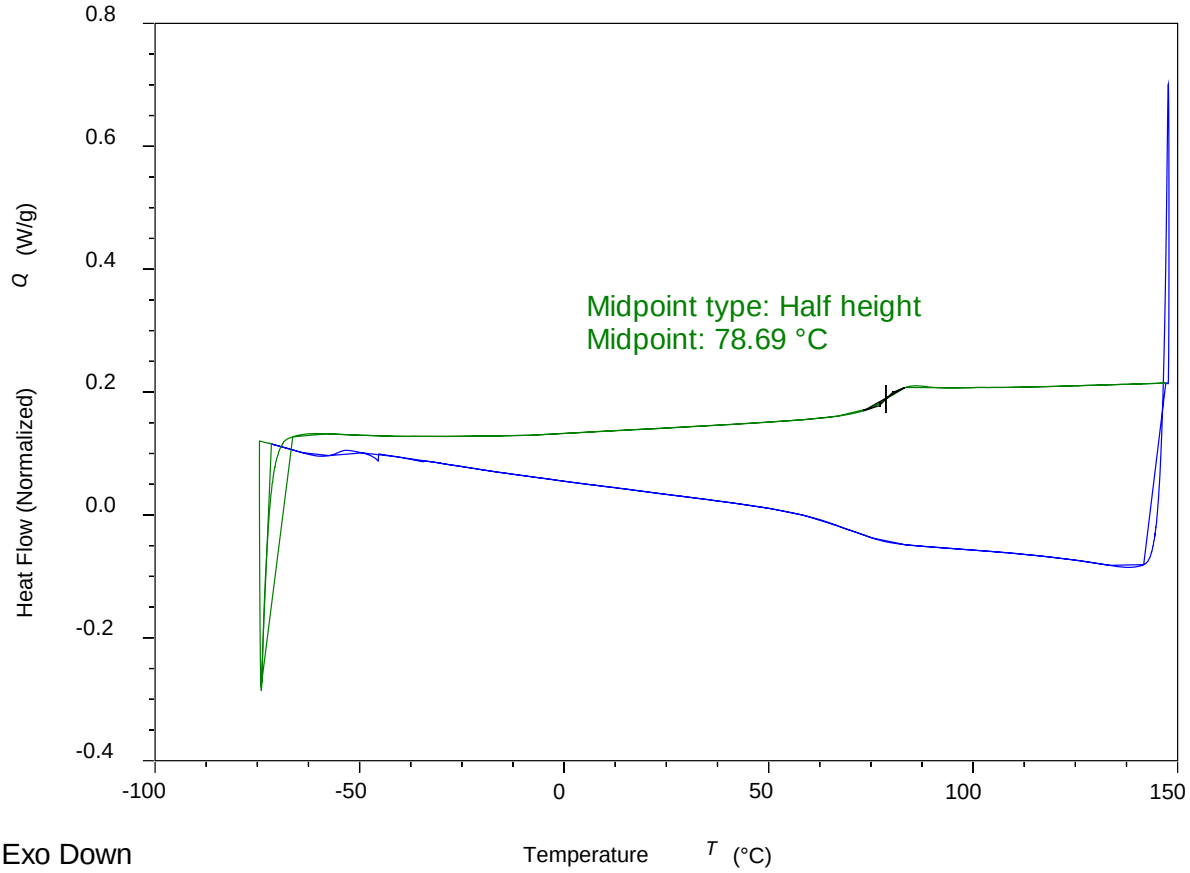


Figure S36: DSC Thermogram of P(**M$_{2A}$**-*alt*-**CTA$_2$**). The green curve shows heating cycle, and the blue curve shows the cooling cycle.

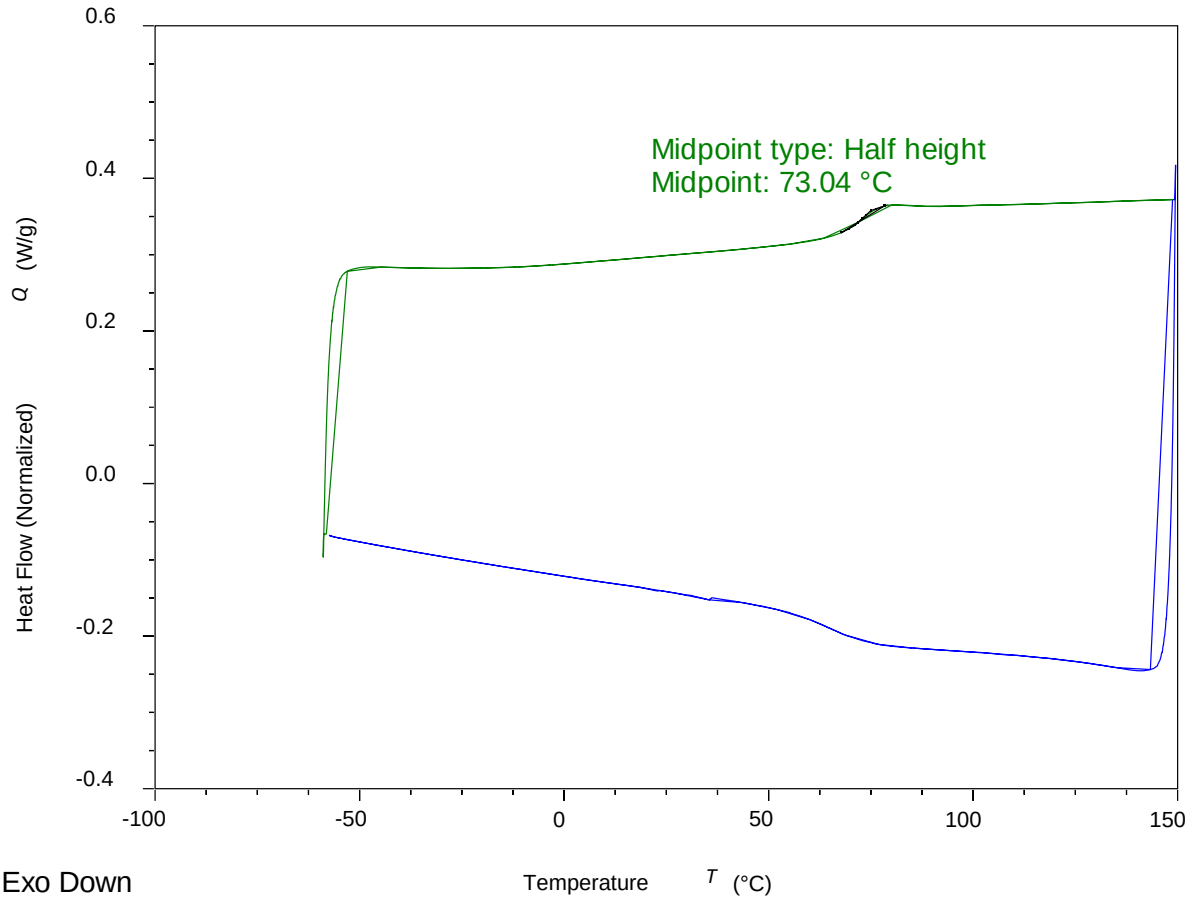


Figure S37: DSC Thermogram of P(**M_{2B}**-*alt*-**CTA_2**). The green curve shows heating cycle, and the blue curve shows the cooling cycle.

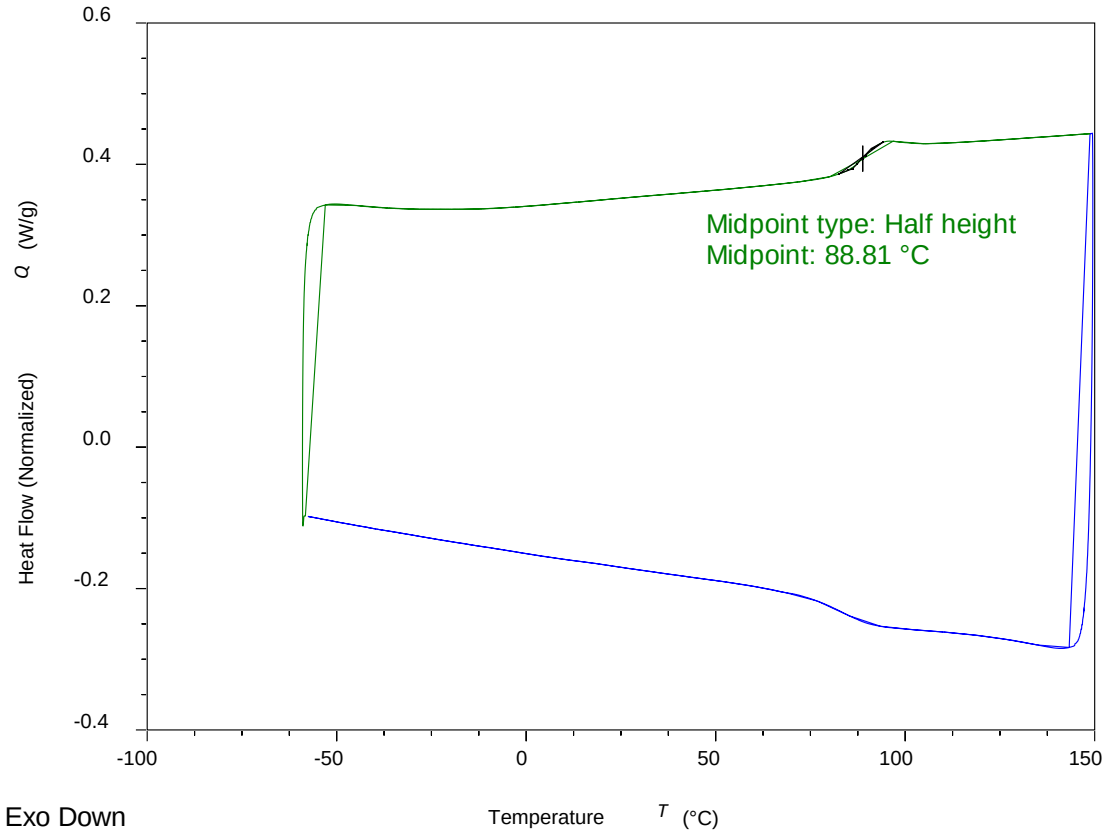


Figure S38: DSC Thermogram of P(**M$_{2C}$**-*alt*-**CTA$_2$**). The green curve shows heating cycle and the blue curve shows the cooling cycle.

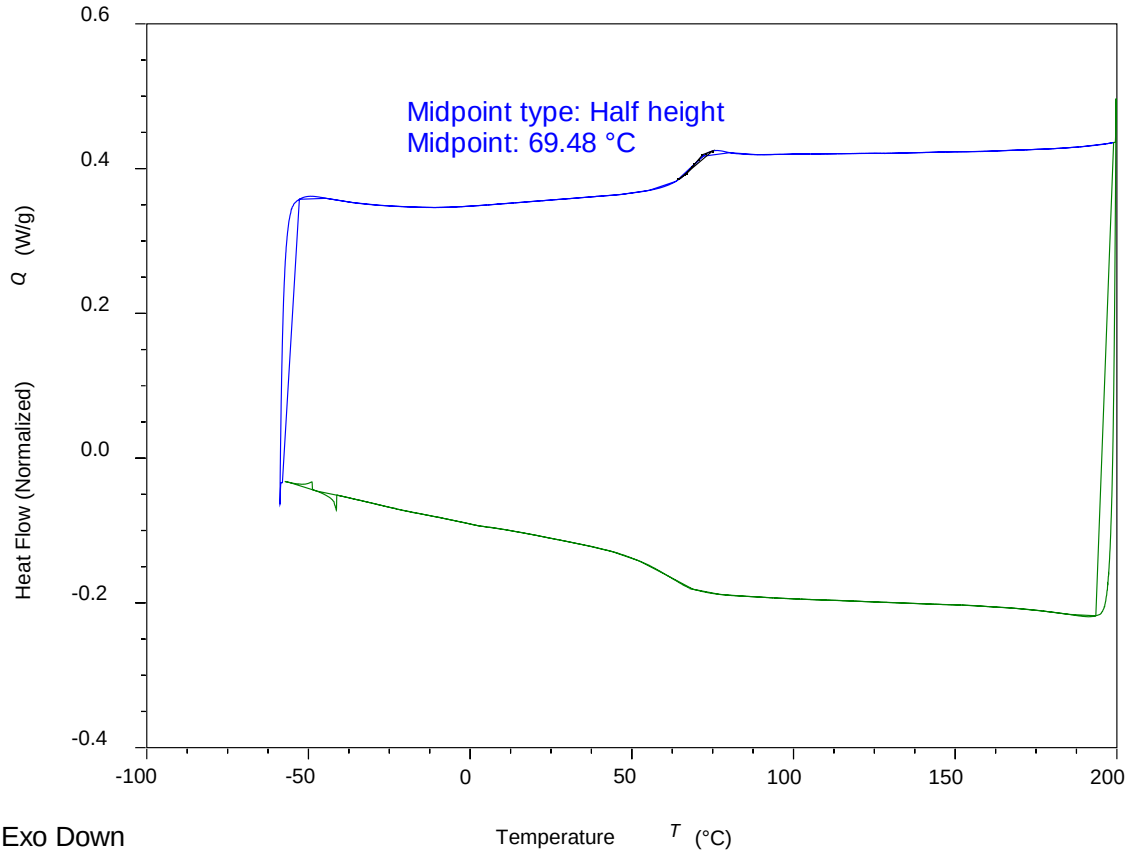
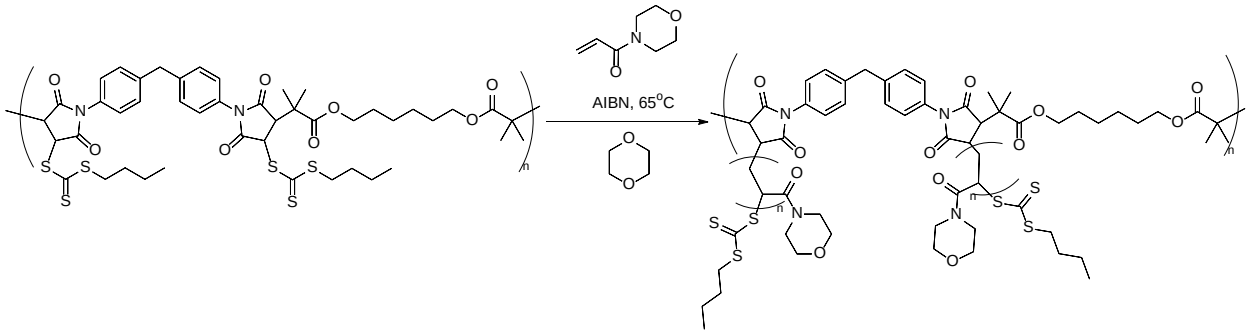


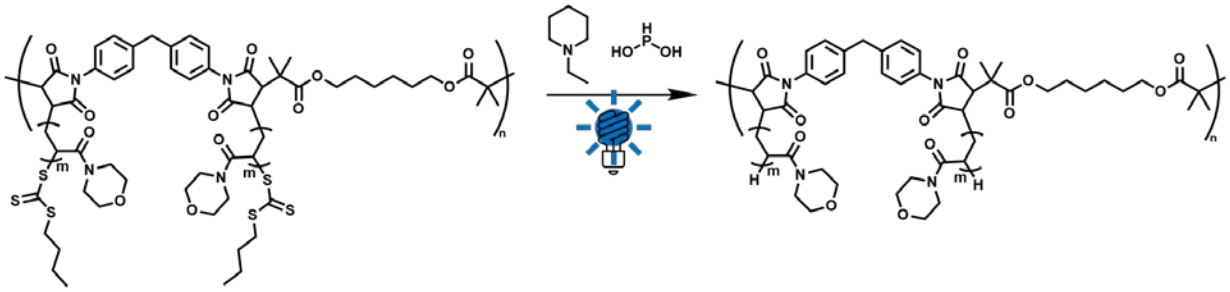
Figure S39: DSC Thermogram of P(**M$_{2D}$**-*alt*-**CTA$_2$**). The blue curve shows heating cycle and the green curve shows the cooling cycle.

Procedure for PNAM graft copolymer synthesis:



Isolated P(**M$_{2A}$**-*alt*-**CTA$_2$**) (1254 mg, 2.7 mmol) was charged into a 100 ml round bottom flask, followed by 4-acryloylmorpholine (15.0 g, 106 mmol). Next, 21.5 ml dioxane was added by weight (22.2 g) and then 545 µl AIBN stock solution (20mg/ml in dioxane) was added using a micropipette, targeting molar concentrations of $[NAM]_0$: $[CTA]_0$: $[I]_0$ = 3 M : 0.075 M : 0.00188 M (taking into account volume of the monomer). The vial was then equipped with a magnetic stir bar and secured by rubber septum. The solution was purged with argon for 10 minutes, prior to placing the reaction mixture in an oil bath set to 65°C. After 2.5 hours the monomer conversion reached 99% and the polymer was isolated by precipitating into diethyl ether.

Procedure CTA end group removal on PNAM graft copolymer:



Removal of Z-group was carried out following a reported procedure:[3] Briefly, isolated P(**M$_{2A}$**-*alt*-**CTA$_2$**)-*g*-PNAM (250 mg, 0.0408 mmol CTA, 1 equivalence) was charged into a 20 ml vial, followed by N-ethyl piperidine hypophosphate (109 mg, 0.612 mmol, 15 equivalence). Next, 2.5 ml dioxane was added. Following dissolution, the mixture was transferred to 3.7 ml vial. The vial was then equipped with a magnetic stir bar and secured by rubber septum. The solution was purged with argon for 10 minutes, prior to irradiation with blue LED light for 24 hours. The polymer (192 mg recovered) was isolated by precipitating into diethyl ether.

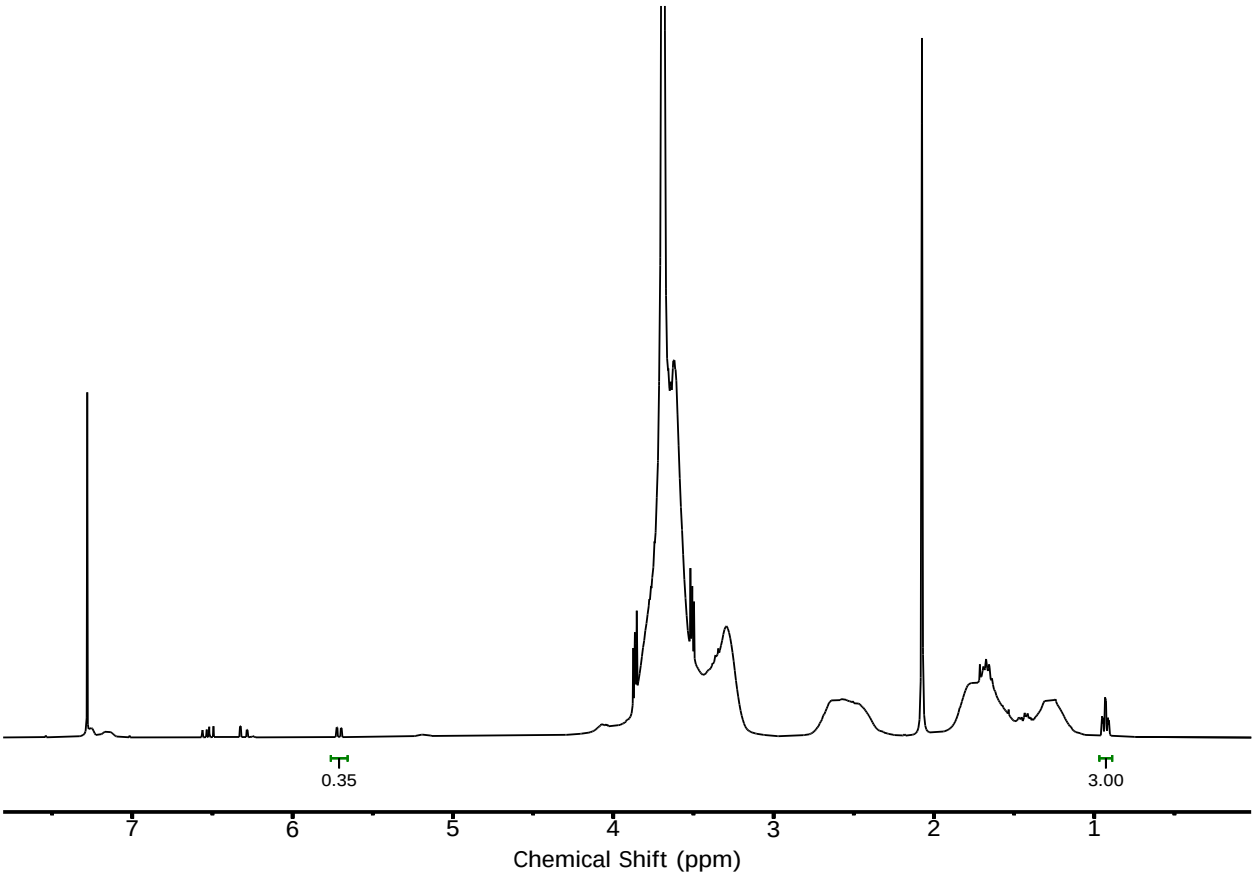


Figure S40: ^{1}H-NMR ($CDCl_3$, 400 MHz) of P(**M_{2A}**-*alt*-**CTA_2**)-*g*-PNAM synthesis, using conditions described above. The conversion of NAM (from 5.73 ppm) was determined using C*H*$_3$ at 0.93 ppm as a reference for end-group.

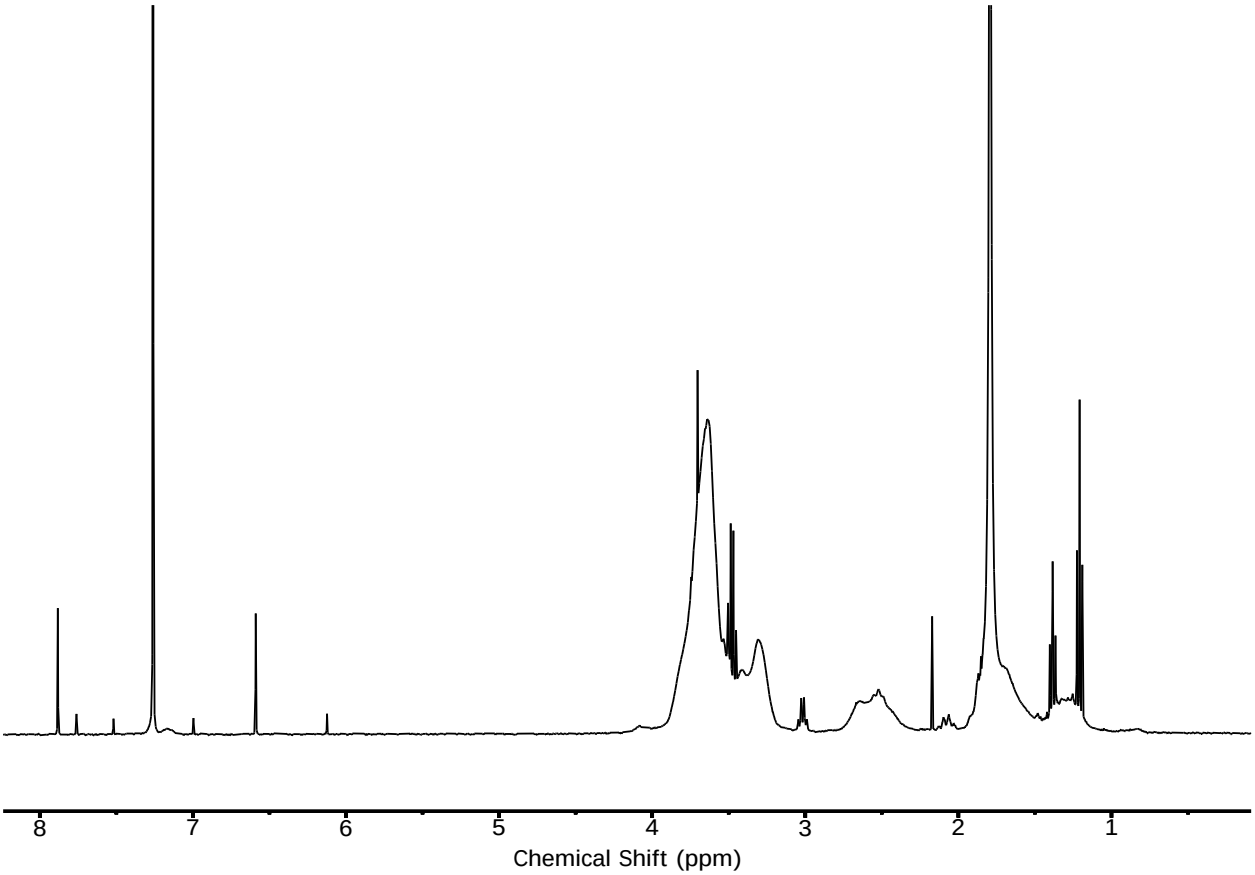


Figure S41: ^{1}H-NMR ($CDCl_3$, 400 MHz) of P(**M_{2A}**-*alt*-**CTA_2**)-*g*-PNAM synthesis after CTA end group removal described above. Note the disappearance of C*H*$_3$ at 0.93 ppm corresponding to the Z-group.

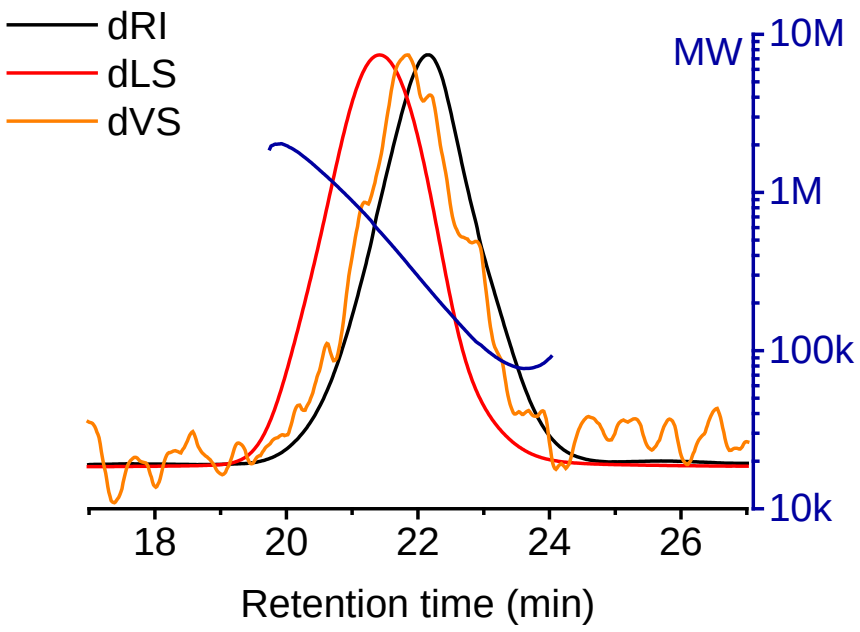


Figure S42: Normalized response from multidetector SEC analysis (dRI, dLS, dVS) of purified P(**M$_{2A}$**-*alt*-**CTA$_2$**)-*g*-PNAM in THF. The molecular weight was determined from the LS-detector with dn/dc value of 0.164 from 100 % mass recovery. M_n = 205k, M_w = 381k, M_z = 702k.

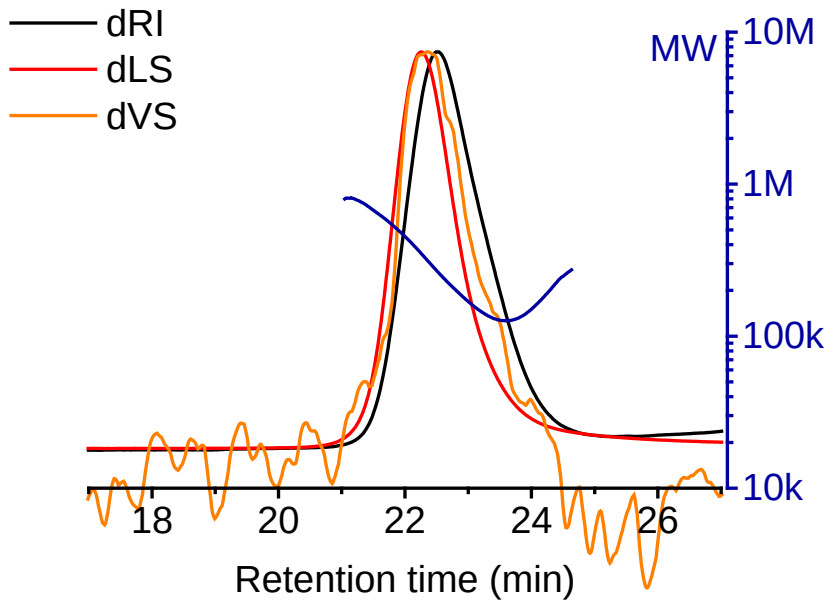


Figure S43: Normalized response from multidetector SEC analysis (dRI, dLS, dVS) in THF of purified P(**M$_{2A}$**-*alt*-**CTA$_2$**)-*g*-PNAM after CTA end group removal. The molecular weight was determined from the LS-detector with assumed dn/dc value of 0.164 from. M_n = 218k, M_w = 268k, M_z = 334k.

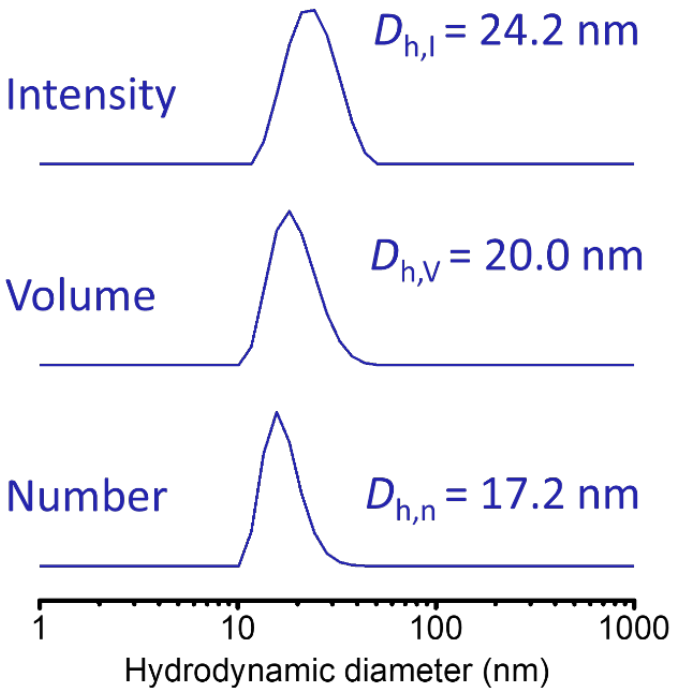


Figure S44: DLS traces (intensity, volume and number distribution) of the P(M_{2A}-alt-CTA_2-*g*-PNAM) in DMF (10 mg/ml) after end group removal. Z-average hydrodynamic radius = 21.3 nm, PdI = 0.212.

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