Electronic Supplementary Information for

Accessing broader vinyl ether scope for sequential cationic-anionic block copolymers

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I. General information

A. Instrumentation and methods

The synthesized polymers were named on the basis of monomer loading and not actual degrees of polymerization (i.e., p(IBVE)$_{50}$ was made using 50 eq of IBVE monomer relative to **TCT1**). Cationic polymerizations were run open to air in sealed 1 dram screw top vials. Vinyl ether monomers were passed through a plug of basic alumina prior to polymerization to remove inhibitors. Thioacyl anionic group transfer polymerizations (TAGTs) were carried out inside an MBraun Unilab glovebox with a nitrogen atmosphere. For polymerizations in the glovebox, vials were oven-dried and allowed to cool under active vacuum. Column chromatography was performed with silica gel (particle size 3–200 μm, 70–320 mesh) using mixtures of ethyl acetate (EtOAc) and hexanes. All work-up and purification was carried out in reagent grade solvents (purchased from Fisher, Oakwood, Sigma Aldrich, and TCI) in air.

Centrifugation of precipitated polymers was performed in 15 mL centrifuge tubes using a VWR 76019-132 Fixed Angle General Purpose Centrifuge with a 12 x 15 mL rotor spun at 4500 revolutions per minute (RPM) for 15 minutes.

Dialysis of polymers was performed using ThermoScientific SnakeSkin^{TM} dialysis tubing (3.5 kDa MWCO) in MeOH for 2 days with complete solvent changes every 24 hours.

Differential scanning calorimetry (DSC) analyses were performed on a TA Q1000 under a nitrogen atmosphere. Samples were sealed inside TA Tzero pans. Heating and cooling rates were set to 10 °C/min. Glass transition temperature (T_g) features were determined during the second heating cycle.

Drying of polymer samples was performed using a Fisherbrand Isotemp Model 281A Vacuum Oven at 60 ºC overnight equipped with an external trap attached to a Welch 1402B-01 DuoSeal Vacuum Pump.

NMR spectra were recorded on a Bruker 500 MHz Avance III HD instrument with a Prodigy TCI cryoprobe [(^{1}H, 500 MHz)] with shifts reported relative to the residual solvent peak [$CDCl_3$: 7.26 ppm (^{1}H), D_2O: 4.79 ppm (^{1}H)] or a Bruker 400 MHz Avance III HD instrument with a BBFO

SmartProbe [(^{1}H, 400 MHz)]. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, n = nonet, m = multiplet), coupling constants (in Hz), and integration. Deuterated chloroform and water was purchased from Cambridge Isotope Laboratories.

SEC analyses of p(POPS) homopolymers were performed using an Agilent 1260 LC system with two Agilent PolarGel-M (diameter: 7.5 mm, length: 30 cm, particle size: 8 μm) columns in series at 40 °C and a flow rate of 1 mL/min with 0.025 M LiBr in DMF as the eluent. Wyatt Optilab differential refractive index (dRI), DAWN 8 angle light scattering (MALS), and Agilent 1260 Infinity UV detectors were used. The SEC was calibrated with poly(methyl methacrylate) (PMMA) standards in the same solvent. DMF (HPLC grade) was purchased from VWR and lithium bromide was purchased from Sigma Aldrich. Samples were filtered through 0.2 μm poly(tetrafluoroethylene) (PTFE) syringe filters.

Size-exclusion chromatography (SEC) analyses for polymers soluble in tetrahydrofuran (THF) were performed on one of two SEC instruments: (1) Tosoh EcoSEC Elite HPLC system with two Tosoh Bioscience TSKgel GMHhr-M columns (diameter: 7.8 mm, length: 30 cm, particle size: 5 μm) in series at 40 °C and a flow rate of 1 mL/min with THF as the eluent. dRI measured using the integrated detector in the HPLC. (2) Waters Arc HPLC with three Agilent PL-Gel Mixed C columns (diameter: 7.5 mm, length: 30 cm, particle size: 5 μm polystyrene-divinylbenzene matrix) with Wyatt Optilab dRI detector with a flow rate of 1 mL/min with THF as the eluent. The SECs were calibrated with poly(styrene) (PS) standards in the same solvent. Samples were filtered through 0.2 μm poly(tetrafluoroethylene) (PTFE) syringe filters.

Solubility tests were conducted by combining polymer (0.2–4.6 mg) and solvent (10 mg/mL) in a 1 dram vial and vortex mixing for 5 min. Polymers that were insoluble after vortex mixing were then sonicated for 15 min. Polymers that were still insoluble were diluted to 2 mg/mL followed by 1 mg/mL with the vortex and sonication procedures repeated at each concentration. Polymers were deemed soluble at a given concentration if the solution was clear and homogenous and insoluble if the solution was not. Solubility was then classified into one of three semiquantitative categories defined by You and coworkers:[1] soluble (≥ 10 mg/mL), partially soluble (1–10 mg/mL), and insoluble (< 1 mg/mL).

Solvent purification system was purchased from Pure Process Technology (PPT) and features two packed columns of neutral alumina for each solvent. Argon is used as the inert gas. Solvents were sparged to degas prior to loading onto columns.

Thermogravimetric analyses (TGA) were performed on a TA TGA 5500 with the sample placed in an aluminum TA Classic pan inside TA platinum TGA pans (for ease of cleaning) at a heating rate of 10 °C/min under a nitrogen atmosphere. Extrapolated onset temperatures of degradation (T_o) were calculated by the intersection of the tangent lines of the pre-degradation baseline and the point of maximum gradient using the TA TRIOS software (Figure S1).

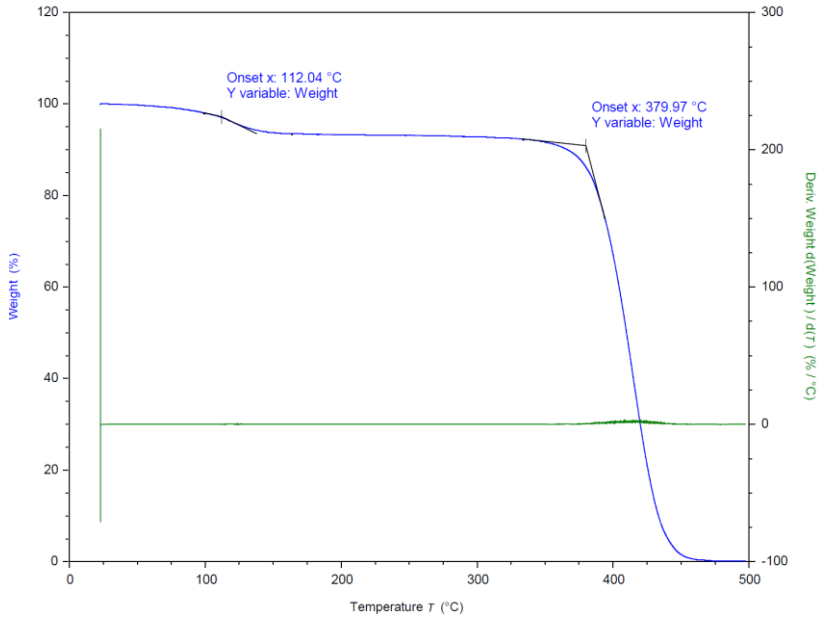


Figure S1. Example calculation of T_o using TRIOS software.

Ultraviolet and visible (**UV-Vis)** light absorbance measurements were performed on a Varian Cary 100 Bio UV-Vis spectrophotometer using a deuterium lamp (for UV range,190–350 nm) and halogen lamp (for visible range, 330–1100 nm) with a silicon photodiode detector and double beam optical system. Quartz cuvettes were used for measurements of solutions in DCM. Samples were diluted until peaks corresponding to **TCT1** were below 1 a.u.

B. Sources of solvents and reagents

2-(Phenoxymethyl)thiirane/3-Phenoxypropylene sulfide (POPS) was synthesized according to previous literature.[2]

2,3-Dihydrofuran (DHF) was purchased from Thermo Fisher Scientific and filtered through basic alumina prior to use.

3,5-Bis(trifluoromethyl)aniline was purchased from Synthonix and used as received.

Acetic Acid (glacial) was purchased from VWR and used as received.

Acetonitrile (MeCN) was purchased from Sigma Aldrich and used as received.

Aluminum oxide, activated, basic, Brockmann I (basic alumina) was purchased from Sigma Aldrich and used as received.

Ammonium chloride was purchased from Thermo Fisher Scientific and was made into a saturated aqueous solution prior to use.

Benzyltrimethylammonium chloride was purchased from Sigma Aldrich and used as received.

***n*-Butylamine** was purchased from Sigma Aldrich and used as received.

Calcium Hydride (CaH_2) was purchased from Sigma Aldrich and stored in a desiccator.

Cyclohexyl vinyl ether (CyVE) was purchased from TCI and filtered through basic alumina prior to use.

Cyclopentanone was purchased from TCI and dried over CaH_2 for 24 hours before being vacuum transferred into a Schlenk bomb and degassed via freeze-pump-thaw cycles (3x) prior to being brought into the glovebox.

Dichloromethane (DCM) was purchased from Sigma Aldrich and used as received.

Diethyl ether, anhydrous (Et_2O) was purchased from Thermo Fisher Scientific and used as received.

Dimethyl acetylenedicarboxylate was purchased from Sigma Aldrich and used as received.

Dimethyl malonate was purchased from Sigma Aldrich and used as received.

Ethyl 1-(2-methylpropoxy)ethyl carbonotrithioate (TCT1) was synthesized (see Section SIV.B) using a modified procedure.[3] For use in TAGT, it was dried under high vacuum for 12 hours, brought into the glovebox under vacuum and stored at −20 °C.

Ethyl acetate (EtOAc) was purchased from Sigma Aldrich and dried over CaH_2 for 24 hours before being vacuum transferred into a Schlenk bomb and degassed via freeze-pump-thaw cycles (3x) prior to being brought into the glovebox.

Ethyl vinyl ether (EVE) was purchased from Sigma Aldrich and filtered through basic alumina prior to use.

Hydrochloric acid (37% in H_2O) was purchased from VWR and used as received.

Isobutyl vinyl ether (IBVE) was purchased from Sigma Aldrich, filtered through basic alumina when used for cationic polymerization and dried over CaH_2, vacuum transferred and freeze-pump-thawed (3x) prior to use in TCT synthesis (see Section SIV.B).

Magnesium sulfate (anhydrous) was purchased from Thermo Fisher Scientific and used as received.

***N*,*N*-Dimethylacetamide (DMAc) (99.8%, anhydrous)** was purchased from Thermo Fisher Scientific and used as received.

***n*-Butyl vinyl ether (NBVE)** was purchased from Thermo Fisher Scientific and filtered through basic alumina prior to use.

Pentacarbomethoxycyclopentadiene (PCCP) was synthesized according to previous literature.[4]

Potassium carbonate was purchased from Fisher Scientific and made into a saturated aqueous solution prior to use.

Potassium thiocyanate was purchased from Oakwood Chemical and used as received.

Propyl vinyl ether (PVE) was purchased from TCI and filtered through basic alumina prior to use.

Pyridine was purchased from Acros Organics and used as received.

Sodium S′-ethyl trithiocarbonate (TCT salt) was synthesized (see Section SIV.A) using a modified procedure.[3]

***tert*-Butyl vinyl ether (TBVE)** was purchased from Thermo Fisher Scientific and filtered through basic alumina prior to use.

Tetrahydrofuran (THF) was purchased from Sigma Aldrich and used as received.

Tetraphenylphosphonium chloride (PPh_4Cl) was purchased from AA Blocks and used as received.

Toluene was purchased from Sigma Aldrich and used as received.

Triethylamine was purchased from Fisher Scientific and was freshly distilled prior to use.

Tris(3,5-bis(trifluoromethyl)phenyl) thiophosphotriamide (HBD) was synthesized according to previous literature.[5]

C. Polymerization Mechanisms

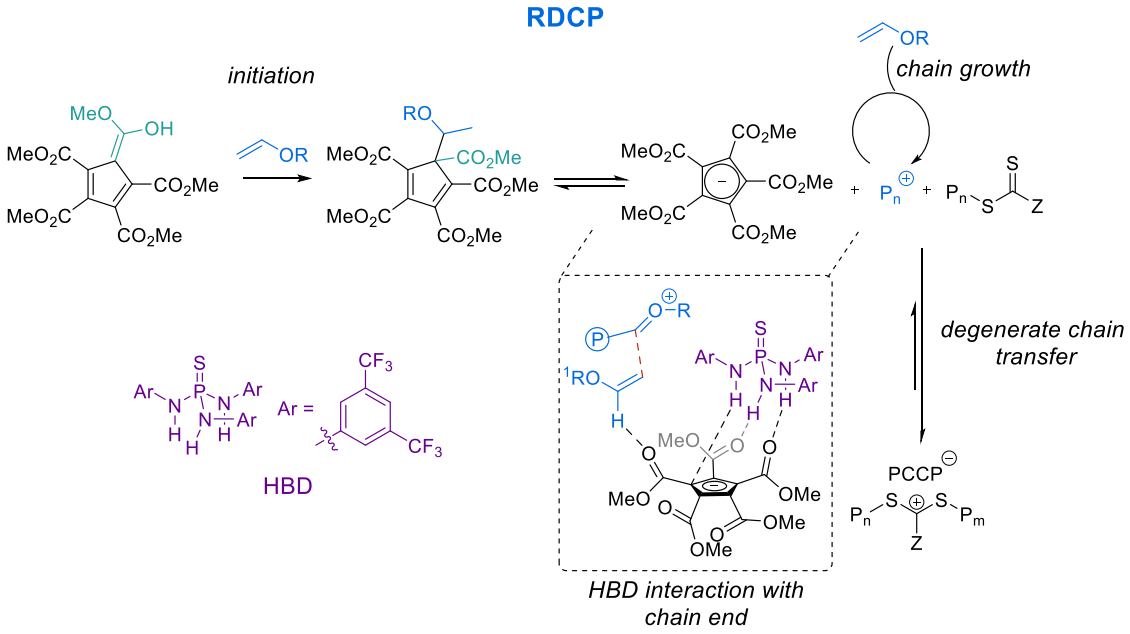


Figure S2. Mechanism for RDCP adapted from previous reports.[6,7]

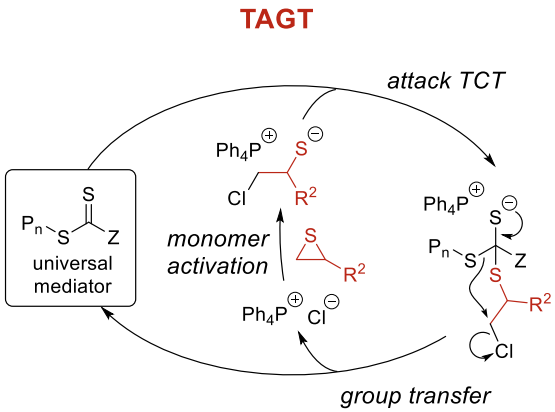


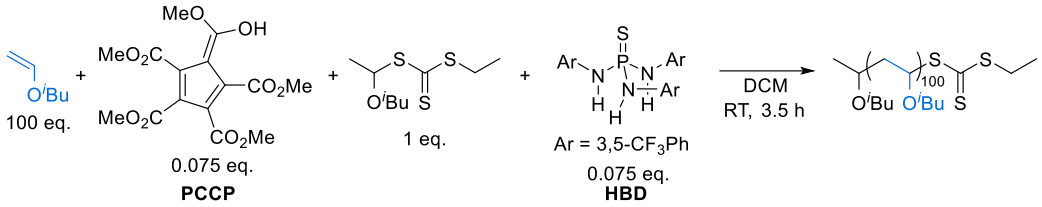
Figure S3. Mechanism for TAGT.[8]

II. Supplemental data

A. Effect of atmosphere on RDCP

While the initial reports of RDCP stated the polymerizations can be run open to air when using **TCT2**,[6] we wanted to verify the performance of the polymerization using **TCT1** open to air compared to a nitrogen atmosphere. Ultimately, there was little difference between the atmospheres (Table S1), so all future RDCP polymerizations were run open to air for ease of use.

Table S1. Effect of atmosphere on RDCP of IBVE



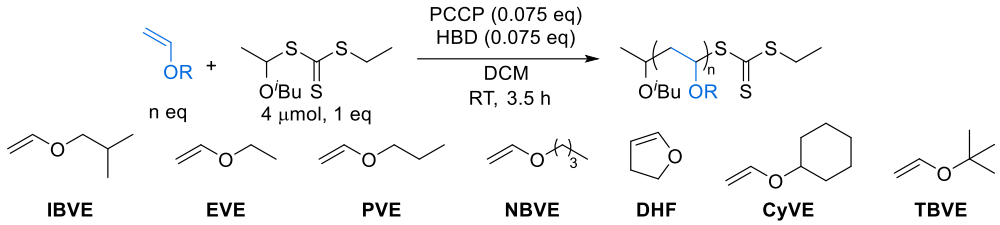
entry	atmosphere	% conv.[c]	$M_{n,theo}$ (kDa)	M_n (kDa)[d]	M_w (kDa)[d]	$Đ$[d]
1	Air	99	10.2	13.7	16.2	1.18
2	N_2[b]	99	10.2	12.6	15.2	1.21

[a] Standard reaction conditions: **TCT1** (0.038 mmol, 1 eq), IBVE (100 eq), PCCP (0.0029 mmol, 0.075 eq), HBD (0.0029 mmol, 0.075 eq), DCM (1:2 DCM:IBVE by volume), 3.5 h, RT. [b] Polymerization set up in a septa-cap vial. Prior to addition of IBVE, the headspace of the vial was purged with N_2 for 5 minutes. [c] Determined via ^{1}H NMR spectroscopy of the crude reaction mixture. [d] Determined via SEC in THF against PS standards.

B. Vinyl ether monomer screen and associated SEC traces

Please note that entries 1–7 are reproduced from Table 1 in the main text for ease of comparison.

Table S2. Vinyl ether monomer scope for RDCP



entry	polymer	conv. (%)[c]	$M_{n,theo}$ (kDa)	M_n (kDa)[d]	M_w (kDa)[d]	$Đ$[d]
1	p(IBVE)$_{100}$	99	10.2	12.4	14.7	1.18
2	p(EVE)$_{100}$[a]	>99	7.5	10.3	11.9	1.13
3	p(PVE)$_{100}$	>99	8.8	7.6	10.2	1.34
4	p(NBVE)$_{100}$	>99	10.2	11.7	13.7	1.17
5	p(DHF)$_{100}$[a]	>99	7.2	7.5	9.8	1.30
6	p(CyVE)$_{100}$[b]	>99	12.9	13.1	21.9	1.67
7	p(TBVE)$_{100}$[a]	>99	10.3	9.0	13.5	1.50
8	p(IBVE)$_{50}$	>99	5.2	8.7	9.6	1.10
9	p(EVE)$_{50}$[a]	>99	3.8	5.0	5.9	1.14
10	p(PVE)$_{50}$	>99	4.5	5.4	6.5	1.20
11	p(NBVE)$_{50}$	>99	5.2	7.3	9.1	1.25
12	p(DHF)$_{50}$[a]	>99	3.7	5.2	6.1	1.18
13	p(CyVE)$_{50}$[b]	>99	6.5	7.9	11.4	1.43
14	p(TBVE)$_{50}$[a]	>99	5.2	6.3	9.9	1.58

Standard reaction conditions: **TCT1** (0.038 mmol, 1 eq), vinyl ether (n eq), PCCP (0.0029 mmol, 0.075 eq), HBD (0.0029 mmol, 0.075 eq), DCM (1:2 DCM:VE by volume), 3.5 h, RT. [a] Reaction run for 16 h. [b] Reaction run at 0 °C for 3 h. [c] Determined via ^{1}H NMR spectroscopy of the crude reaction mixture. [d] Determined via SEC in THF against PS standards.

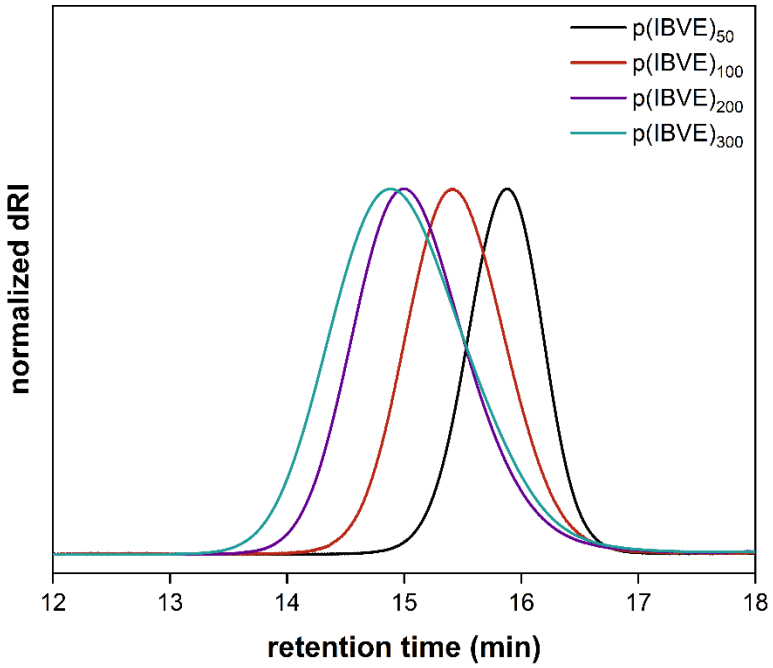


Figure S4. SEC traces of p(IBVE) at various [IBVE]:[**TCT1**] ratios.

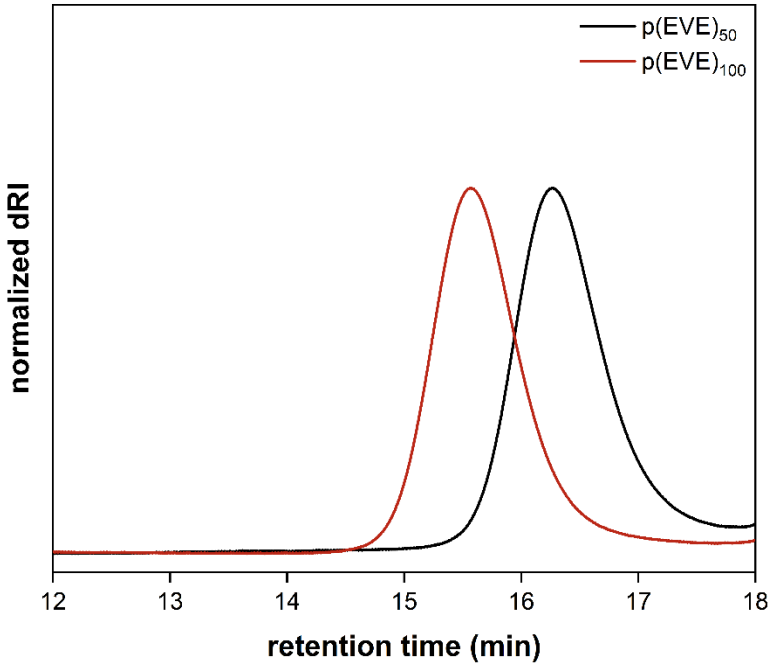


Figure S5. SEC traces of p(EVE) at various [EVE]:[**TCT1**] ratios.

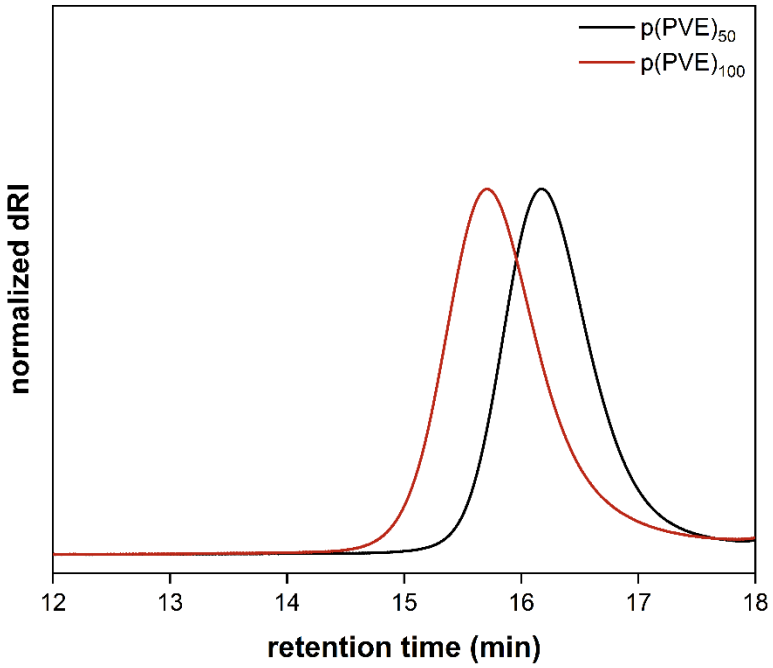


Figure S6. SEC traces of p(PVE) at various [PVE]:[**TCT1**] ratios.

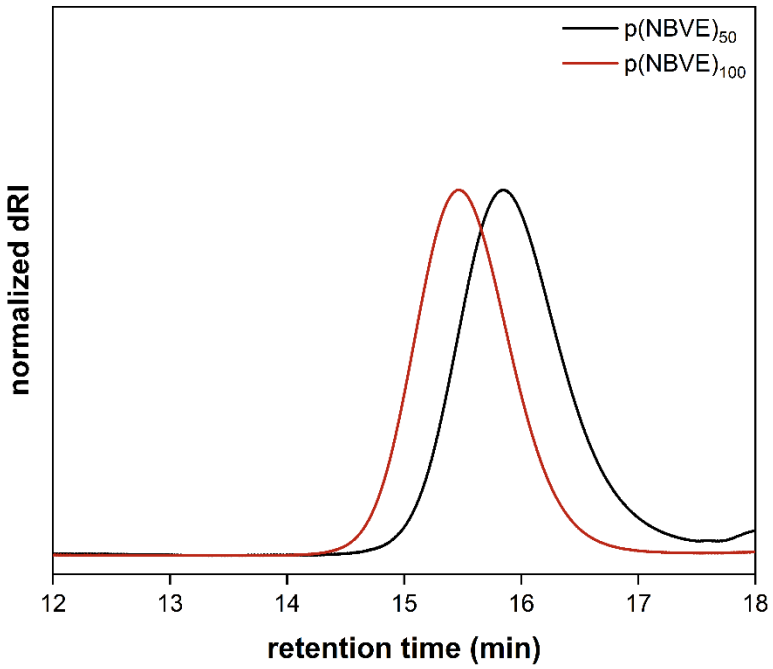


Figure S7. SEC traces of p(NBVE) at various [NBVE]:[**TCT1**] ratios.

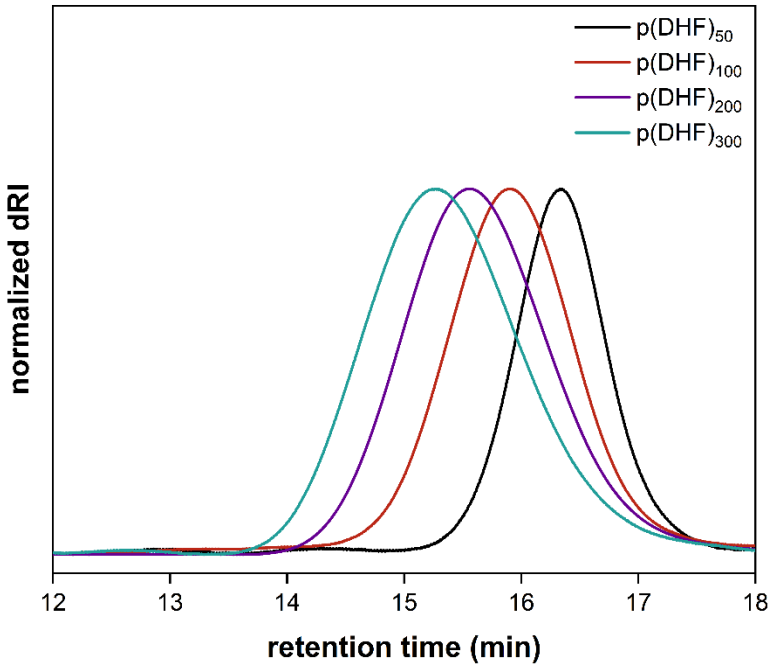


Figure S8. SEC traces of p(DHF) at various [DHF]:[**TCT1**] ratios.

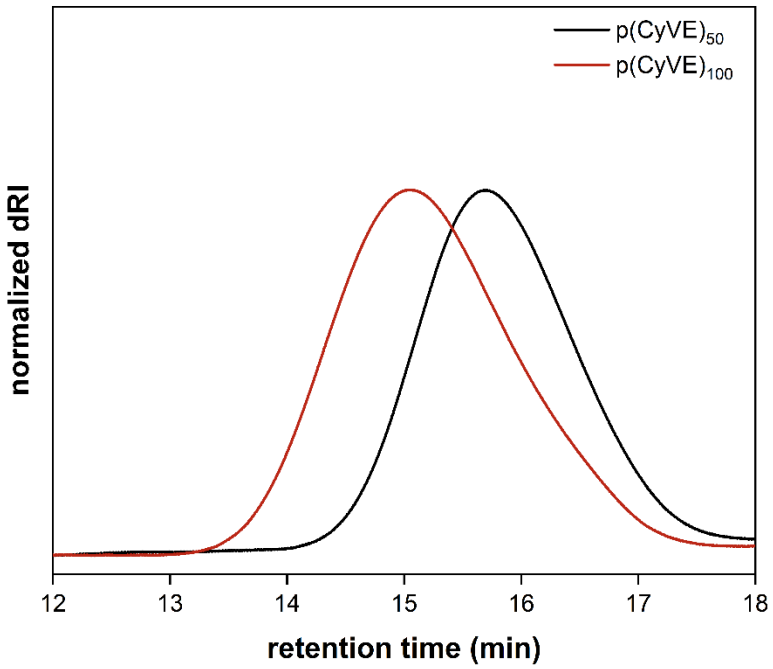


Figure S9. SEC traces of p(CyVE) at various [CyVE]:[**TCT1**] ratios.

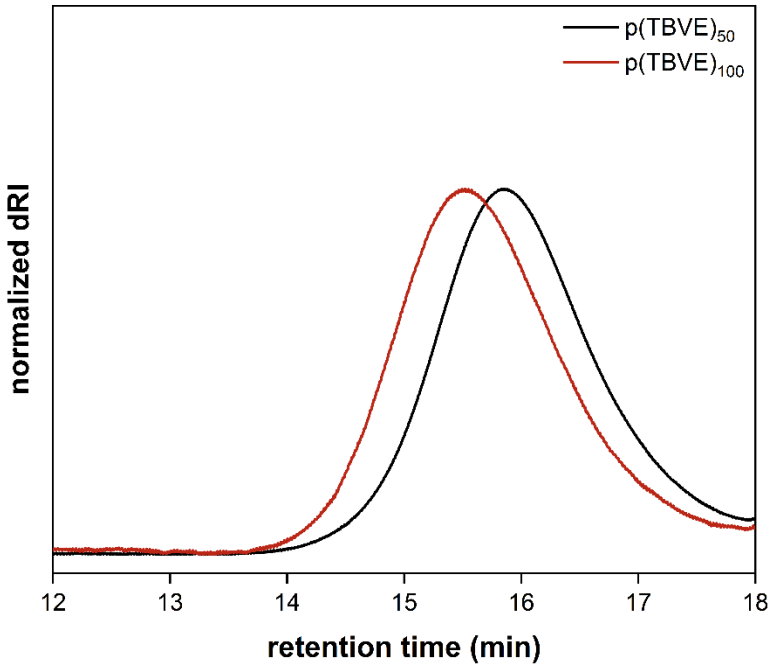
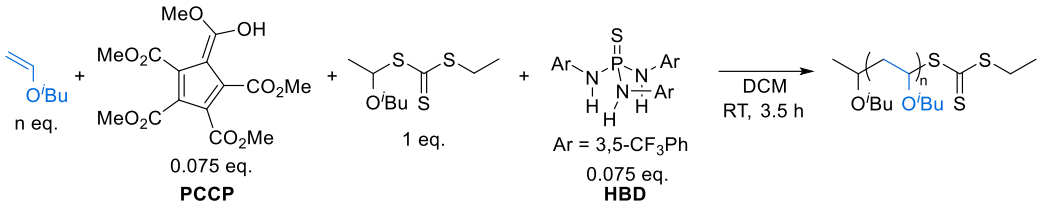


Figure S10. SEC traces of p(TBVE) at various [TBVE]:[**TCT1**] ratios.

C. Isobutyl vinyl ether [M]:[TCT1] screen

Table S3. [IBVE]:[**TCT1**] screen[a]



entry	[M]:[TCT]	% conv.[b]	$M_{n,theo}$ (kDa)	M_n (kDa)[c]	M_w (kDa)[c]	$Đ$[c]
1	50:1	>99	5.2	8.7	9.6	1.10
2	100:1	99	10.2	12.4	14.7	1.18
3	200:1	93	18.6	17.2	21.7	1.26
4	300:1	75	17.3	18.2	24.7	1.36

[a] Standard reaction conditions: **TCT1** (0.038 mmol, 1 eq), IBVE (n eq), PCCP (0.0029 mmol, 0.075 eq), HBD (0.0029 mmol, 0.075 eq), DCM (1:2 DCM:IBVE by volume), 3.5 h, RT. [b] Determined via ^{1}H NMR spectroscopy of the crude reaction mixture. [c] Determined via SEC in THF against PS standards.

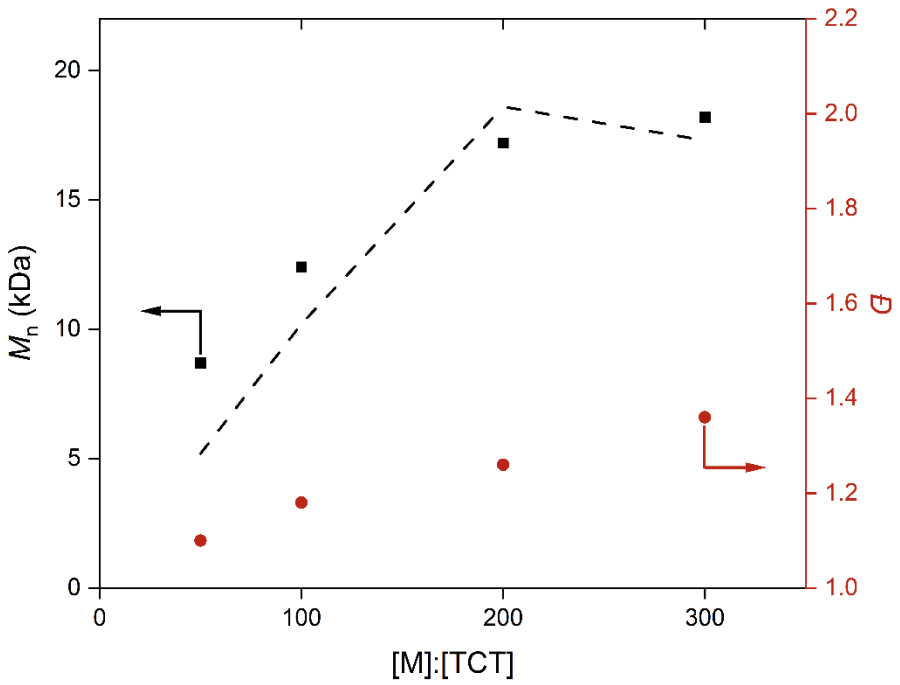
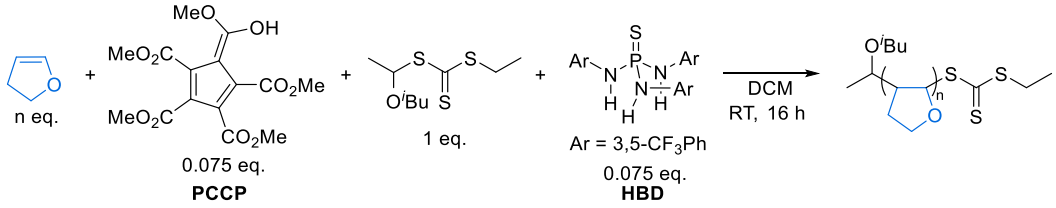


Figure S11. [IBVE]:[**TCT1**] screen of RDCP homopolymerization. Black squares: M_n. Red circles: $Đ$. Black dashed line: $M_{n,theo}$.

D. 2,3-Dihydrofuran [M]:[TCT1] screen

Table S4. [DHF]:[**TCT1**] screen[a]



entry	[M]:[TCT]	% conv.[b]	$M_{n,theo}$ (kDa)	M_n (kDa)[c]	M_w (kDa)[c]	$Đ$[c]
1	50:1	>99	3.7	5.2	6.1	1.16
2	100:1	>99	7.2	7.5	9.8	1.30
3	200:1	>99	14.3	9.3	13.3	1.44
4	300:1	>99	21.3	11.9	17.7	1.49

[a] Standard reaction conditions: **TCT1** (0.038 mmol, 1 eq), IBVE (n eq), PCCP (0.0029 mmol, 0.075 eq), HBD (0.0029 mmol, 0.075 eq), DCM (1:2 DCM:IBVE by volume), 16 h, RT. [b] Determined via ^{1}H NMR spectroscopy of the crude reaction mixture. [c] Determined via SEC in THF against PS standards.

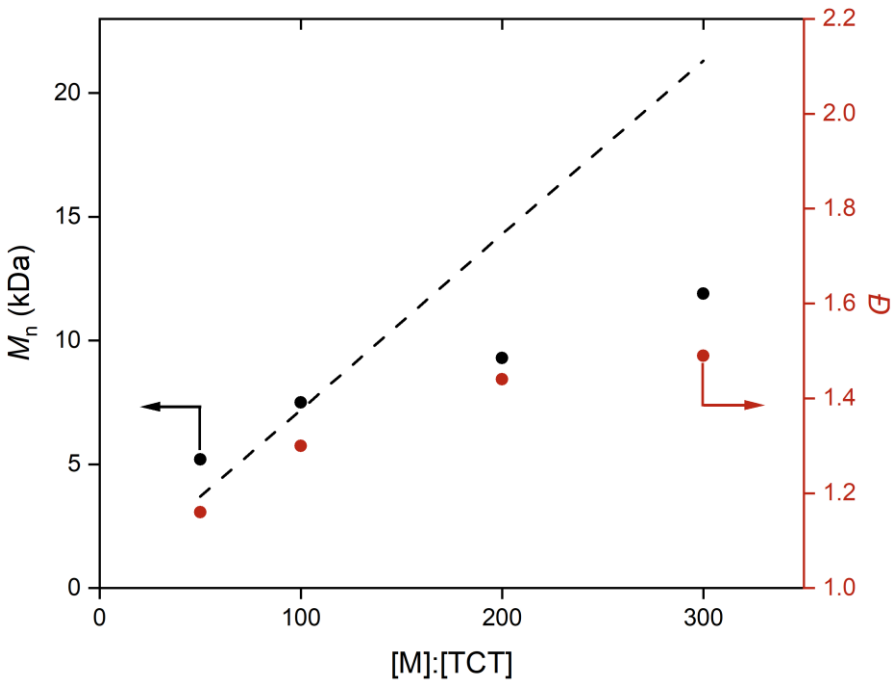
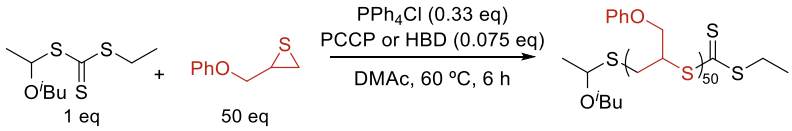


Figure S12. [DHF]:[**TCT1**] screen of RDCP homopolymerization. Black squares: M_n. Red circles: $Đ$. Black dashed line: $M_{n,theo}$.

E. Effect of PCCP and HBD on TAGT homopolymerization

In order to determine if purification of p(VE) is necessary prior to chain extension, the effect of PCCP and HBD on TAGT homopolymerization was investigated. To do this, TAGT was performed using standard conditions (see Section SIII.B) with PCCP and HBD added separately (in the amount that would be present in a chain extension assuming no loss from RDCP homopolymerization (0.075 eq to **TCT1**)). Unfortunately, the presence of PCCP in the TAGT polymerization severely hindered reactivity, resulting in just 11% monomer conversion after 6 hours. The addition of HBD resulted in 97% conversion – slightly higher than a typical TAGT homopolymerization – but SEC analysis revealed significant bimodality indicating a loss of control (Figure S13). With this information, it is important to purify the p(VE) to remove these components.



Scheme S1. TAGT homopolymerization with PCCP or HBD (0.075 eq) added.

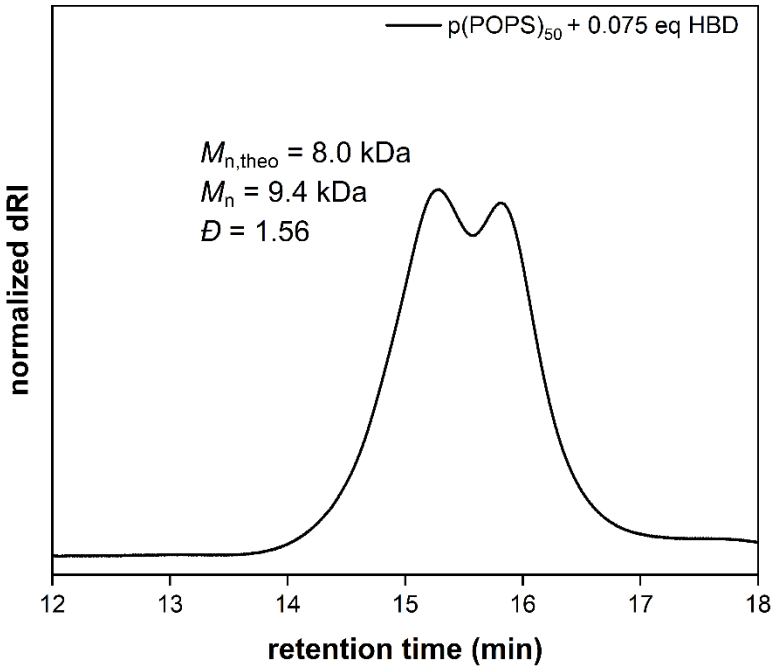
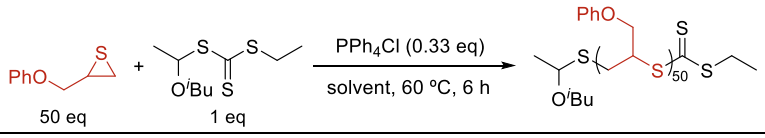


Figure S13. SEC chromatogram of TAGT performed with 0.075 eq of HBD relative to **TCT1**.

F. TAGT solvent screen for chain extensions of less soluble poly(vinyl ethers)

The solubility of $p(IBVE)_{50}$ and $p(DHF)_{50}$ in various solvents was evaluated, and found to be soluble in THF, EtOAc, and cyclopentanone. These solvents were evaluated for performance in TAGT in combination with DMAc in various ratios (Table S5).

Table S5. Solvent screen for TAGT homopolymerization



entry	solvent	conv. (%)[b]	$M_{n,theo}$ (kDa)	M_n (kDa)[c]	$Đ$[c]
1	DMAc	91	7.8	10.7	1.33
2	THF:DMAc (1:5)	76	6.3	7.5	1.28
3	THF:DMAc (1:4)	61	5.1	11.0	1.44
4	THF:DMAc (1:1)	66	5.7	7.4	1.51
5	EtOAc:DMAc (1:5)	86	7.4	8.8	1.48
6	EtOAc:DMAc (1:4)	90	7.3	8.9	1.47
7	EtOAc:DMAc (1:1)	76	6.5	11.4	1.73
8	cyclopentanone:DMAc (1:4)	96	8.5	10.3	1.58

[a] Standard reaction conditions: **TCT1** (0.004 mmol, 1 eq), POPS (50 eq), PPh_4Cl (0.33 eq), DMAc + co-solvent (15 mM), 6 h, 60°C. [b] Determined via ^{1}H NMR spectroscopy of the crude reaction mixture. [c] Determined via SEC in DMF with 0.025 M LiBr against PMMA standards.

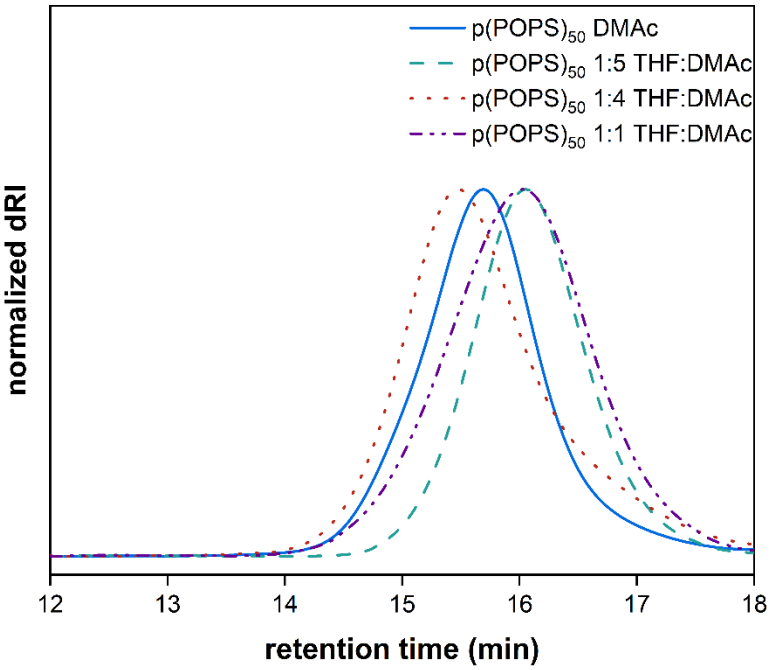


Figure S14. SEC traces of TAGT with various ratios of THF:DMAc.

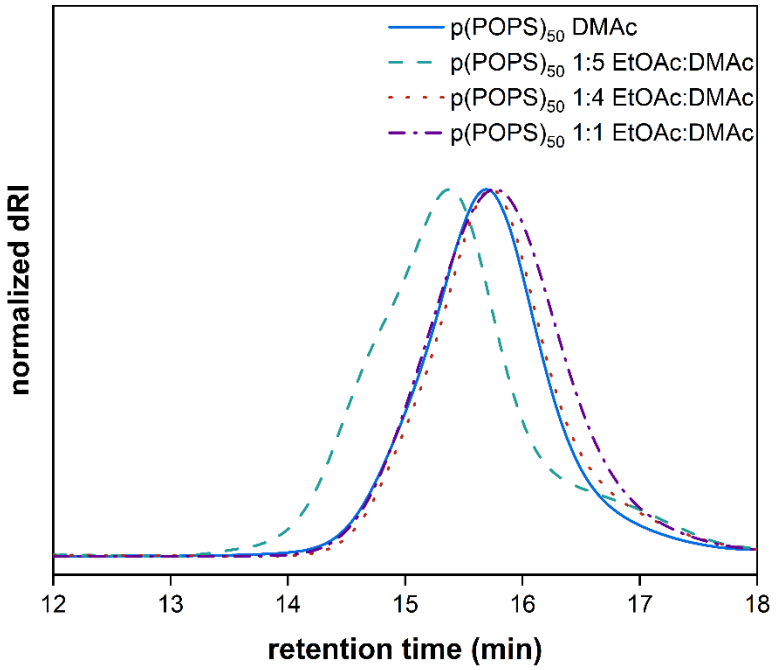


Figure S15. SEC traces of TAGT with various ratios of EtOAc:DMAc.

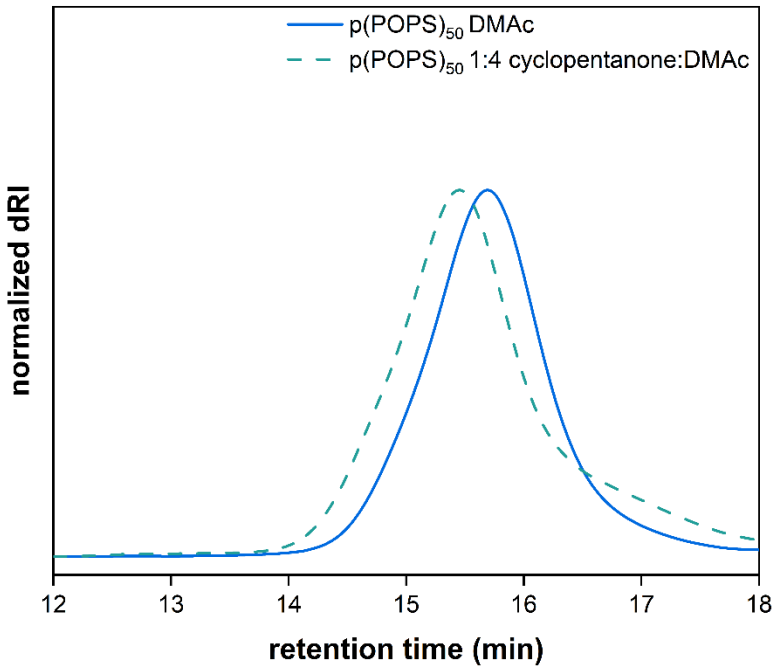
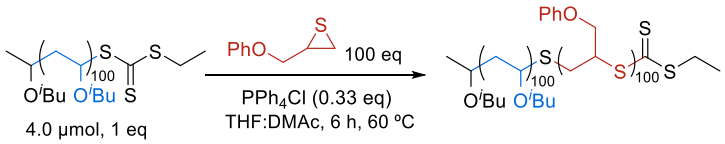


Figure S16. SEC traces of TAGT with various ratios of cyclopentanone:DMAc.

G. Concentration and THF:DMAc ratio screen for TAGT chain extension of p(IBVE)$_{100}$

To probe the effect of concentration and amount of THF on TAGT BCP formation, a series of polymerizations were performed to chain extend p(IBVE)$_{100}$ homopolymer with POPS. A DP of 100 was chosen to make the polymer being chain-extended more difficult to dissolve completely.

Table S6. TAGT chain extension of p(IBVE)$_{100}$ concentration and solvent screen[a]



entry	concentration (mM)	THF:DMAc	% conv.[b]	$M_{n,theo}$ (kDa)	M_n (kDa)[c]	$Đ$[c]
1	7.5	1:2	76	14.0	40.1	1.90
2	7.5	1:1	74	13.9	41.4	1.71
3	7.5	3:5	72	11.1	37.4	1.59
4	7.5	7:10	74	14.8	44.1	1.83
5	5	1:2	62	9.4	28.5	1.58
6	5	1:1	60	10.3	32	1.67
7	5	3:5	61	11.5	35.1	1.75
8	5	7:10	60	10.9	35.9	1.74

[a] Standard reaction conditions: p(IBVE)$_{100}$ (0.002 mmol, 1 eq), POPS (0.2 mmol, 100 eq), PPh_4Cl (0.66 µmol, 0.33 eq), 6 h, 60 °C. [b] Determined via ^{1}H NMR spectroscopy of the crude reaction mixture. [c] Determined via SEC in THF against PS standards.

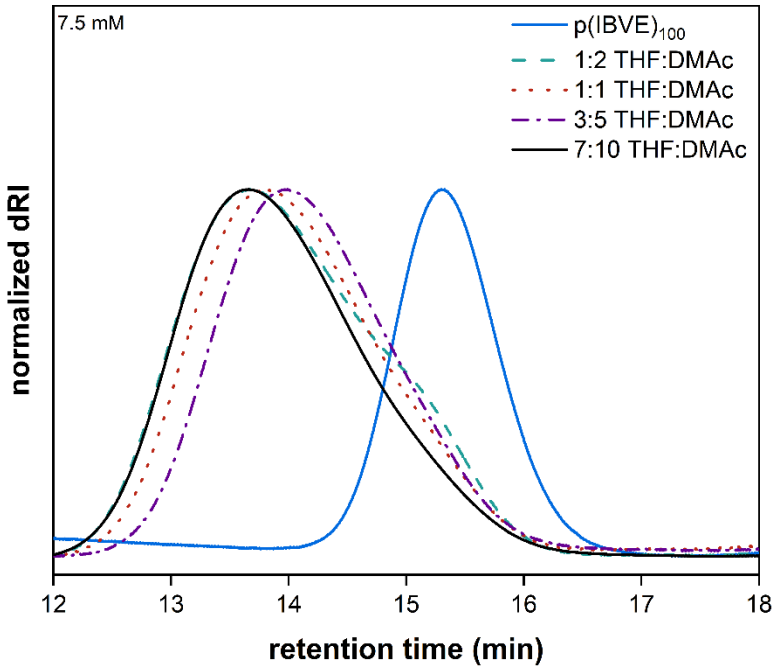


Figure S17. SEC traces of 7.5 mM TAGT chain extension of p(IBVE)$_{100}$ altering THF:DMAc.

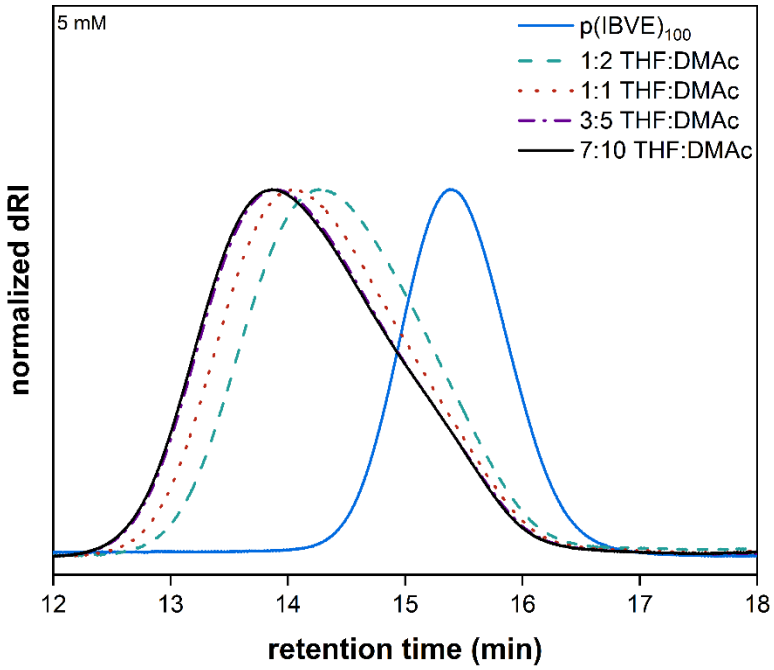


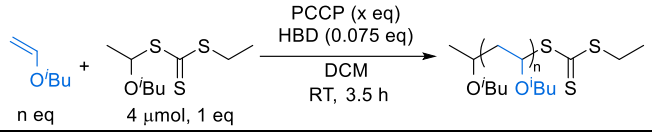
Figure S18. SEC traces of 5 mM TAGT chain extension of $p(IBVE)_{100}$ altering THF:DMAc.

H. Optimization of PCCP amounts for chain extension

During chain extension trials of $p(IBVE)_{50}$, a low molar mass shoulder was observed for homopolymers made using the standard PCCP loading of 0.075 eq relative to **TCT1**. We hypothesized that this shoulder is the result of detrimental side-reactions of the TCT chain-end that could be minimized by lowering the concentration of the propagating cation, which is controlled by the PCCP loading. Thus, we performed RDCP with decreasing amounts of PCCP (Table S7). It was found that well-controlled polymerization with >99% conversion was achieved using between 0.050–0.20 eq of PCCP (entries 1–3). For the synthesis of $p(IBVE)_{100}$ and $p(IBVE)_{50}$ using 0.025 and 0.013 eq of PCCP, respectively, conversion was slightly lower (93%), but good control was still achieved (entries 4 and 8), indicating good performance with small amounts of PCCP catalyst.

Subsequently, chain extensions of these homopolymers were performed. For chain extensions with $p(IBVE)_{50}$ polymerized using 0.050 eq and 0.025 eq of PCCP, a low molar mass shoulder can still be seen (Figure S19 and Figure S20). However, $p(IBVE)_{50}$ polymerized using 0.013 eq of PCCP featured minimal tailing (Figure S21). Therefore, chain extensions of p(IBVE), p(TBVE), and p(DHF) are performed with homopolymers made using 0.013 eq of PCCP relative to **TCT1**. p(CyVE) was successfully chain-extended when made with 0.025 eq of PCCP during RDCP.

Table S7. Effect of PCCP amount on RDCP homopolymerization of IBVE



entry	IBVE eq	PCCP eq	conv. (%)[a]	$M_{n,theo.}$ (kDa)	M_n (kDa)[b]	$Đ$[b]
1	100	0.075	>99	10.2	10.9	1.16
2	100	0.2	>99	10.2	11.0	1.20
3	100	0.05	>99	10.2	10.6	1.14
4	100	0.025	93	9.6	10.7	1.24
5	50	0.075	>99	5.2	3.9	1.12
6	50	0.05	>99	5.2	4.3	1.15
7	50	0.025	>99	5.2	4.3	1.15
8	50	0.013	93	4.9	4.4	1.19

Standard reaction conditions: **TCT1** (0.038 mmol, 1 eq), IBVE (n eq), PCCP (x eq), HBD (0.0029 mmol, 0.075 eq), DCM (1:2 DCM:IBVE by volume, 125–250 μL), 3.5 h, RT. [a] Determined via ^{1}H NMR spectroscopy of the crude reaction mix. [b] Determined via SEC in THF against PS standards.

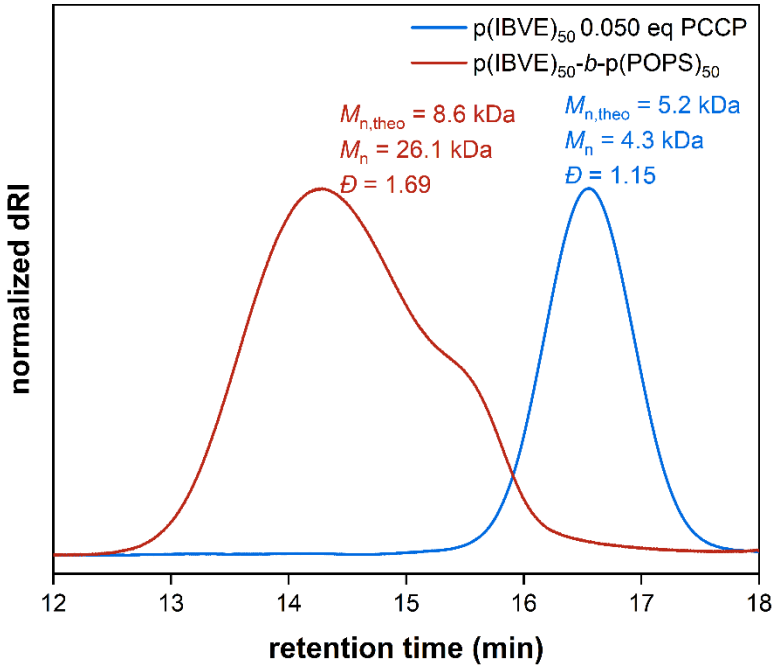


Figure S19. SEC traces of chain extension of p(IBVE)$_{50}$ polymerized using 0.050 eq PCCP rel. **TCT1**.

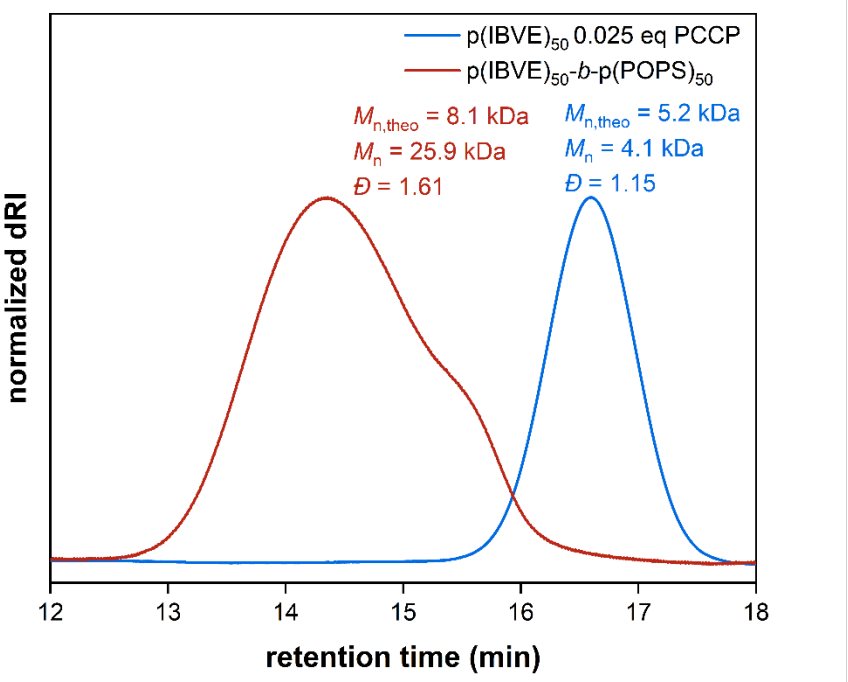


Figure S20. SEC traces of chain extension of p(IBVE)$_{50}$ polymerized using 0.025 eq PCCP rel. **TCT1**.

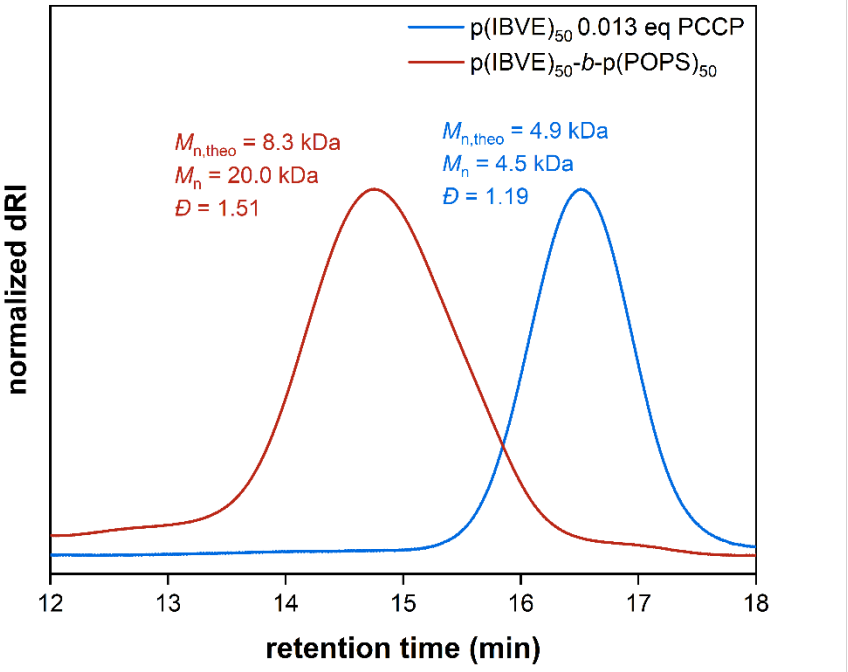


Figure S21. SEC traces of chain extension of p(IBVE)$_{50}$ polymerized using 0.013 eq PCCP rel. **TCT1**.

I. Effect of quench conditions for p(DHF)$_{50}$ chain extension

When optimizing the TAGT chain extension of p(DHF)$_{50}$, it was found that all attempts led to bimodal SEC traces (Figure S22), indicating a significant population of p(DHF)$_{50}$ chains that were not extended. This bimodality implies that there was a population of homopolymer without the correct TCT chain end. It was hypothesized that the sterically-crowded active p(DHF) chain end was more difficult to quench with the **TCT salt** than other pVEs. By quenching with an equimolar (rel. **TCT1**) amount of **TCT salt** in a 1:1 MeCN:DCM (1 mg/mL) solution, followed by stirring at 35 °C for 30 minutes, the subsequent TAGT chain extension was unimodal (Figure S23) – indicating a significantly smaller population of dead p(DHF)$_{50}$ chains.

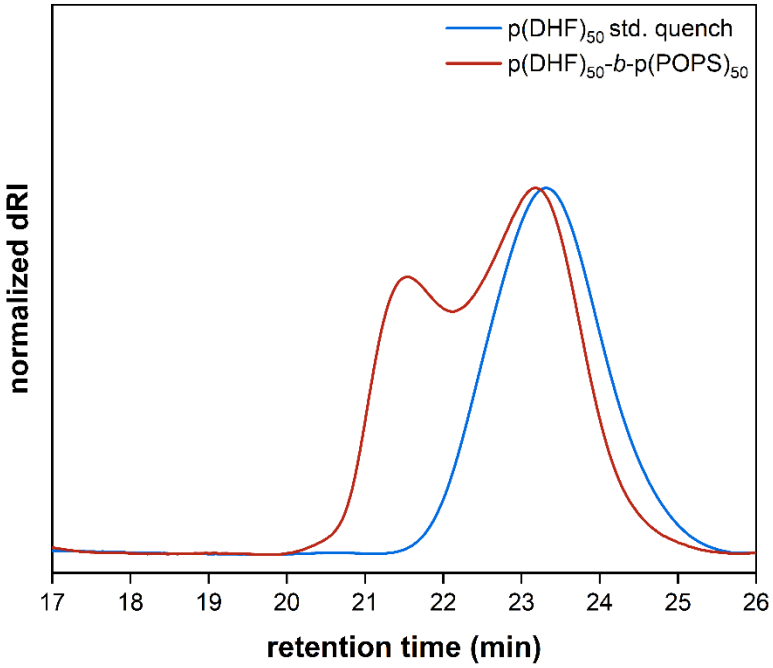


Figure S22. SEC of p(DHF)$_{50}$-*b*-p(POPS)$_{50}$ from p(DHF)$_{50}$ quenched with standard procedure.

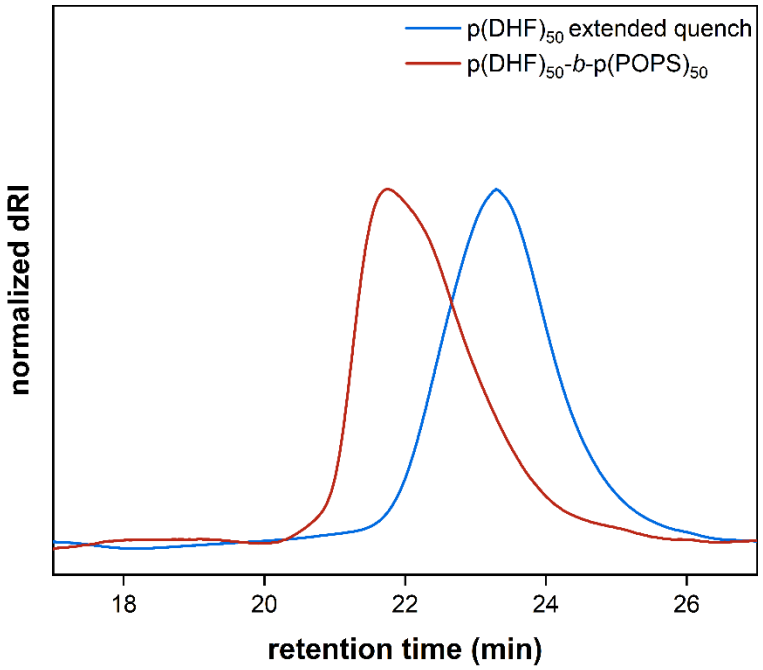


Figure S23. SEC of p(DHF)$_{50}$-*b*-p(POPS)$_{50}$ from p(DHF)$_{50}$ quenched for 30 minutes at 35 °C.

J. Purification of pVE and p(VE)-*b*-p(POPS) BCPs

Because the pVE homopolymers have drastically different solubilities, the purification of both the homopolymers and BCPs need to be optimized for each monomer.

p(EVE), p(PVE), and p(NBVE) are soluble in MeOH, and thus cannot be precipitated in this solvent. Therefore, either H_2O:MeOH mixtures or dialysis are needed to purify these homopolymers. The corresponding BCPs can similarly not be precipitated in MeOH due to fractionation on the basis of solubility.[2] For example, the relative integration of p(PVE) in p(PVE)$_{50}$-*b*-p(POPS)$_{50}$ decreases from 1.71 to 0.70 upon precipitation in cold MeOH (Figure S24). Fractionation was also seen during precipitation of p(EVE)-*b*-p(POPS) and p(NBVE)-*b*-p(POPS) in cold MeOH. Therefore, precipitation in mixtures of H_2O:MeOH were tested to minimize fractionation and allow for purified polymers for thermal analysis (Table S8 and Figure S25). In contrast, p(IBVE), p(DHF), p(CyVE), and p(TBVE) and the corresponding BCPs could be purified via precipitation in cold methanol. The optimized purification method for all polymers tested can be found in Table S9.

Table S8. Solvent used in precipitation for each more soluble BCP and p(VE):p(POPS) integral ratios comparison between crude polymers and precipitants

Entry	BCP	H_2O:MeOH ratio	p(VE):p(POPS) ratio in crude[a]	p(VE):p(POPS) ratio in precipitant[a]
1	$p(PVE)_{50}$-*b*-$p(POPS)_{50}$	0:1	1.71:1	0.71:1
2	$p(PVE)_{50}$-*b*-$p(POPS)_{50}$	1:1	1.26:1	1.17:1
3	$p(EVE)_{50}$-*b*-$p(POPS)_{50}$	8:2	2.31:1	2.30:1
4	$p(NBVE)_{50}$-*b*-$p(POPS)_{50}$	1:1	1.18:1	0.70:1

[a] Determined via ^{1}H NMR spectroscopy of the crude reaction mixtures.

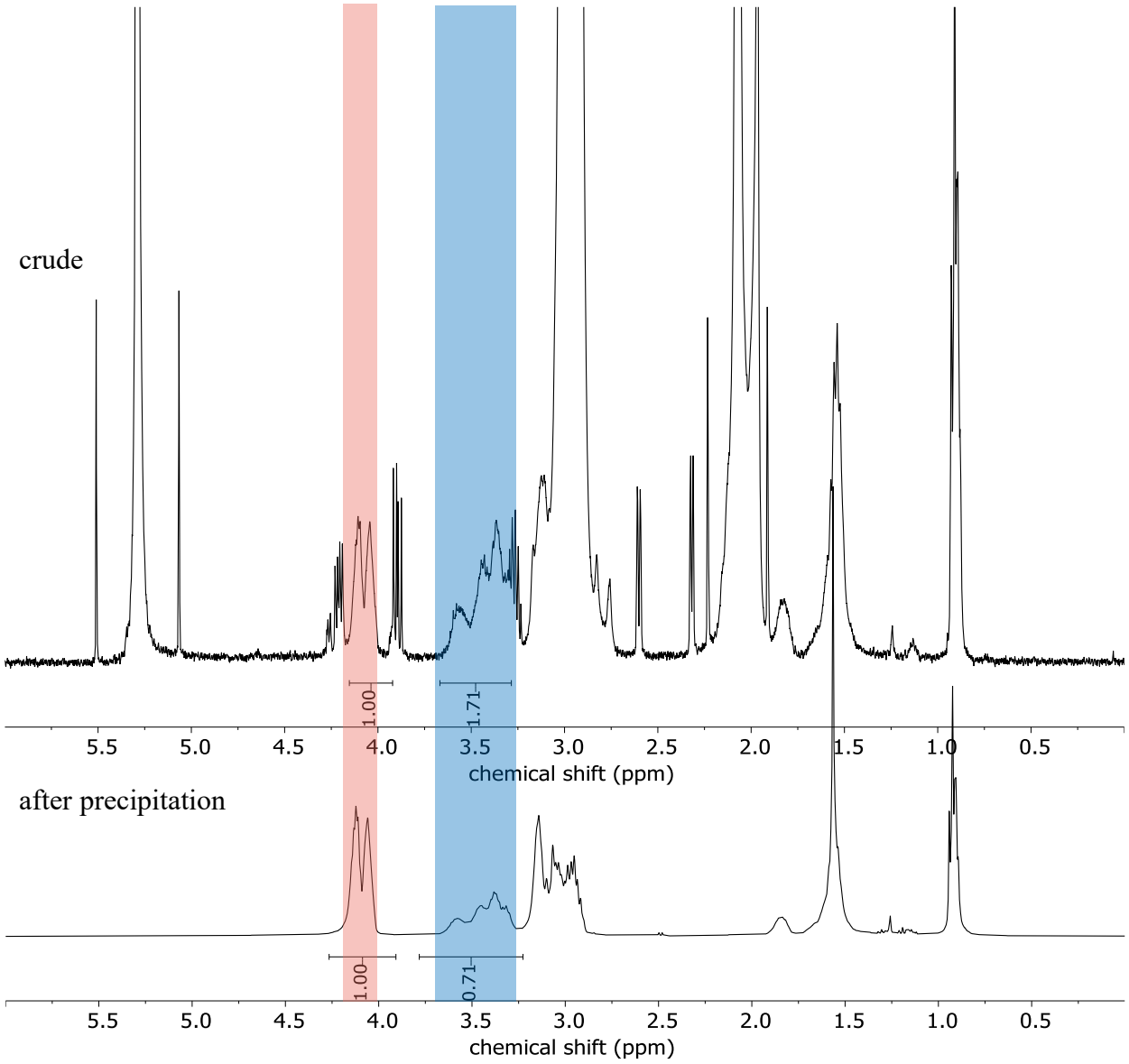


Figure S24. Comparison of p(PVE) integration in the ^{1}H NMR spectra of $p(PVE)_{50}$-*b*-$p(POPS)_{50}$ of crude polymer verses after precipitation in MeOH (Table S8, entry 1).

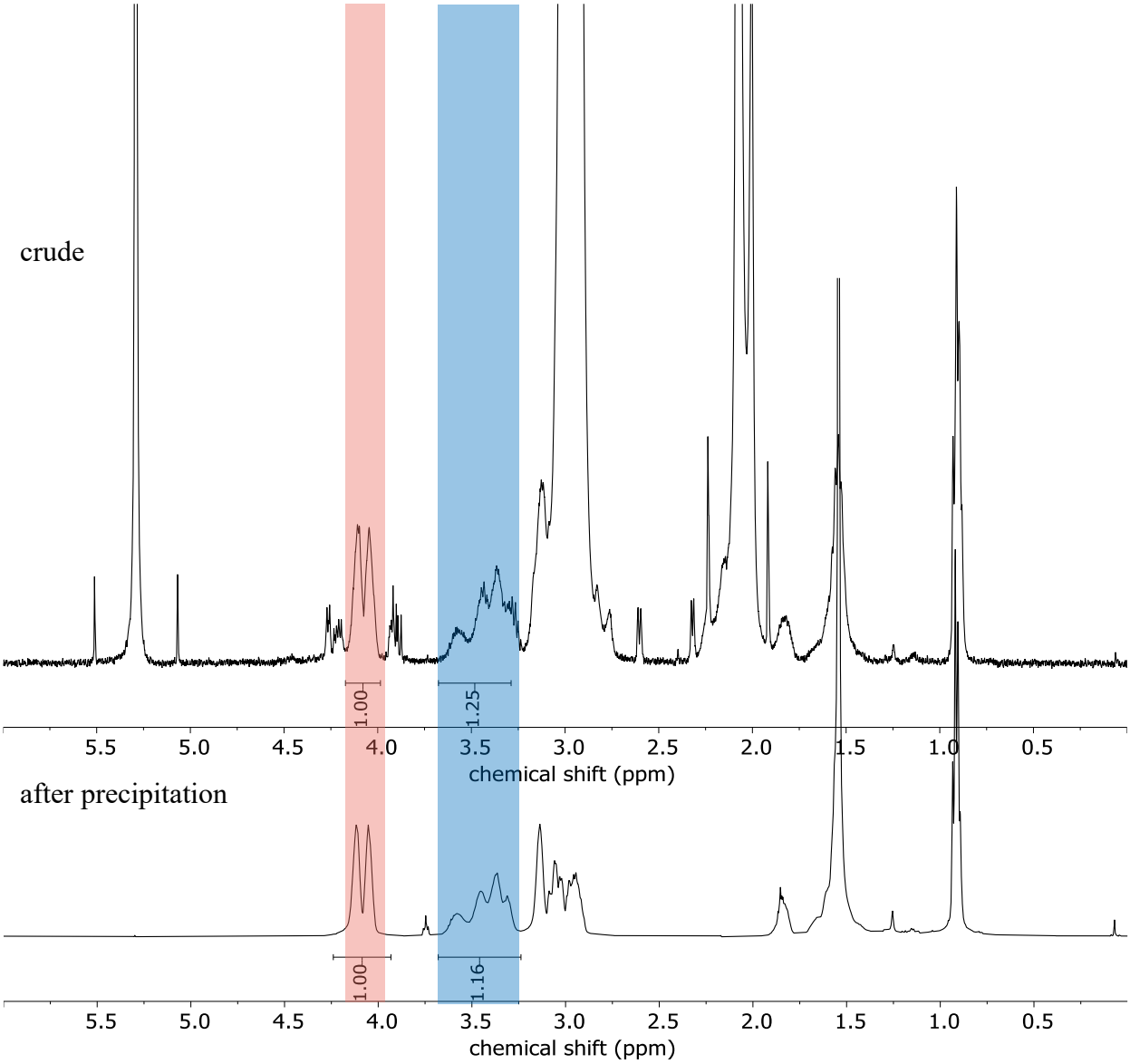


Figure S25. Comparison of p(PVE) integration in the ^{1}H NMR spectra of p(PVE)$_{50}$-*b*-p(POPS)$_{50}$ of crude polymer verses after precipitation in 1:1 H_2O:MeOH (Table S8, entry 2).

Table S9. Summary of chain extension and purification procedures

entry	BCP	PCCP eq for RDCP	TAGT solvent concentration (mM)	p(VE) purification	BCP purification
1	$p(EVE)_{50}$-*b*-$p(POPS)_{50}$	0.075	15	precipitation in 8:2 H_2O:MeOH	precipitation in 8:2 H_2O:MeOH
2	$p(PVE)_{50}$-*b*-$p(POPS)_{50}$	0.075	15	dialysis in MeOH	precipitation in 1:1 H_2O:MeOH
3	$p(NBVE)_{50}$-*b*-$p(POPS)_{50}$	0.075	15	dialysis in MeOH	precipitation in 1:1 H_2O:MeOH
4	$p(IBVE)_{50}$-*b*-$p(POPS)_{50}$	0.013	5	precipitation in MeOH	precipitation in MeOH
5	$p(DHF)_{50}$-*b*-$p(POPS)_{50}$	0.013	5	precipitation in MeOH	precipitation in MeOH
6	$p(CyVE)_{50}$-*b*-$p(POPS)_{50}$	0.025	5	precipitation in MeOH	precipitation in MeOH
7	$p(TBVE)_{50}$-*b*-$p(POPS)_{50}$	0.013	5	precipitation in MeOH	precipitation in MeOH

K. SEC traces of block copolymers

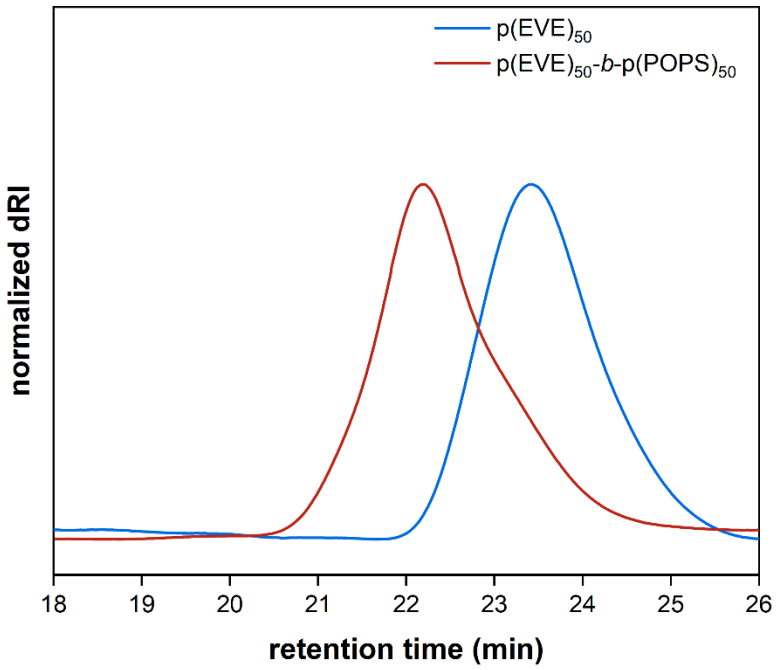


Figure S26. SEC traces of $p(EVE)_{50}$-*b*-$p(POPS)_{50}$.

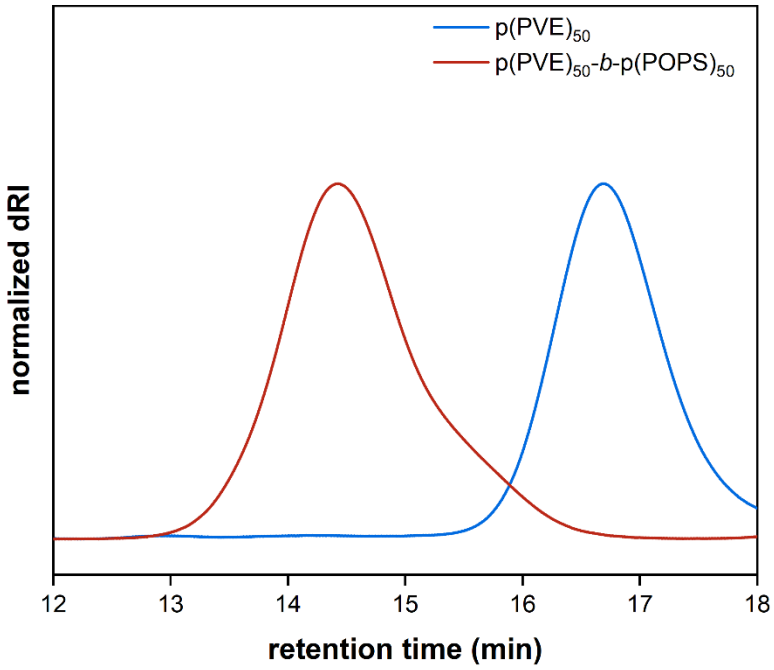


Figure S27. SEC traces of $p(PVE)_{50}$-*b*-$p(POPS)_{50}$.

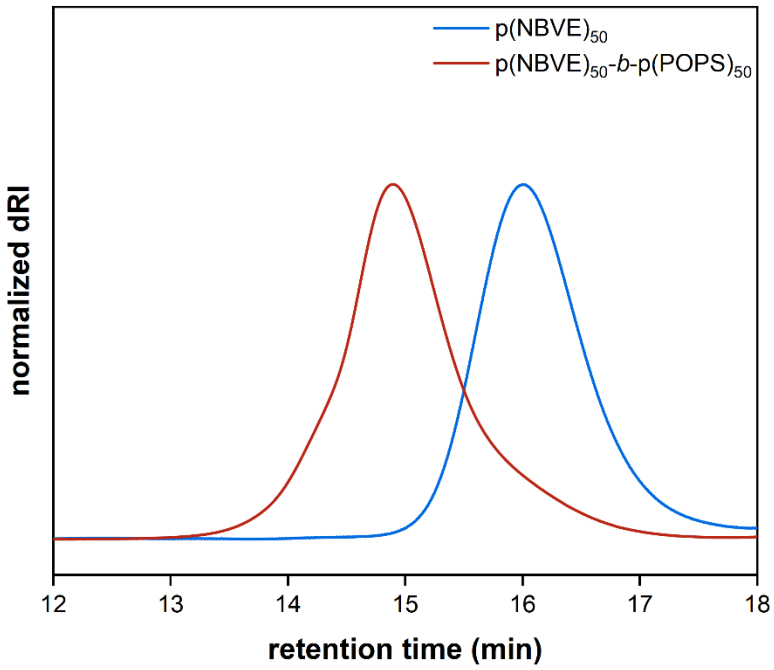


Figure S28. SEC traces of $p(NBVE)_{50}$-*b*-$p(POPS)_{50}$.

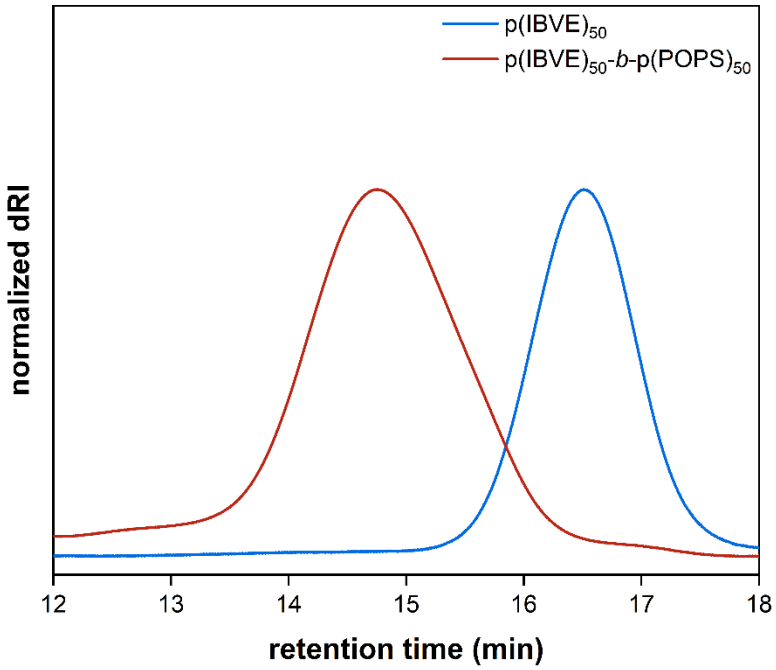


Figure S29. SEC traces of p(IBVE)$_{50}$-*b*-p(POPS)$_{50}$.

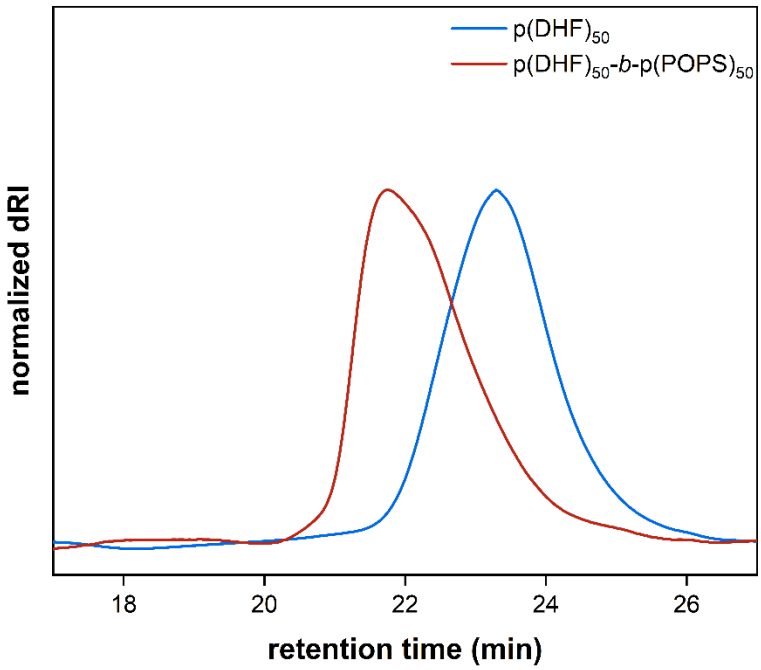


Figure S30. SEC traces of p(DHF)$_{50}$-*b*-p(POPS)$_{50}$.

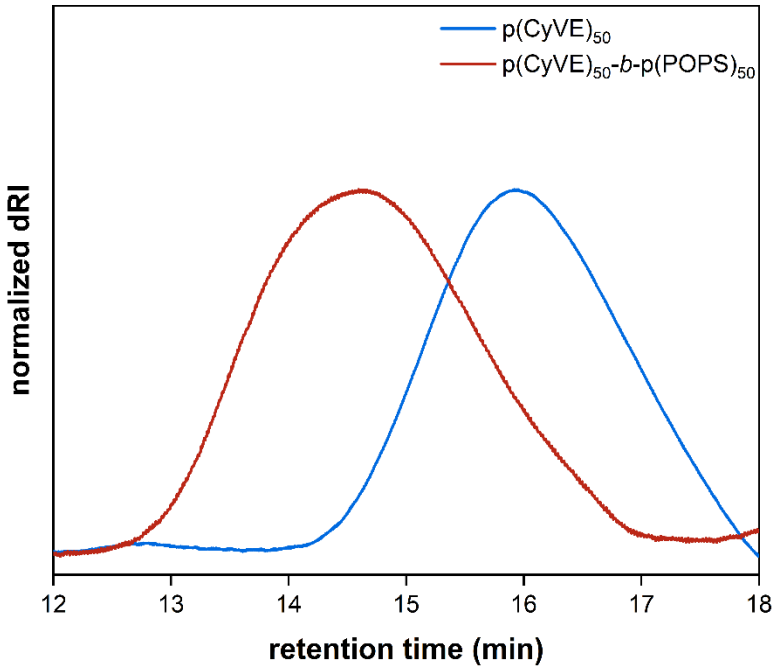


Figure S31. SEC traces of $p(CyVE)_{50}$-*b*-$p(POPS)_{50}$.

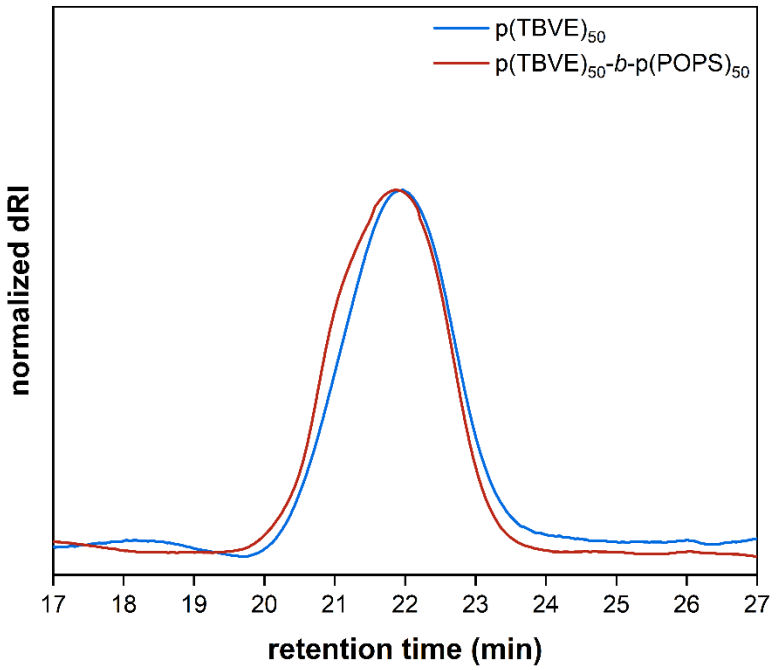


Figure S32. SEC traces of $p(TBVE)_{50}$-*b*-$p(POPS)_{50}$. Note: the minor shift in trace is due to low POPS conversion (12%) for this substrate. Both blocks are observed in ^{1}H NMR spectroscopy (Section SIII.D) and thermal analysis (Figure S49 and Figure S63).

L. Evidence of TAGT chain growth on both sides of TCT and subsequent cleavage of TCT

It was observed that during a prolonged TAGT chain extension (24 hours) of p(IBVE)$_{50}$ there was a significant shifting of the peak in SEC (Figure S33, green dotted line) to a longer retention time compared to the 6 hour chain extension of the same homopolymer (Figure S33, red dashed line).

Because the M_n of the 24-hour sample was nearly half that of the 6-hour chain extension, our initial hypothesis was that the monothioacetal between the blocks was being cleaved. However, ^{1}H NMR analysis of the precipitated polymers shows no difference in integration between the p(IBVE) and p(POPS) blocks from the 6- and 24-hour samples (Figure S34). This evidence combined with the monomodal nature of the SEC traces indicates that we are likely not degrading the linkage between vinyl ether and thiirane blocks during chain extension.

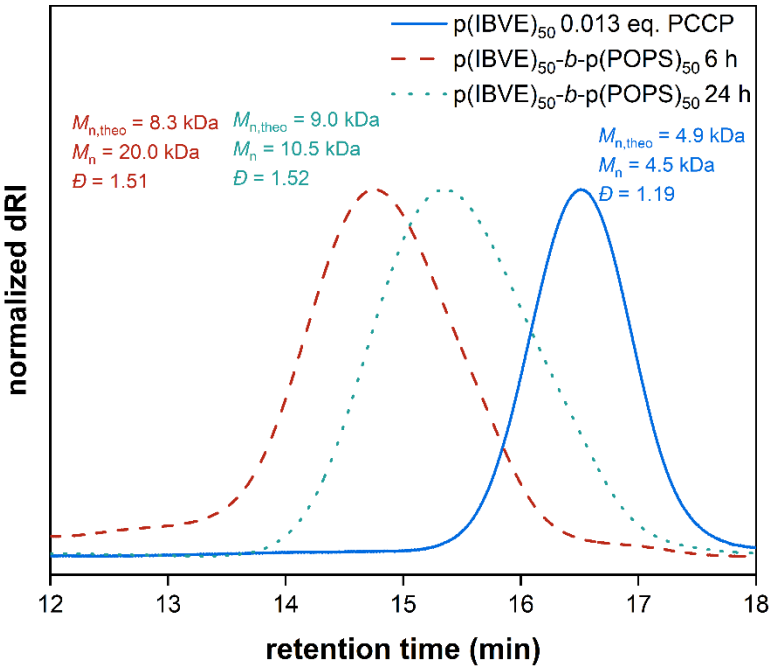


Figure S33. SEC traces of p(IBVE)$_{50}$-*b*-p(POPS)$_{50}$ after 6 or 24 h made using p(IBVE)$_{50}$ polymerized with 0.013 eq PCCP rel. **TCT1** quenched with 7 eq **TCT salt** rel. PCCP.

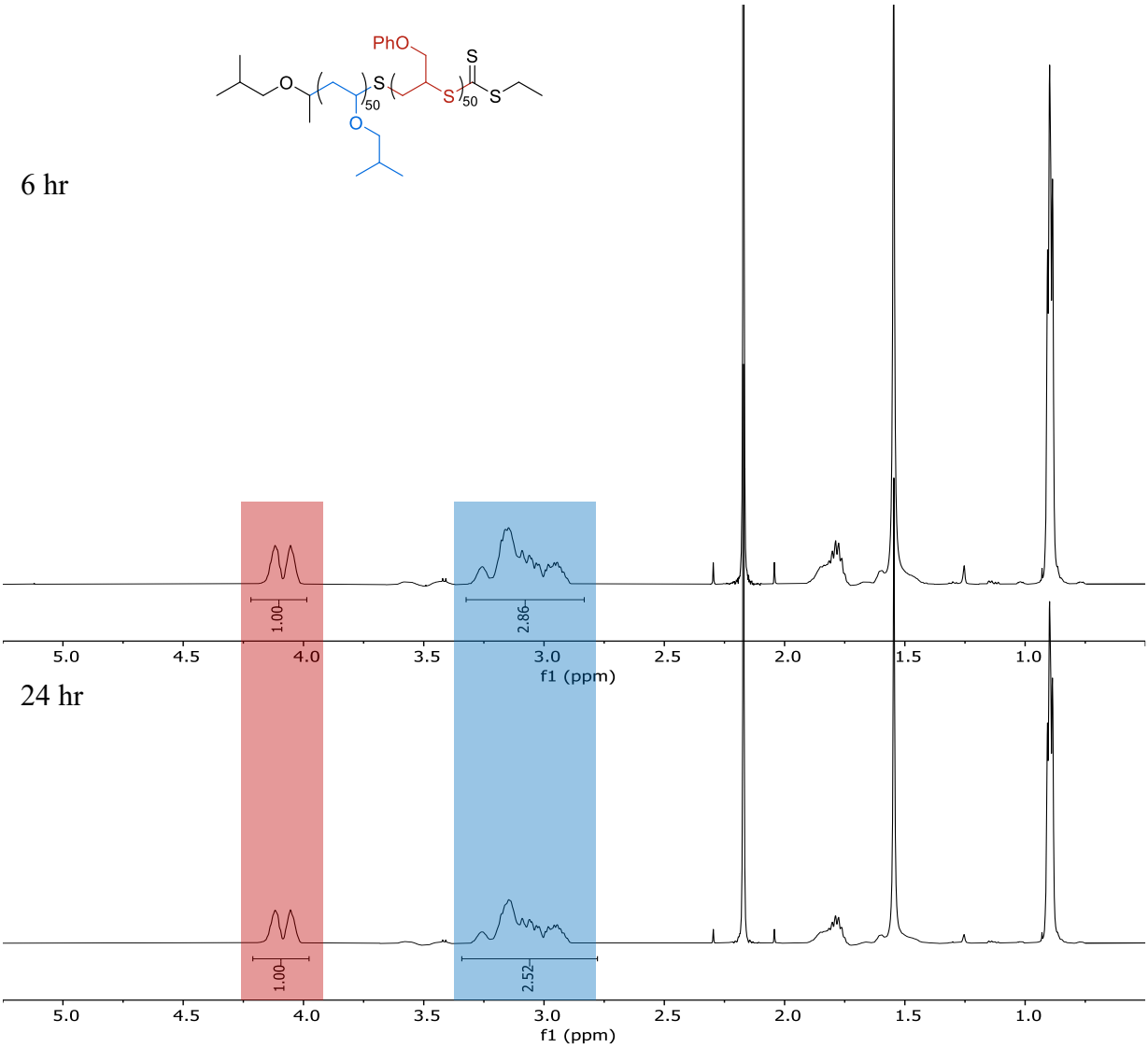
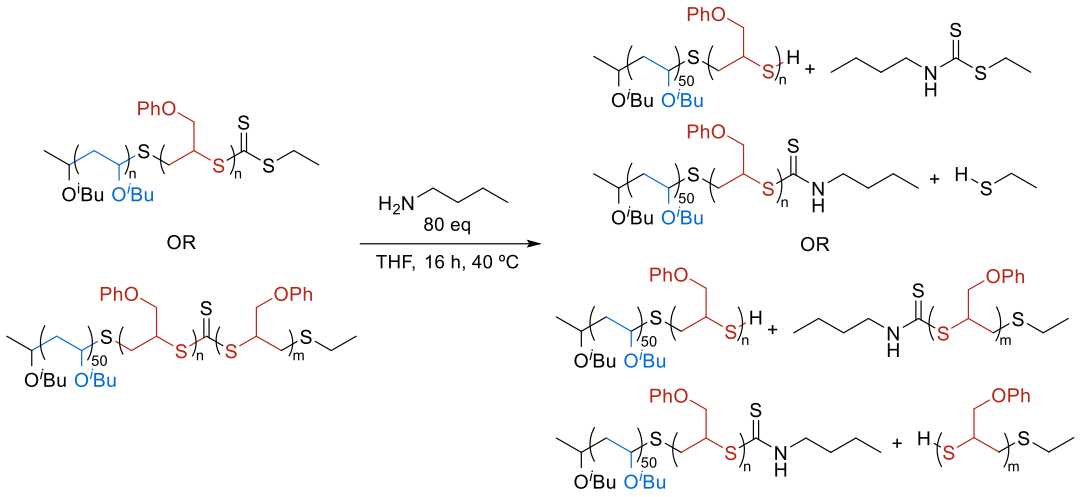


Figure S34. Comparison of ^{1}H NMR spectra of purified p(IBVE)$_{50}$-*b*-p(POPS)$_{50}$ from TAGT for 6 and 24 hours.

Another potential explanation of the discrepancy between SEC traces with the 6- and 24-hour chain extensions is that propagation during TAGT is occurring on both sides of the TCT, and not just the expected side containing the p(IBVE)$_{50}$ block, and over the course of the 24 hour reaction, the TCT is being degraded in a manner similar to aminolysis.[9] To probe this hypothesis, aminolysis on both the 6- and 24-hour TAGT chain extensions of p(IBVE)$_{50}$ were performed using butylamine overnight (Scheme S2; for full procedure, see Section SIII.E).



Scheme S2. Aminolysis of p(IBVE)$_{50}$-*b*-p(POPS)$_{50}$ BCP.

The SEC trace of the post-aminolysis 6-hour TAGT sample (Figure S35A) shows a complete shifting of the SEC trace to a longer retention time, near that of the 24-hour sample, a result reminiscent of the 6-hour vs. 24-hour chain extension described above (Figure S33). SEC analysis of the post-aminolysis 24-hour TAGT sample was largely unchanged (Figure S35B), indicating that the TCT was likely already degraded in a similar manner. The results of this experiment indicate that performing TAGT chain extensions for extended periods of time can result in the TCT being cleaved, and so all chain extensions should be run for 6 hours or less. The cause of this cleavage is not yet known and is currently under investigation.

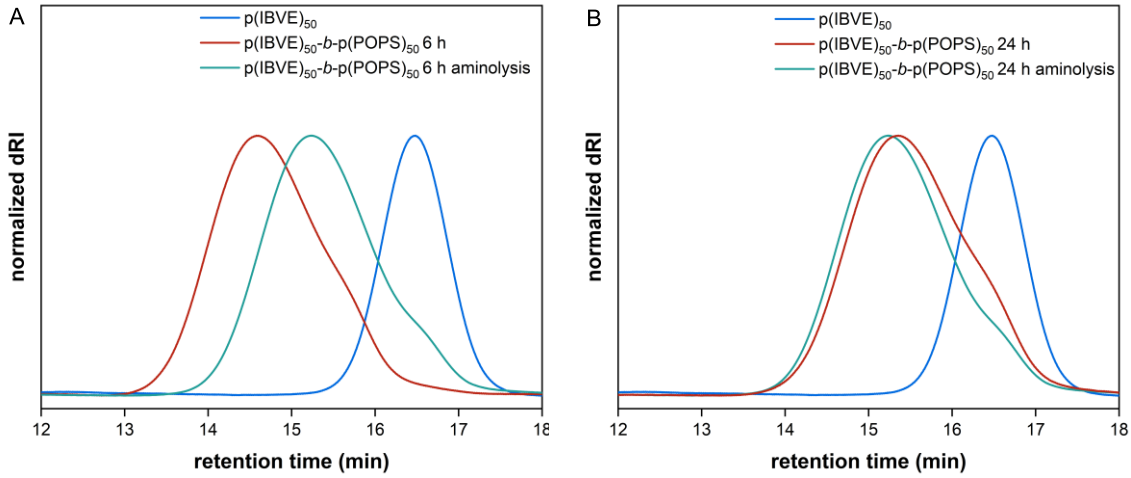


Figure S35. SEC traces of 6- and 24-hour TAGT chain extensions pre- and post-aminolysis.

M. Thermal characterization of polymers

Table S10. Thermal characterization data of homopolymers and BCPs

entry	polymer	T_o (°C)[a]	T_g (°C)[b]
1	$p(EVE)_{100}$	130, 378	−30
2	$p(PVE)_{100}$	147, 412	−43
3	$p(NBVE)_{100}$	159, 391	−54
4	$p(IBVE)_{100}$	160, 401	−19
5	$p(DHF)_{100}$	112, 380	107
6	$p(CyVE)_{100}$	385	43
7	$p(TBVE)_{100}$	119, 276, 400	62
8	$p(EVE)_{50}$-*b*-$p(POPS)_{50}$	168, 294, 388	−31, 20
9	$p(PVE)_{50}$-*b*-$p(POPS)_{50}$	301, 382	−44, 21
10	$p(NBVE)_{50}$-*b*-$p(POPS)_{50}$	302, 383	−58, 18
11	$p(IBVE)_{50}$-*b*-$p(POPS)_{50}$	301, 376	−17, 22
12	$p(DHF)_{50}$-*b*-$p(POPS)_{50}$	305, 386	70
13	$p(CyVE)_{50}$-*b*-$p(POPS)_{50}$	305, 386	24, 54
14	$p(TBVE)_{50}$-*b*-$p(POPS)_{50}$	299, 401	22, 74

[a] Calculated from TGA thermograms. [b] Determined via DSC.

1. TGA thermograms

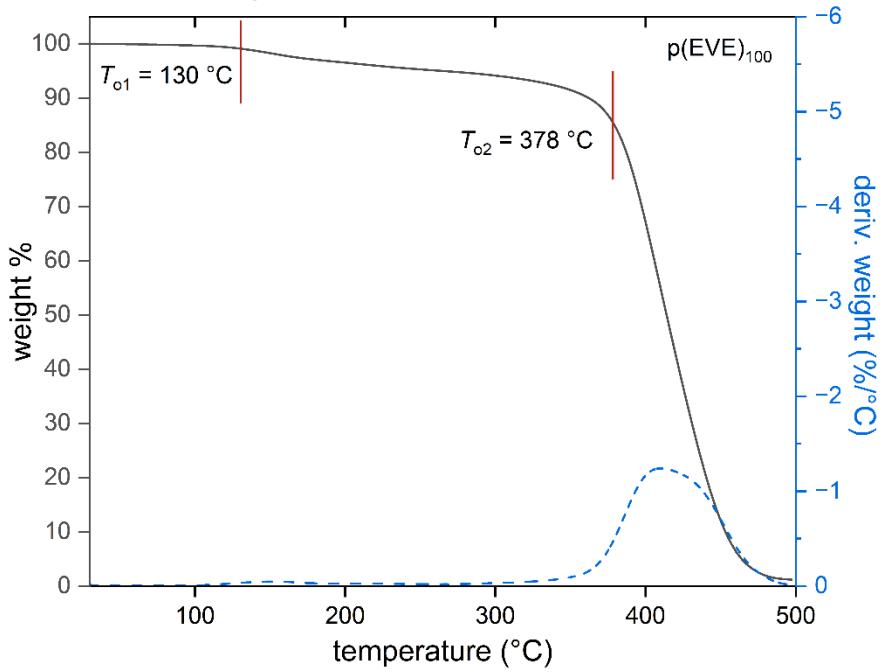


Figure S36. TGA thermogram of $p(EVE)_{100}$.

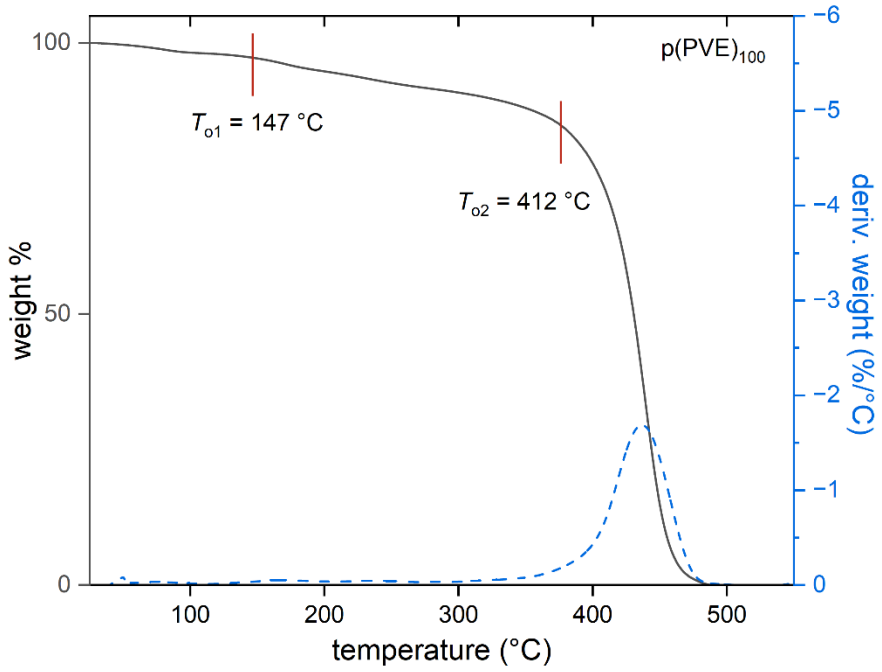


Figure S37. TGA thermogram of $p(PVE)_{100}$.

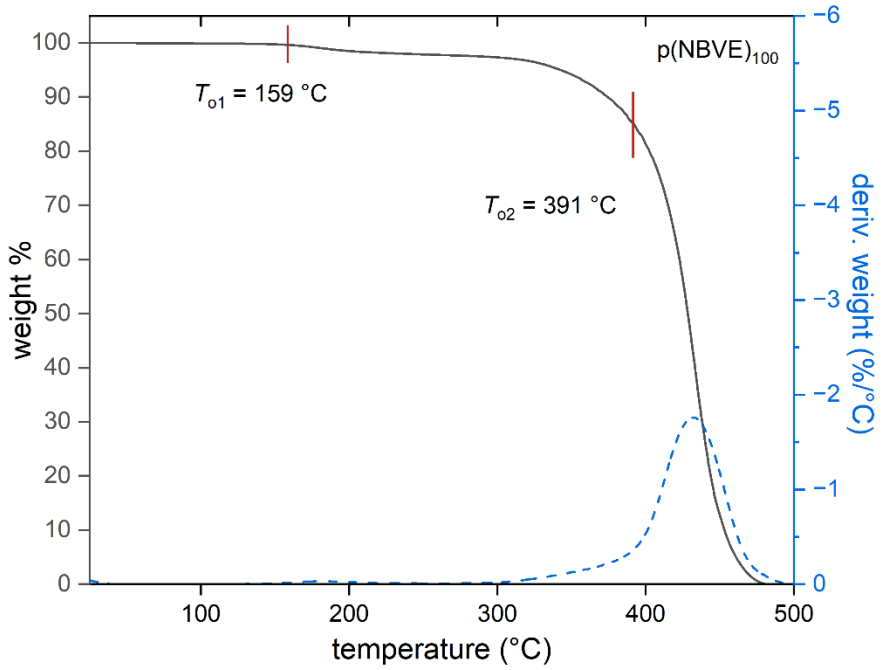


Figure S38. TGA thermogram of $p(NBVE)_{100}$.

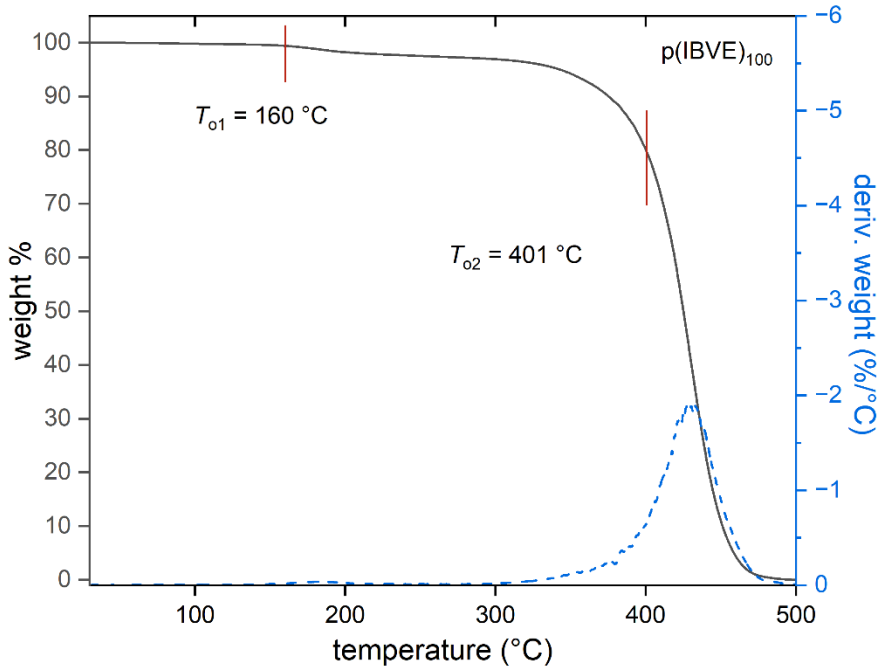


Figure S39. TGA thermogram of $p(IBVE)_{100}$.

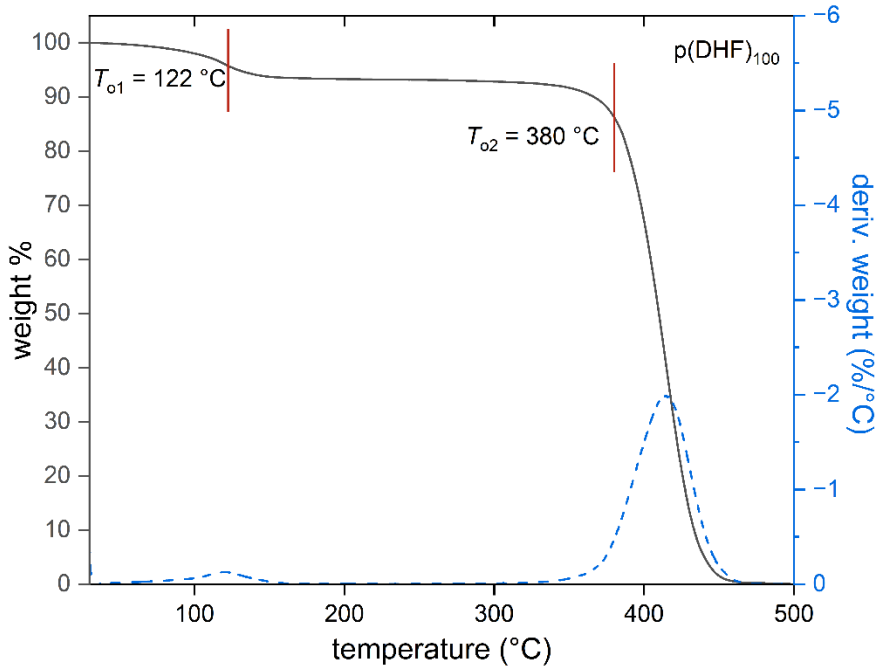


Figure S40. TGA thermogram of $p(DHF)_{100}$.

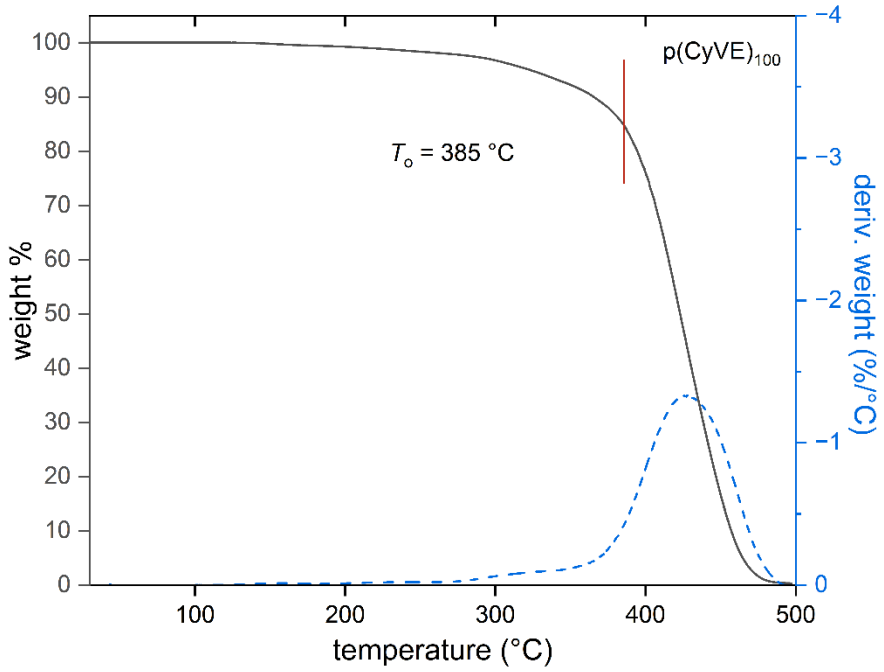


Figure S41. TGA thermogram of $p(CyVE)_{100}$.

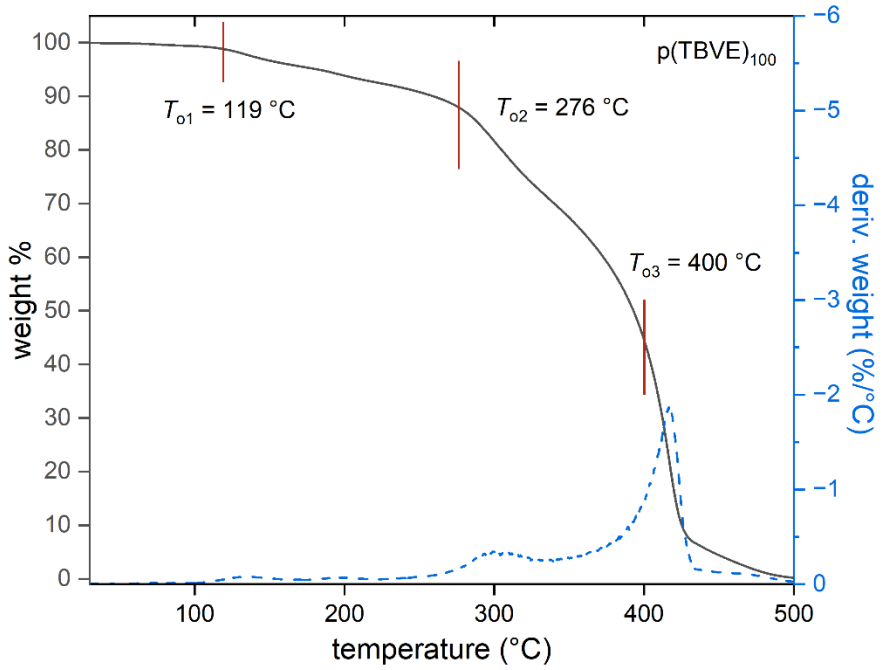


Figure S42. TGA thermogram of $p(TBVE)_{100}$.

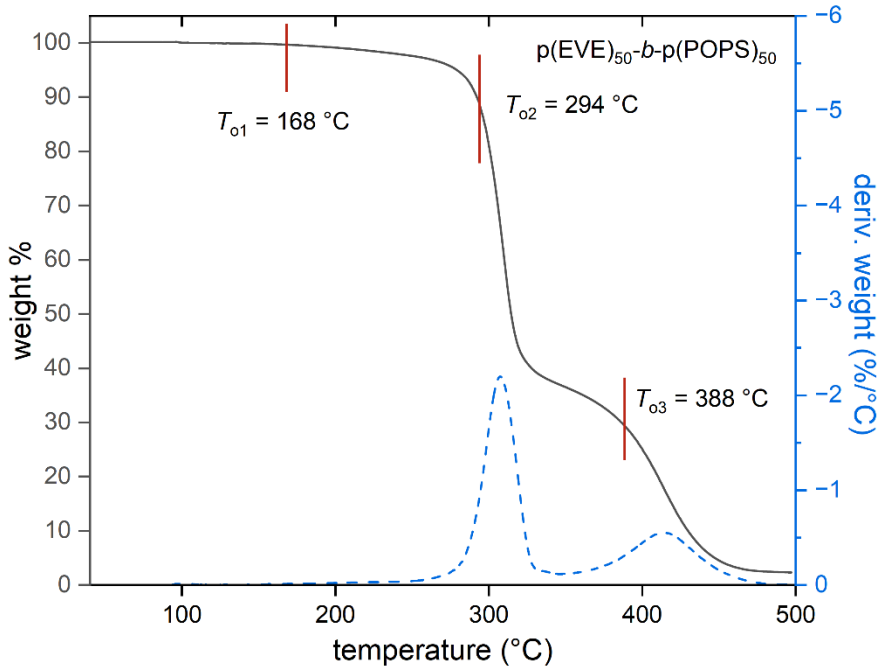


Figure S43. TGA thermogram of p(EVE)$_{50}$-*b*-p(POPS)$_{50}$.

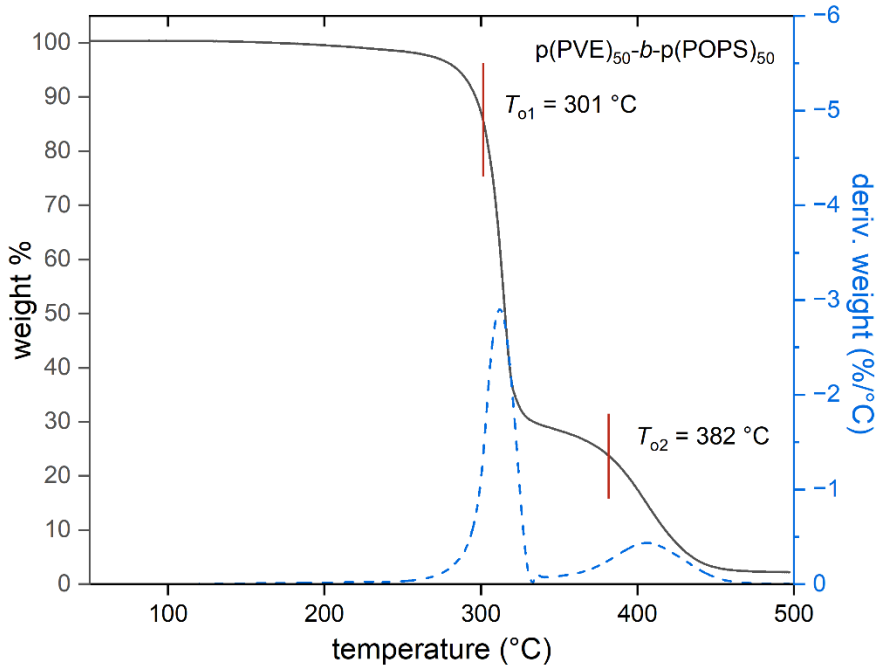


Figure S44. TGA thermogram of p(PVE)$_{50}$-*b*-p(POPS)$_{50}$.

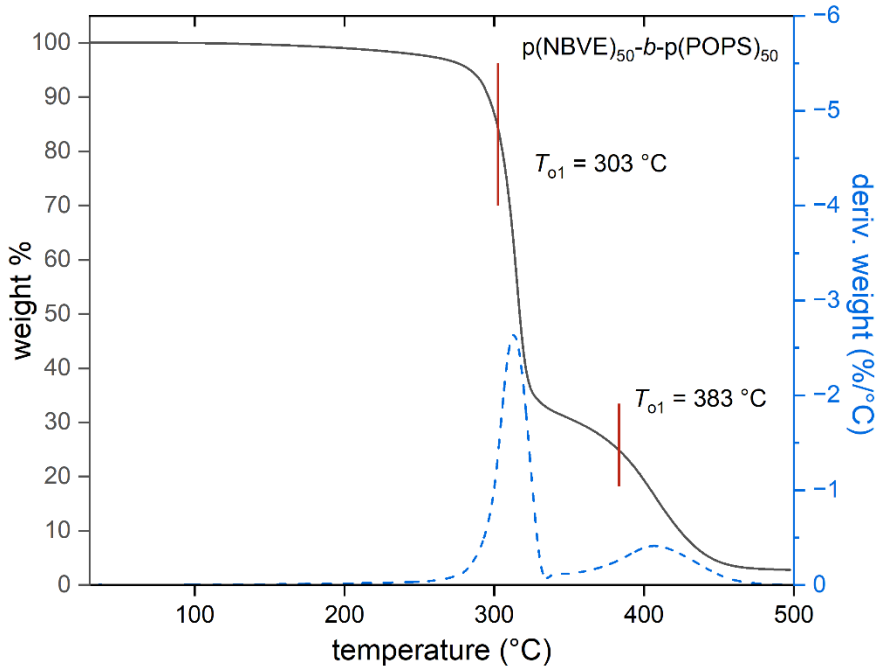


Figure S45. TGA thermogram of p(NBVE)$_{50}$-*b*-p(POPS)$_{50}$.

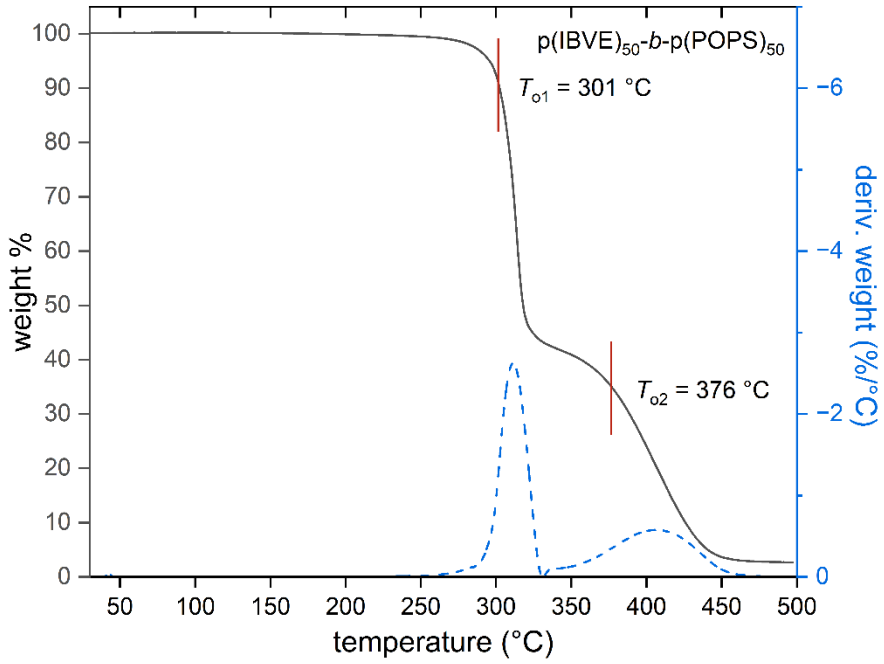


Figure S46. TGA thermogram of p(IBVE)$_{50}$-*b*-p(POPS)$_{50}$.

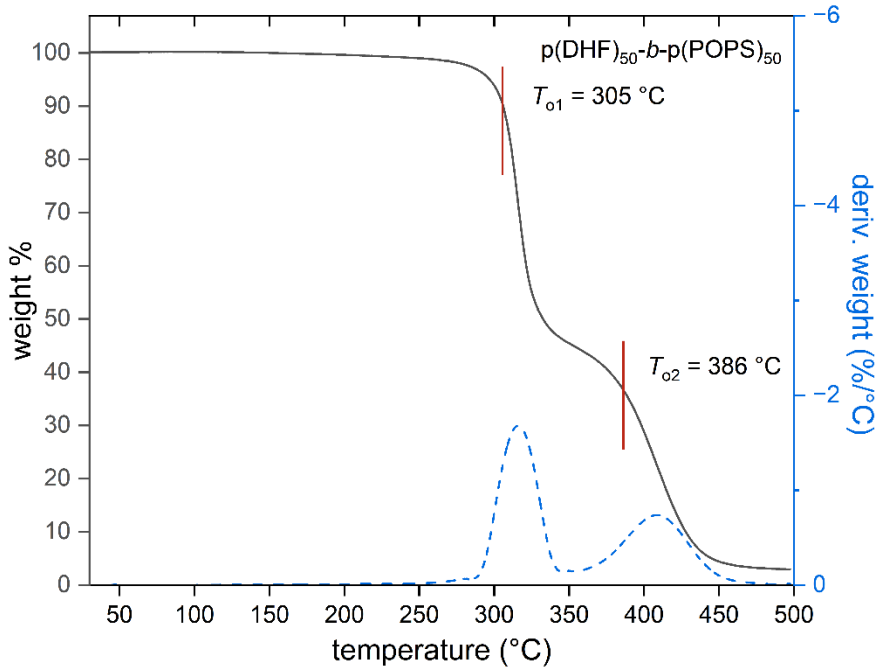


Figure S47. TGA thermogram of p(DHF)$_{50}$-*b*-p(POPS)$_{50}$.

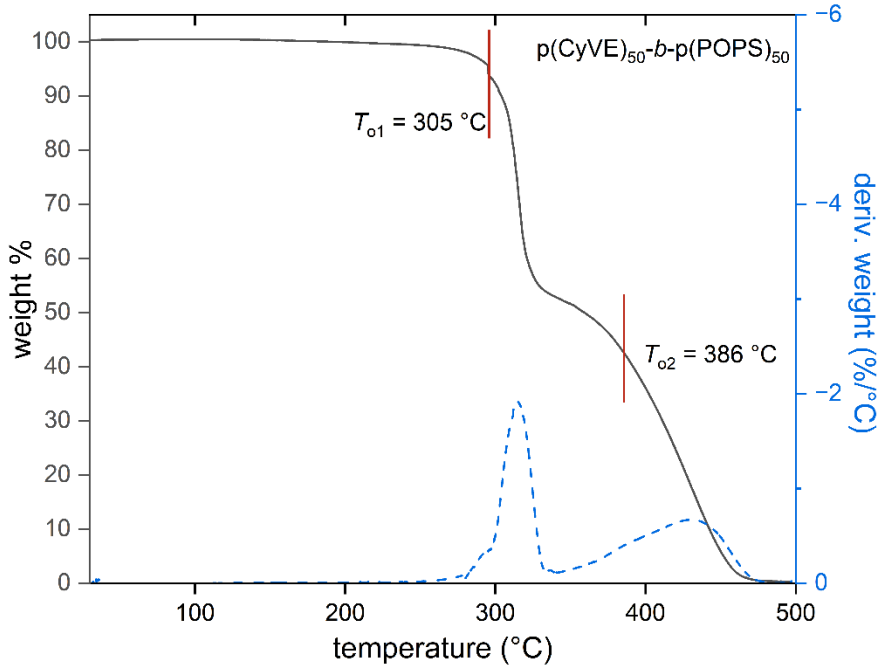


Figure S48. TGA thermogram of p(CyVE)$_{50}$-*b*-p(POPS)$_{50}$.

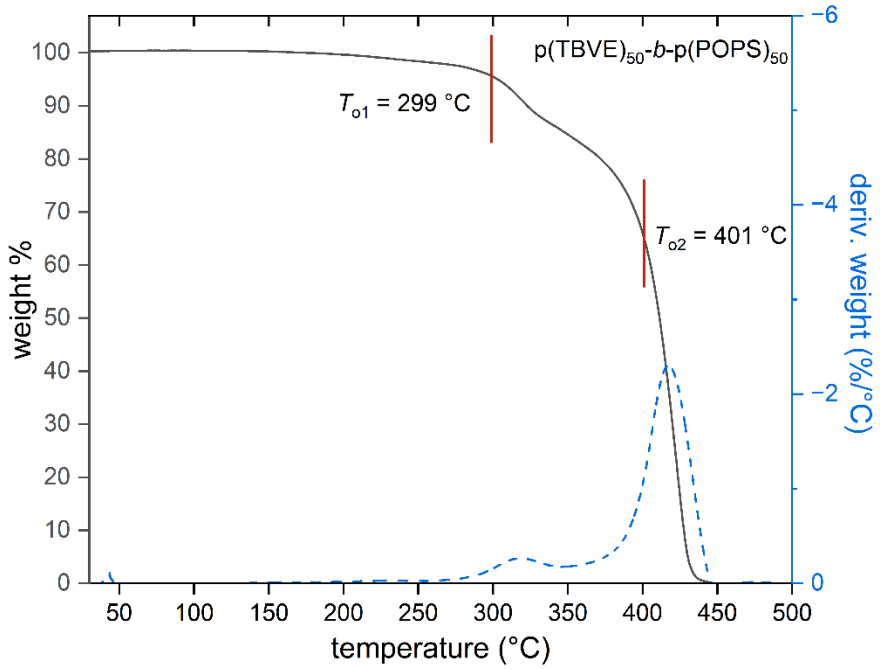


Figure S49. TGA thermogram of $p(TBVE)_{50}$-*b*-$p(POPS)_{50}$.

2. DSC thermograms

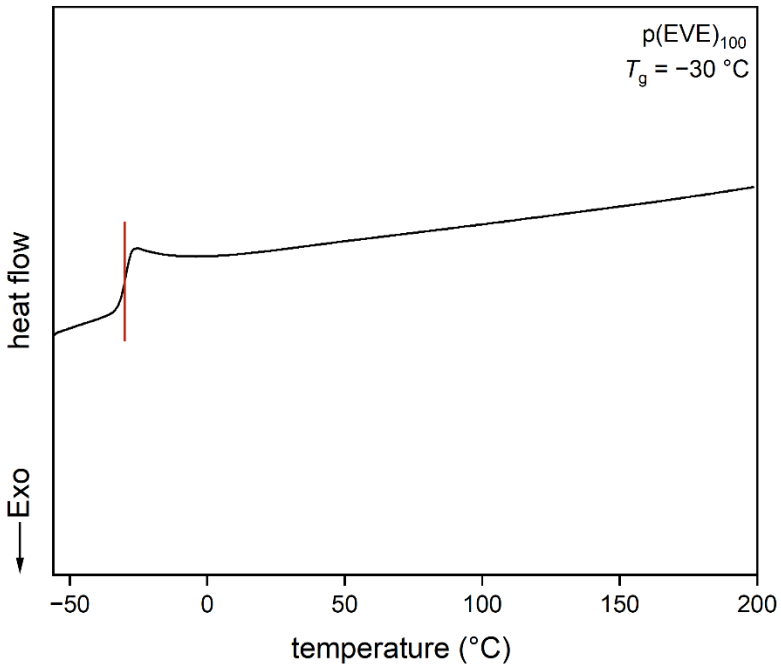


Figure S50. DSC thermogram of $p(EVE)_{100}$.

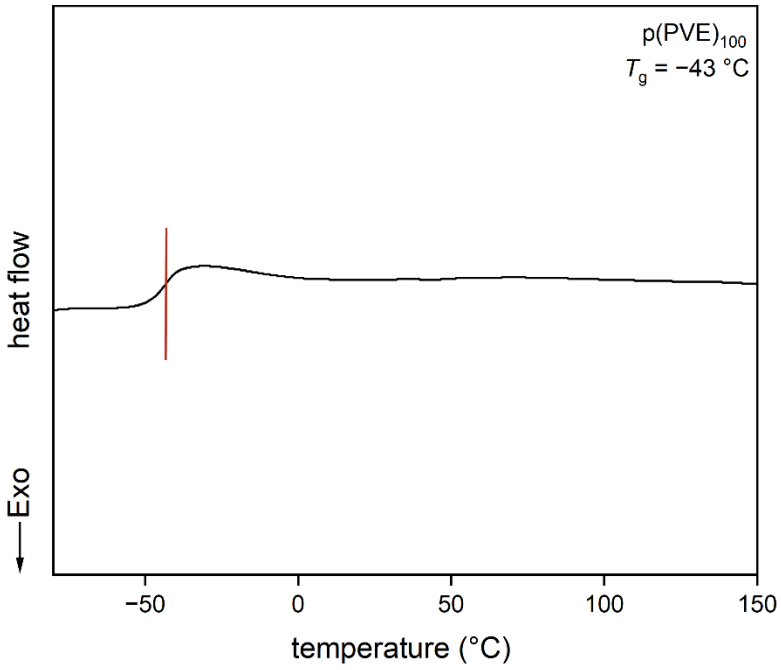


Figure S51. DSC thermogram of $p(PVE)_{100}$.

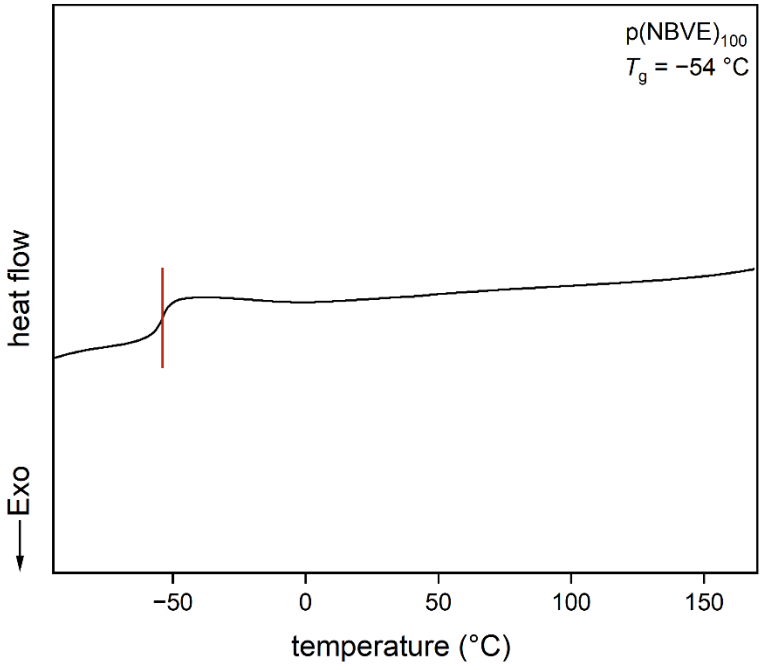


Figure S52. DSC thermogram of $p(NBVE)_{100}$.

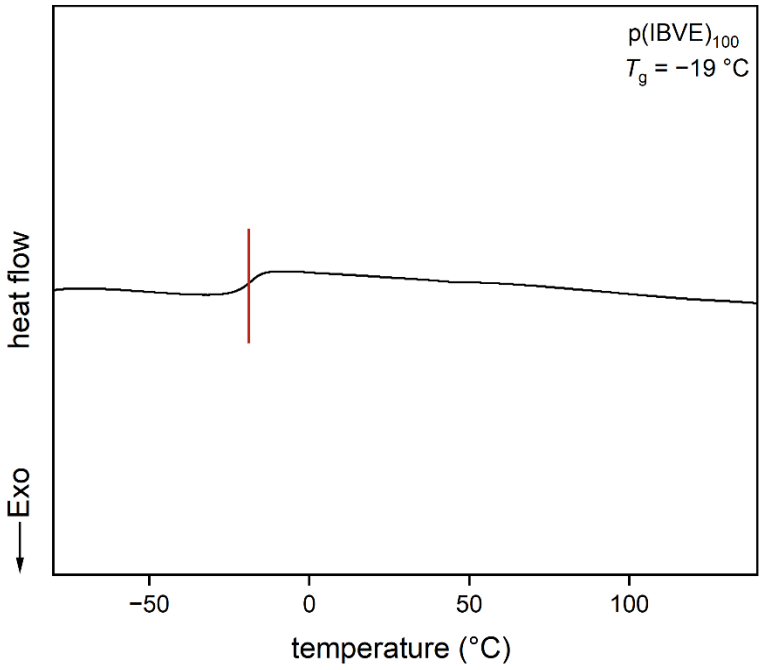


Figure S53. DSC thermogram of $p(IBVE)_{100}$.

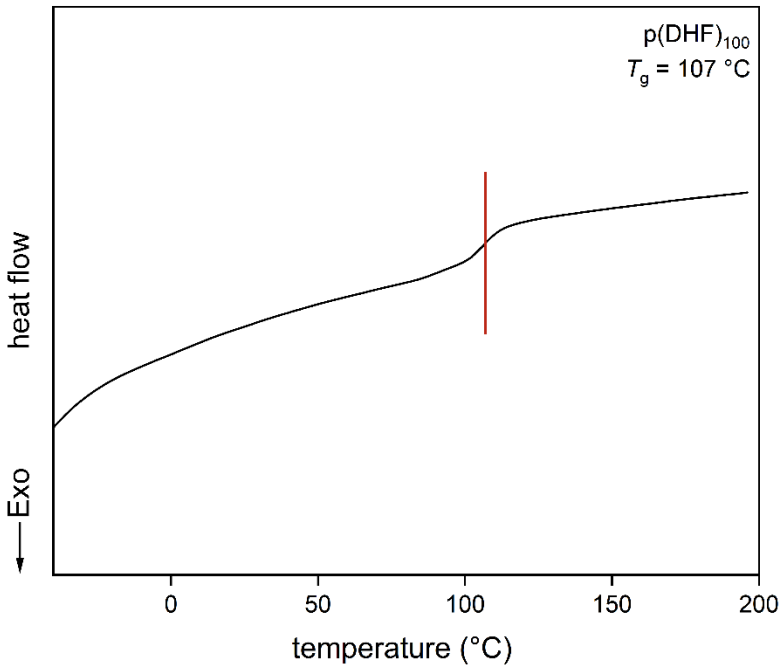


Figure S54. DSC thermogram of $p(DHF)_{100}$.

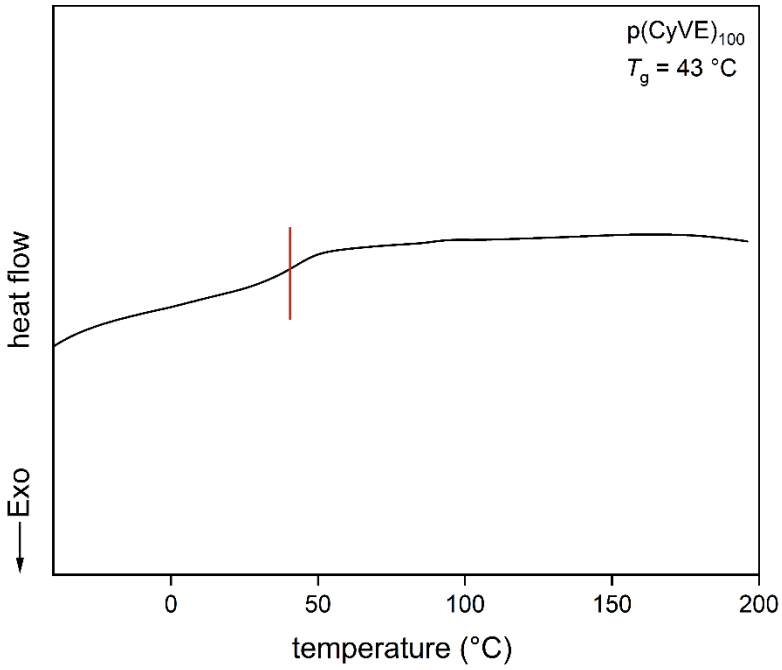


Figure S55. DSC thermogram of $p(CyVE)_{100}$.

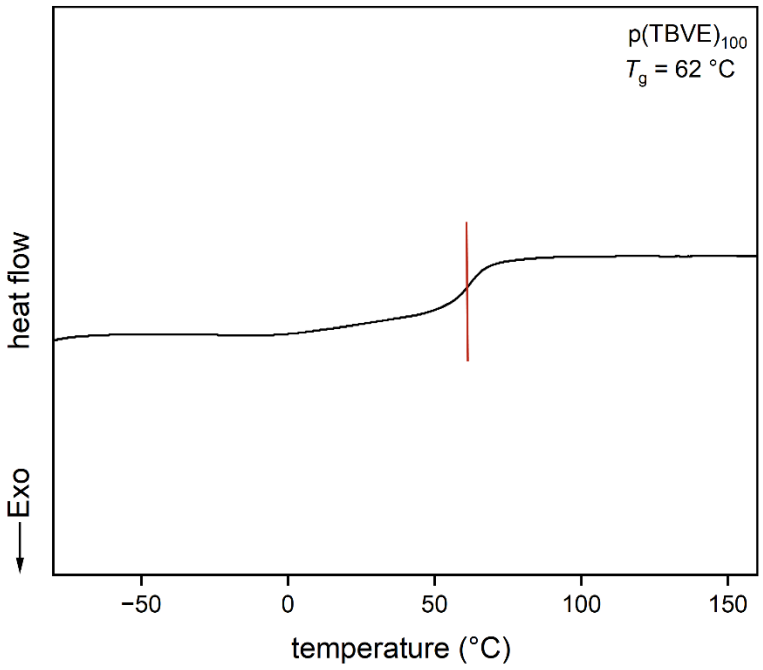


Figure S56. DSC thermogram of $p(TBVE)_{100}$.

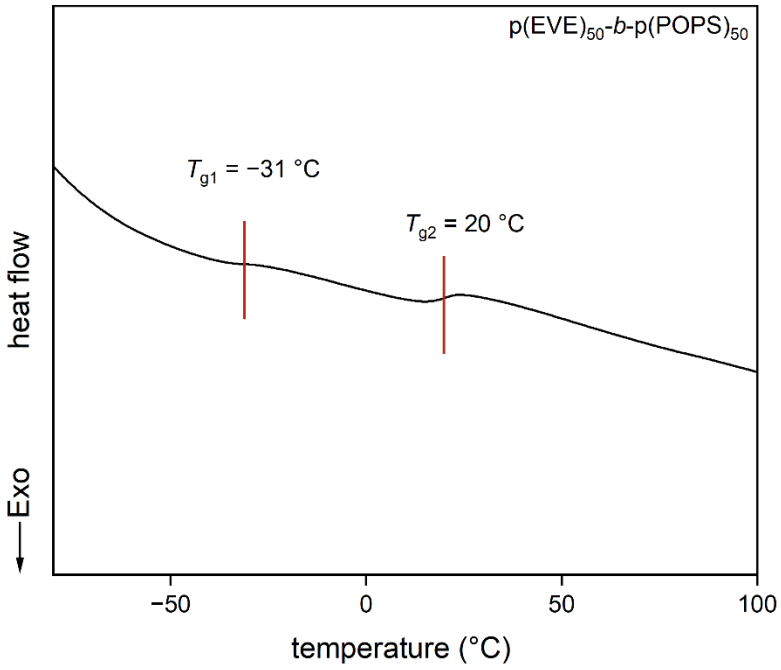


Figure S57. DSC thermogram of $p(EVE)_{50}$-*b*-$p(POPS)_{50}$.

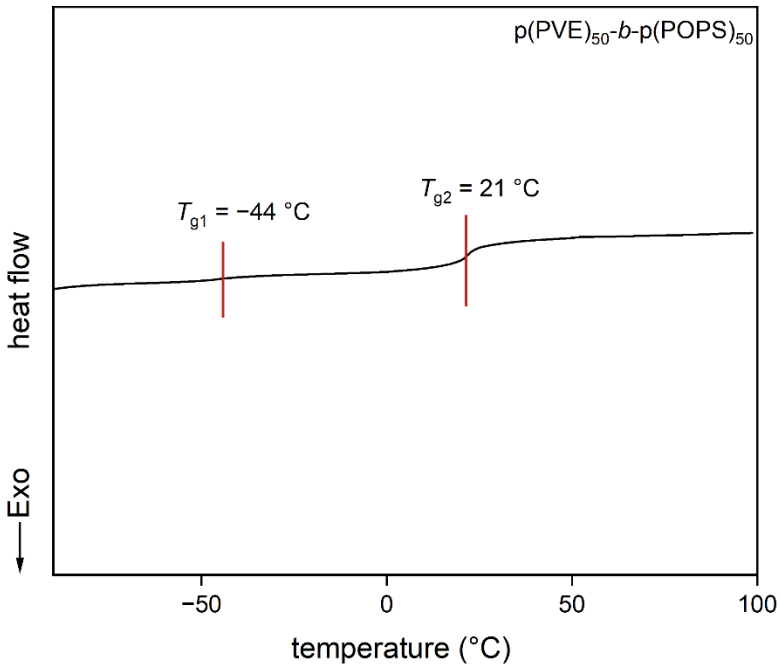


Figure S58. DSC thermogram of $p(PVE)_{50}$-*b*-$p(POPS)_{50}$.

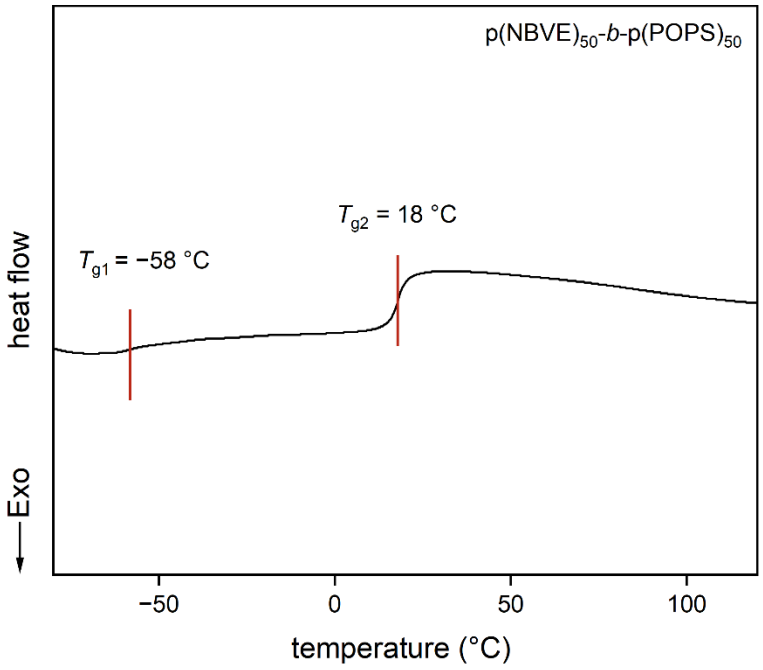


Figure S59. DSC thermogram of p(NBVE)$_{50}$-*b*-p(POPS)$_{50}$.

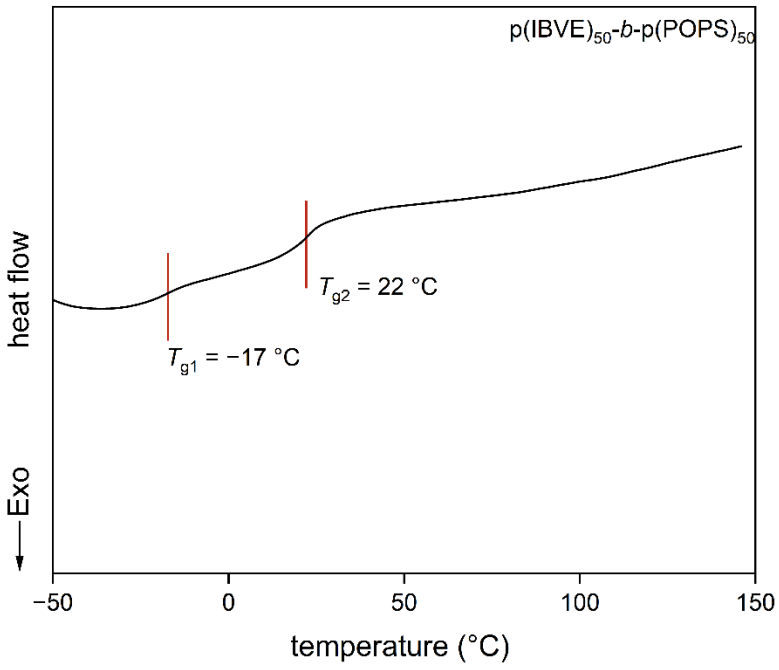


Figure S60. DSC thermogram of p(IBVE)$_{50}$-*b*-p(POPS)$_{50}$.

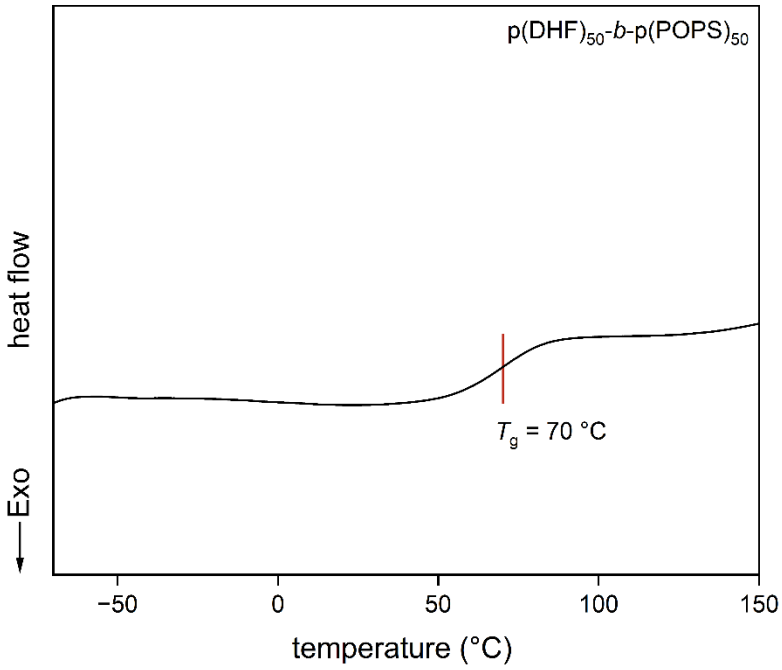


Figure S61. DSC thermogram of $p(DHF)_{50}$-*b*-$p(POPS)_{50}$.

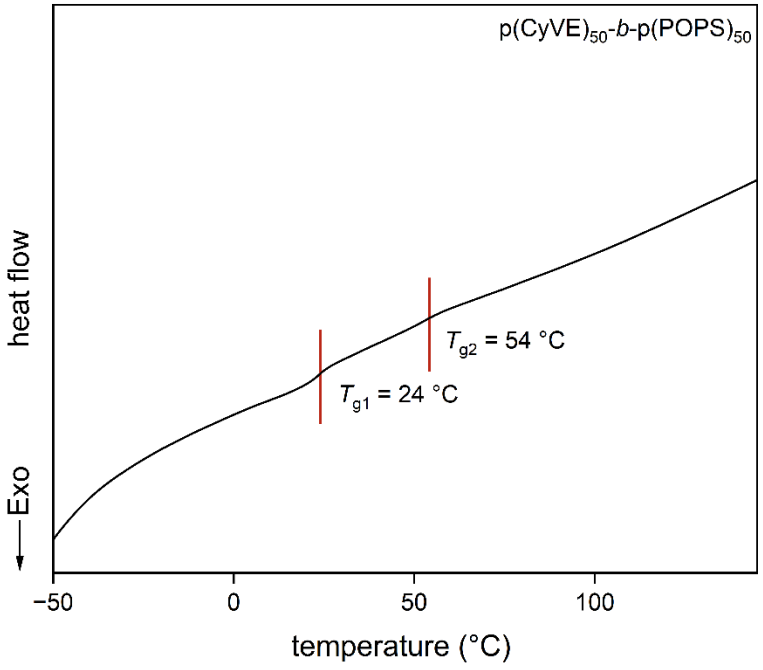


Figure S62. DSC thermogram of $p(CyVE)_{50}$-*b*-$p(POPS)_{50}$.

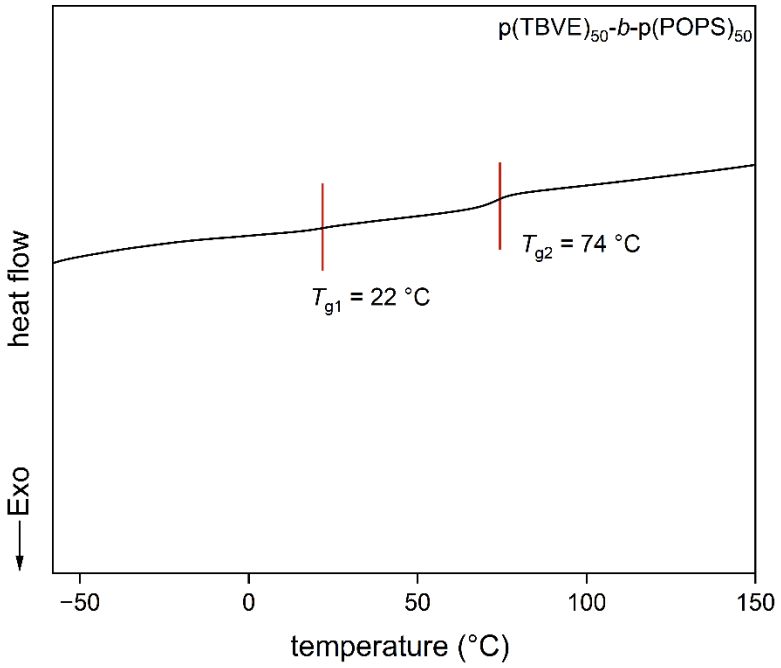


Figure S63. DSC thermogram of p(TBVE)$_{50}$-*b*-p(POPS)$_{50}$.

N. UV-Vis spectroscopy to verify presence of TCT chain-end

To support the retention of the desired TCT chain-end following RDCP and chain-extension with TAGT, UV-Vis spectroscopy was employed to qualitatively determine if TCT was present. Quantitative measurements of the amount of TCT are not possible in this study due to the fact that dRI is being used in SEC analysis, meaning exact molar masses of the polymers are not measured, and thus precise concentrations for UV-Vis analysis cannot be determined. It should also be noted that comparison of the intensity of peaks in UV-Vis cannot be compared due to the same issue – we are only noting the presence or absence of the expected absorbance peaks.

First, absorbance measurements of **TCT1**, IBVE, and POPS were taken (Figure S64). For **TCT1**, peaks at 305 nm and 440 nm are observed, which correspond to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, respectively. IBVE does not absorb strongly in the wavelength region measured, and POPS has absorbance between 290 nm and 240 nm. Looking at the UV-Vis spectrum of p(IBVE)$_{50}$ and p(IBVE)$_{50}$-*b*-p(POPS)$_{50}$ (Figure S65), we can see the retention of the **TCT1** $\pi \rightarrow \pi^*$ absorbance, indicating the presence of the TCT end-group for both polymers.

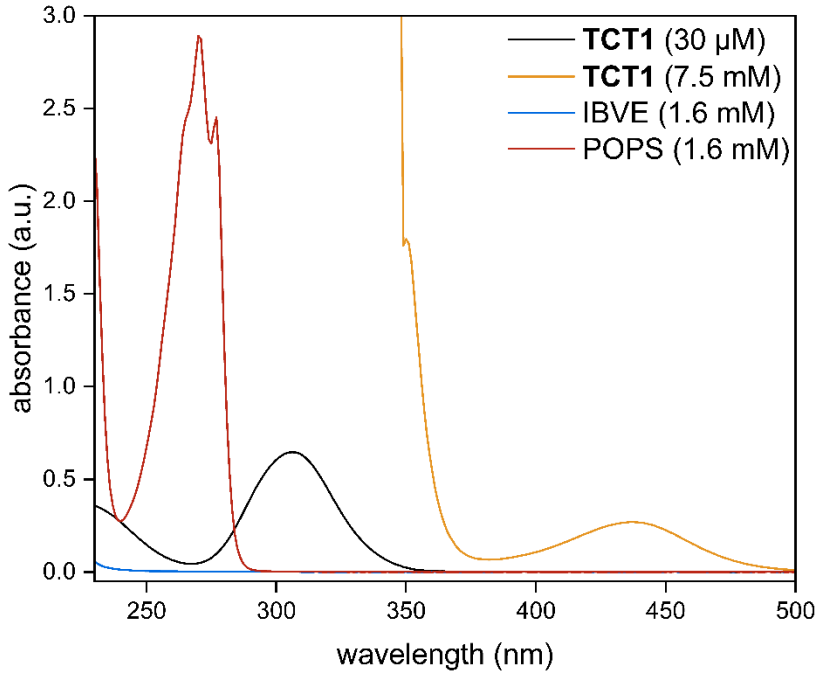


Figure S64. UV-Vis spectra of **TCT1**, IBVE, and POPS.

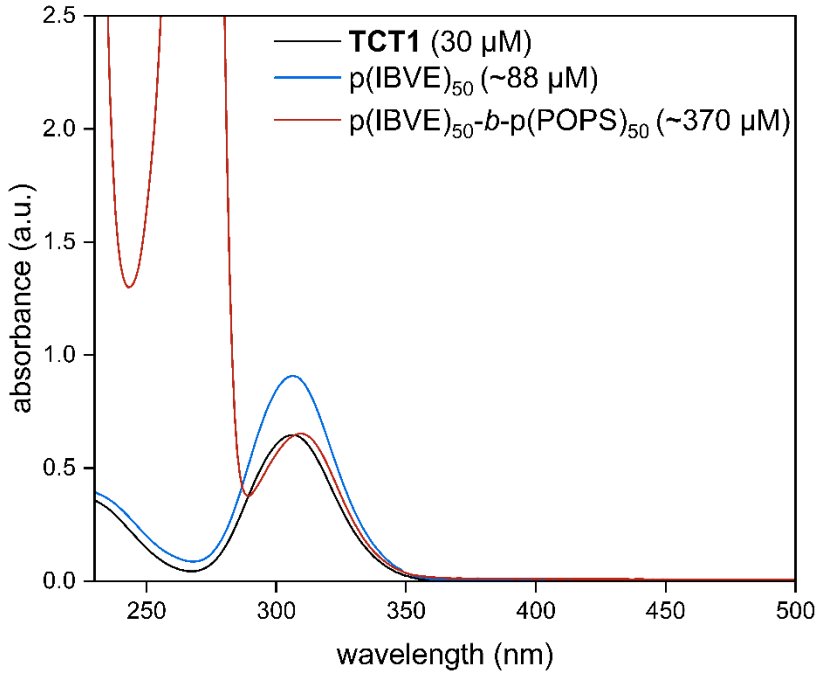
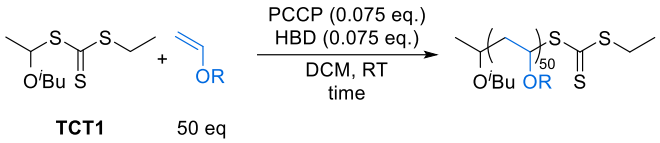


Figure S65. UV-Vis spectra of **TCT1**, p(IBVE)$_{50}$, and p(IBVE)$_{50}$-*b*-p(POPS)$_{50}$.

III. General synthetic procedures

A. General procedure for RDCP of vinyl ethers



This synthesis is adapted from a previous literature procedure.[6] Stock solutions of **TCT1**, HBD, and PCCP are made using DCM (due to the volatility of DCM, the concentrations and volumes are approximate). The exact concentration of these stock solutions can vary depending on the volume of vinyl ether being used (the final volume of DCM in the reaction should be half the volume of the vinyl ether added to ensure sufficient stirring during polymerization). An example IBVE polymerization is as follows: A 1-dram screw-top vial is equipped with a stir bar and charged with 38 μL of a solution of **TCT1** in DCM (1 M, 38 μmol, 1 eq). To this vial, 57 μL of a solution of HBD (50 mM, 2.85 μmol, 0.075 eq) is added, followed by 250 μL of IBVE (192 mg, 1.9 mmol, 50 eq). Next, DCM (15.8 uL) is added, followed by 14.25 μL of a PCCP solution (0.2 M, 2.85 μmol, 0.075 eq) to reach a final DCM volume of 125 μL. The vial is capped and allowed to stir for 3.5 h at room temperature. The polymerization is quenched with 730 μL of a 1 mg/mL (6.2 mM) solution of sodium S′-ethyl trithiocarbonate (**TCT salt**) in 1:1 DCM:MeCN. The resulting polymer is purified via precipitation in cold MeOH and dried in a vacuum oven overnight at 60 °C.

Monomer-specific deviations:

p(EVE) is precipitated in 8:2 H_2O:MeOH (see Section SII.J).

p(PVE) and p(NBVE) is precipitated in 1:1 H_2O:MeOH see Section SII.J).

p(IBVE) for chain-extension is made with 0.013 eq PCCP (see Section SII.J).

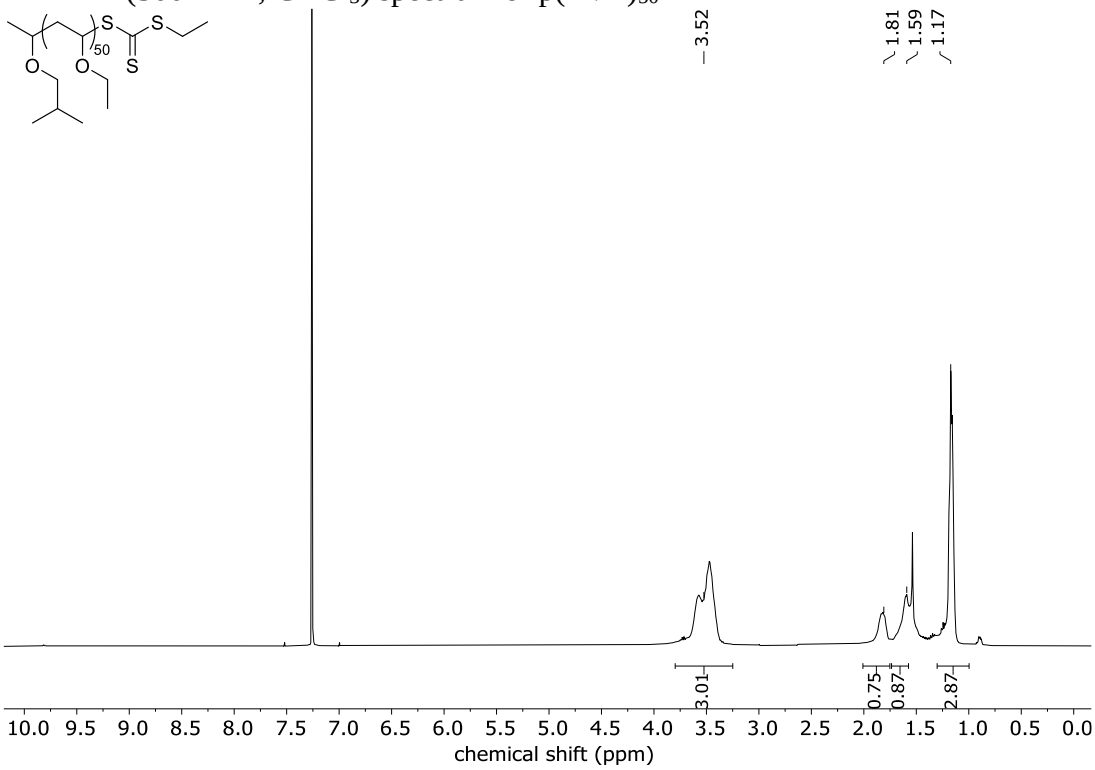
p(DHF) uses a 1:1 DCM:DHF by volume ratio, and is stirred for 16 hours before quenching. If being used for chain-extension, 0.013 eq PCCP is used and is stirred for 6 hours before being quenched with 100 μL of a 1:1 DCM:MeCN solution of **TCT salt** for 30 minutes at 35 °C.

p(CyVE) uses a 1:1 DCM:CyVE by volume ratio, and is stirred at 0 °C for 3 hours. If being used for chain-extension, 0.025 eq PCCP is used.

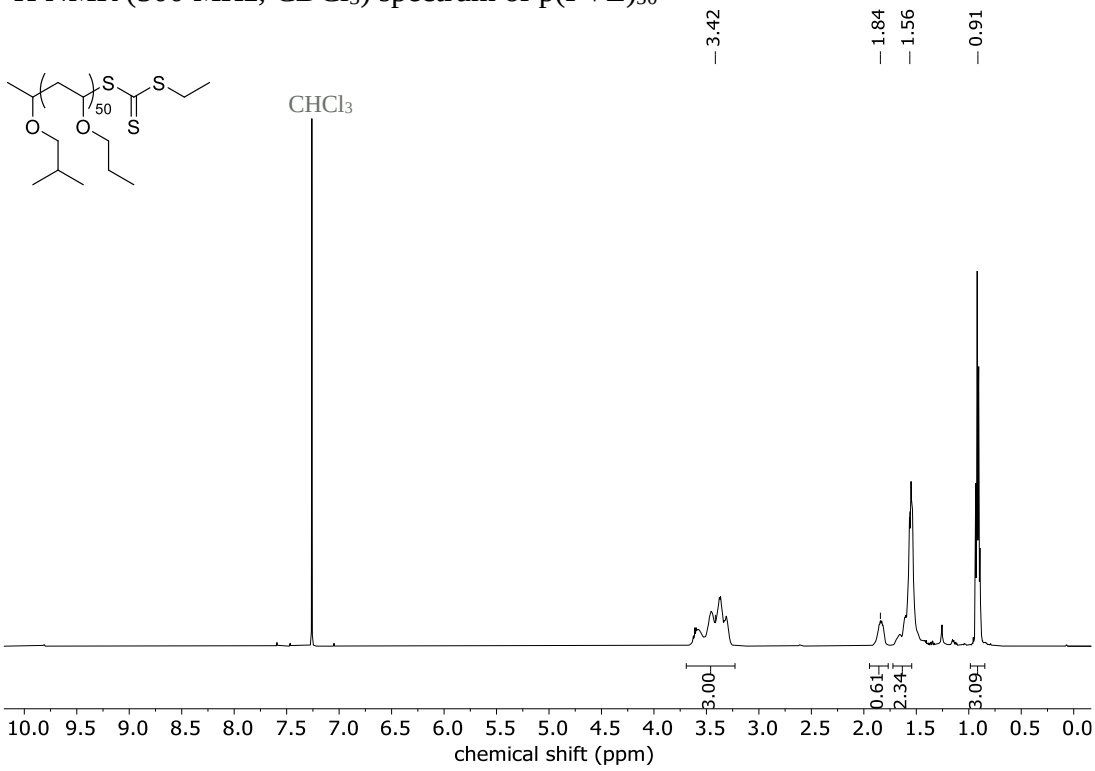
p(TBVE) for chain-extension is made with 0.013 eq PCCP and is stirred for 6 hours.

$CHCl_3$

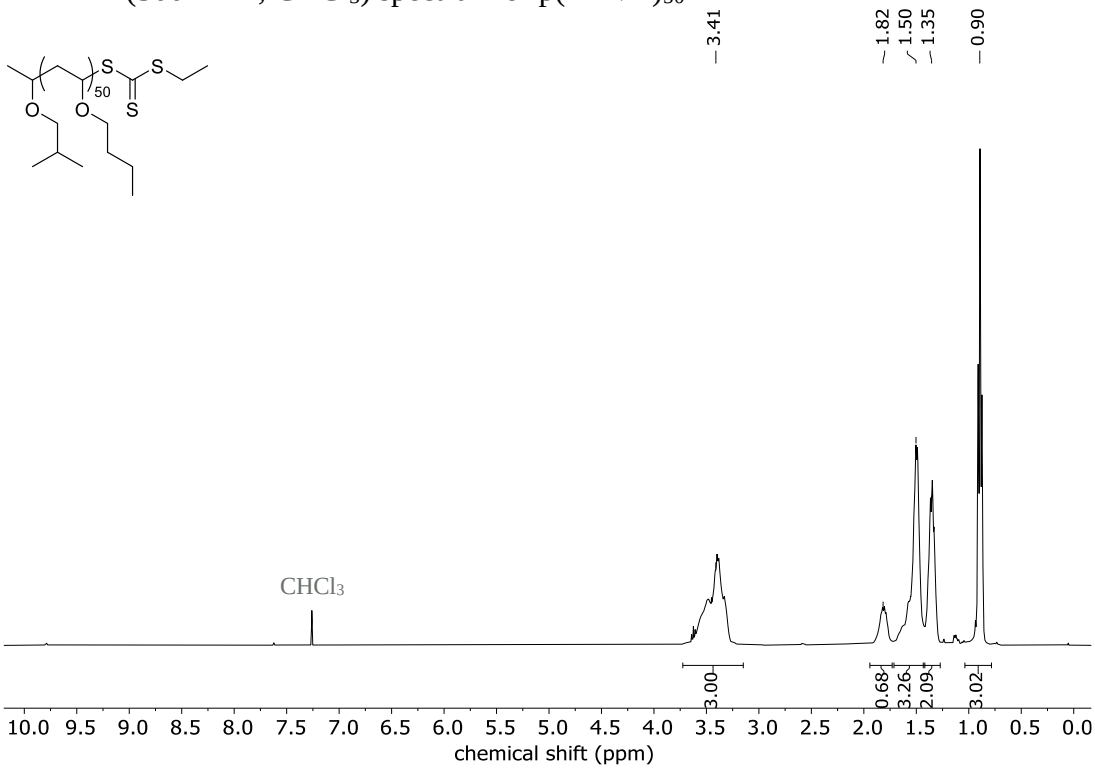
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of $p(EVE)_{50}$



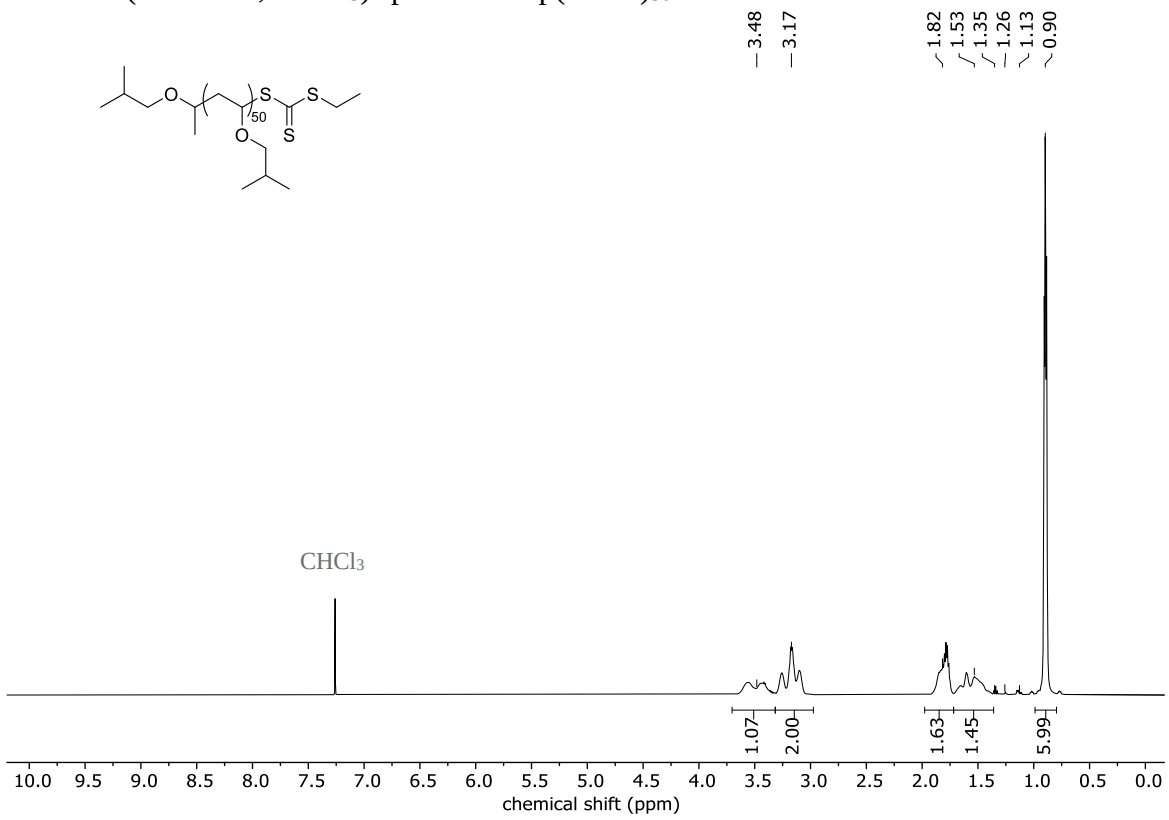
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of $p(PVE)_{50}$



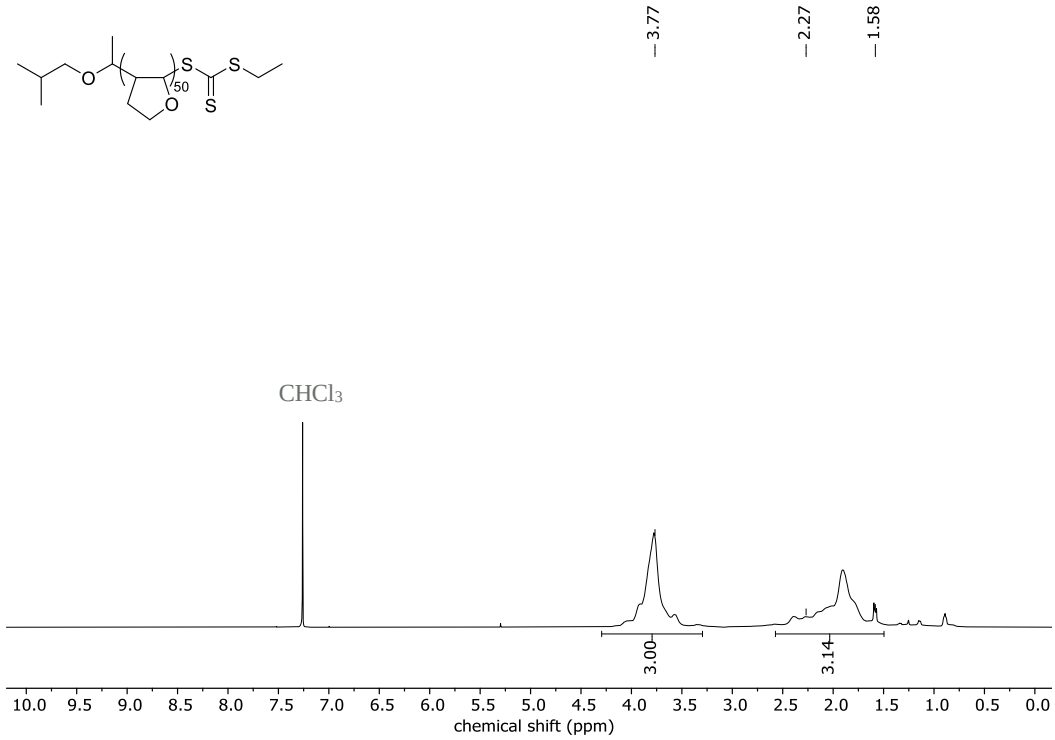
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of $p(NBVE)_{50}$



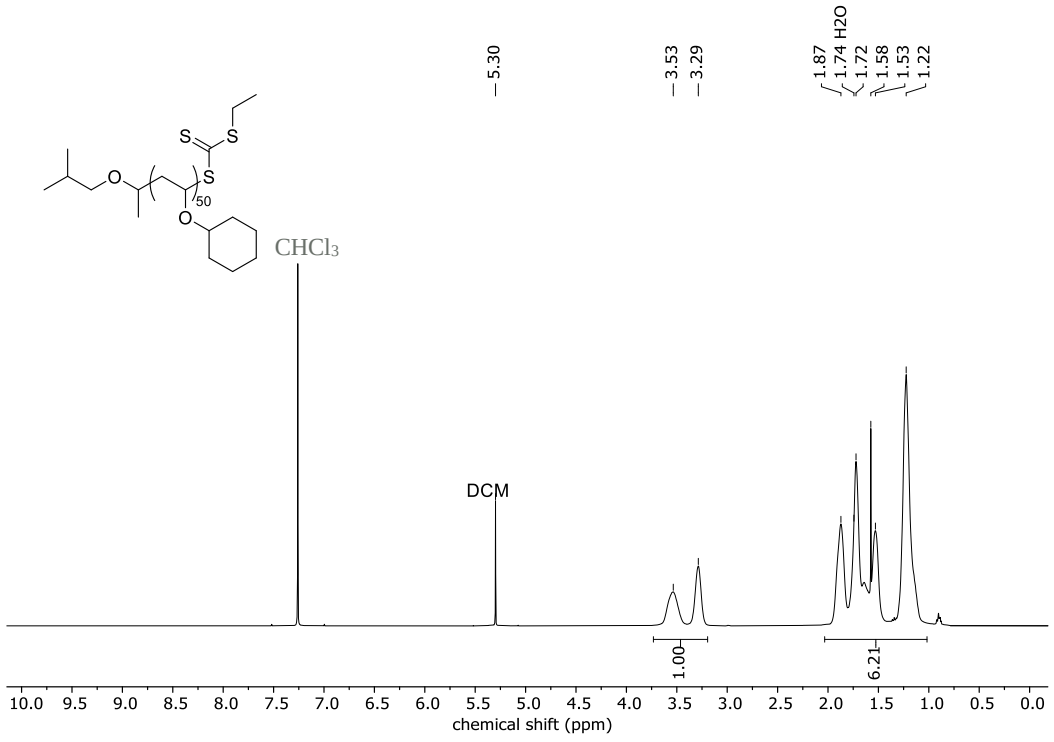
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of $p(IBVE)_{50}$



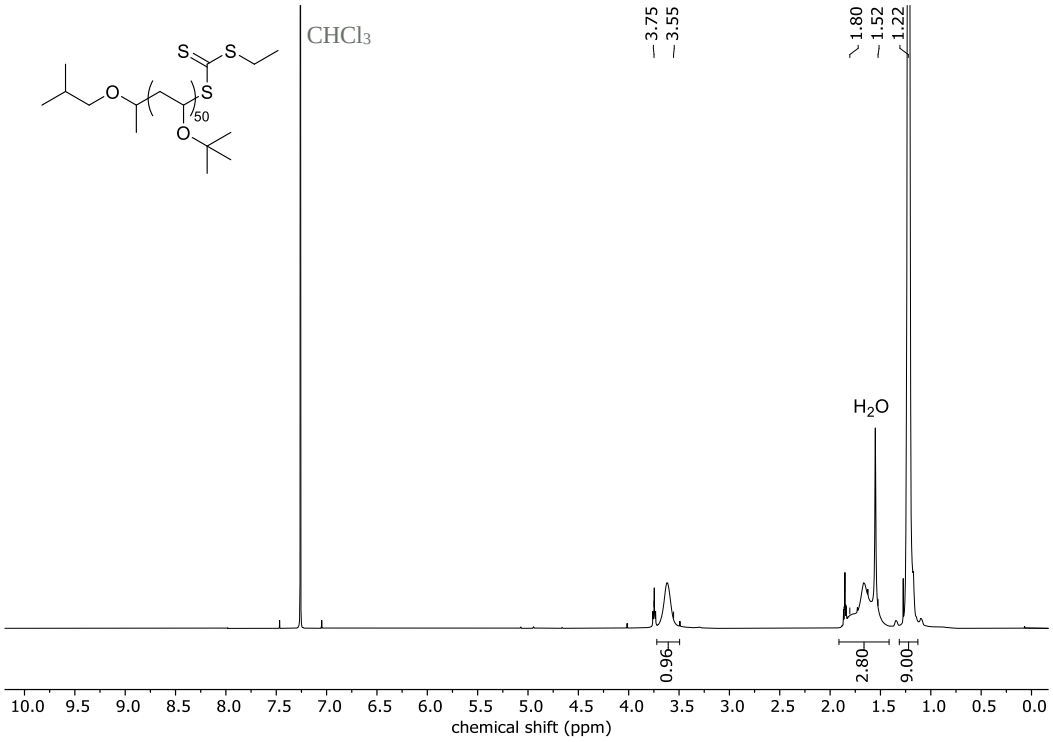
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of $p(DHF)_{50}$



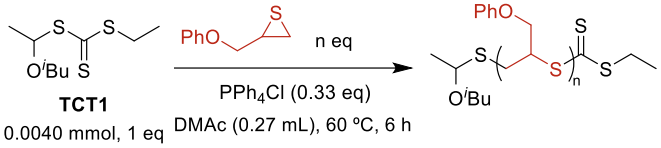
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of $p(CyVE)_{50}$



^{1}H NMR (500 MHz, $CDCl_3$) spectrum of p(TBVE)$_{50}$

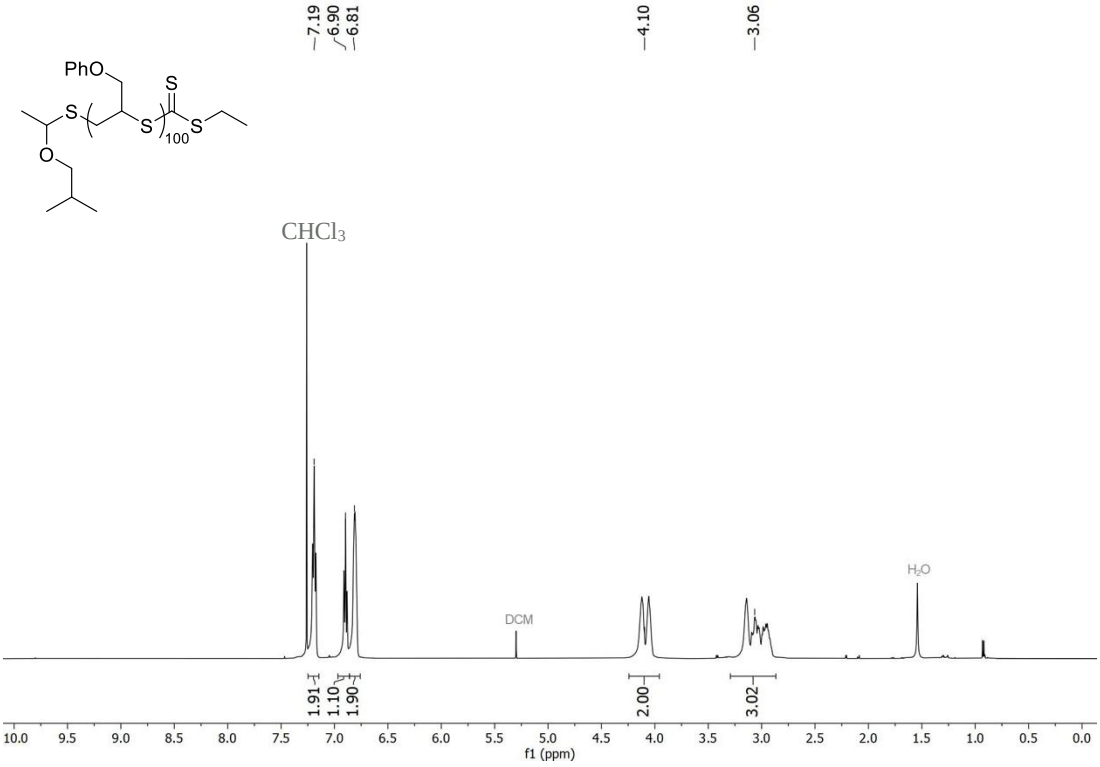


B. General procedure for TAGT homopolymerization of POPS

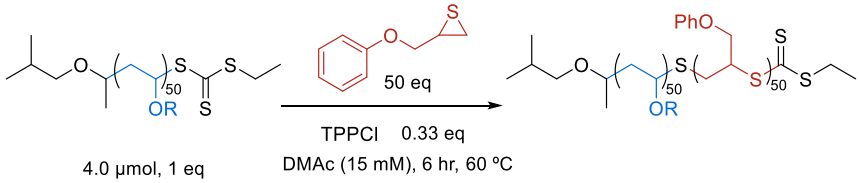


This synthesis was adapted from a previous literature procedure.[8] A 1 dram screw-top vial was charged with 130 µL of a stock solution of **TCT1** in DMAc (0.50 M, 0.0040 mmol, 1 eq) and a stir bar. POPS (50–100 eq) was added to the vial by weight followed by 110 µL of a stock solution of PPh_4Cl in DMAc (12 mM, 0.0013 mmol, 0.33 eq). More solvent was added until the total amount of DMAc was 270 µL. The solution was placed in a pre-heated reaction block at 60 °C. After stirring for 6 hours, the vial was removed from the glovebox, and an aliquot was taken for ^{1}H NMR analysis. The polymerization was then quenched with the addition of DCM (~100 µL), followed by isolation via precipitation in cold methanol. The pellet was redissolved in DCM to transfer to a tared vial. Additionally, an aliquot was taken for SEC analysis. The solvent was removed via drying overnight in a vacuum oven set at 60 °C.

^{1}H NMR (500 MHz, $CDCl_3$) spectrum for p(POPS)$_{100}$



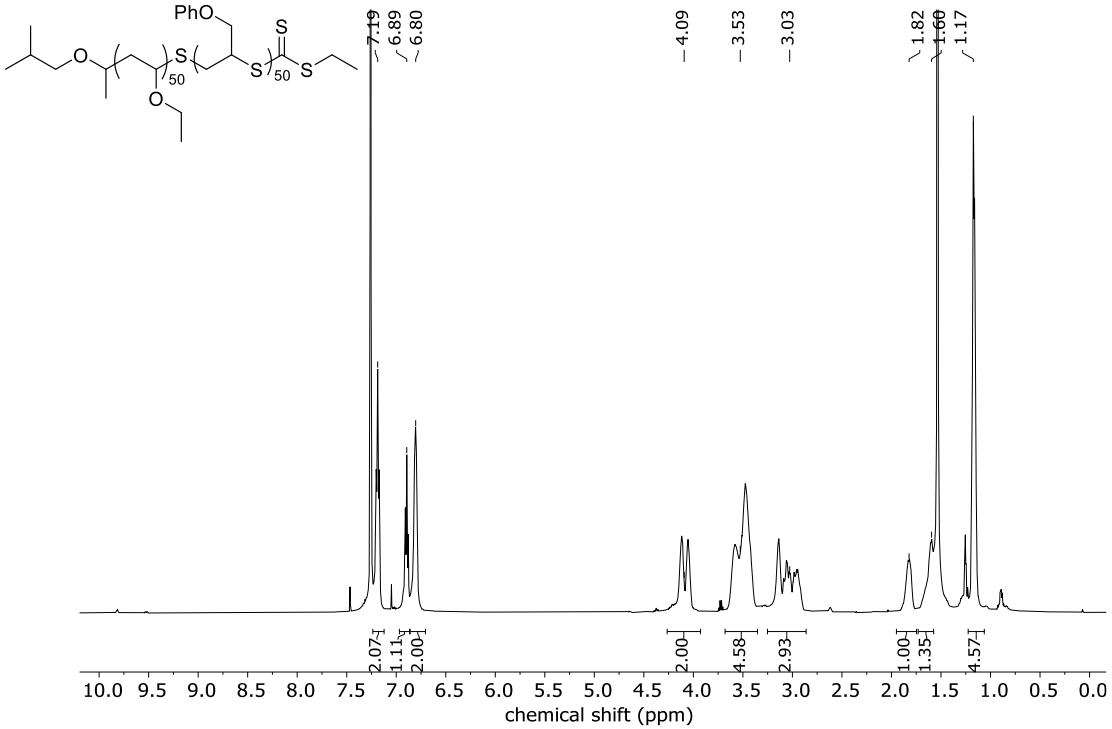
C. General procedure for TAGT chain-extension of DMAc-soluble pVEs



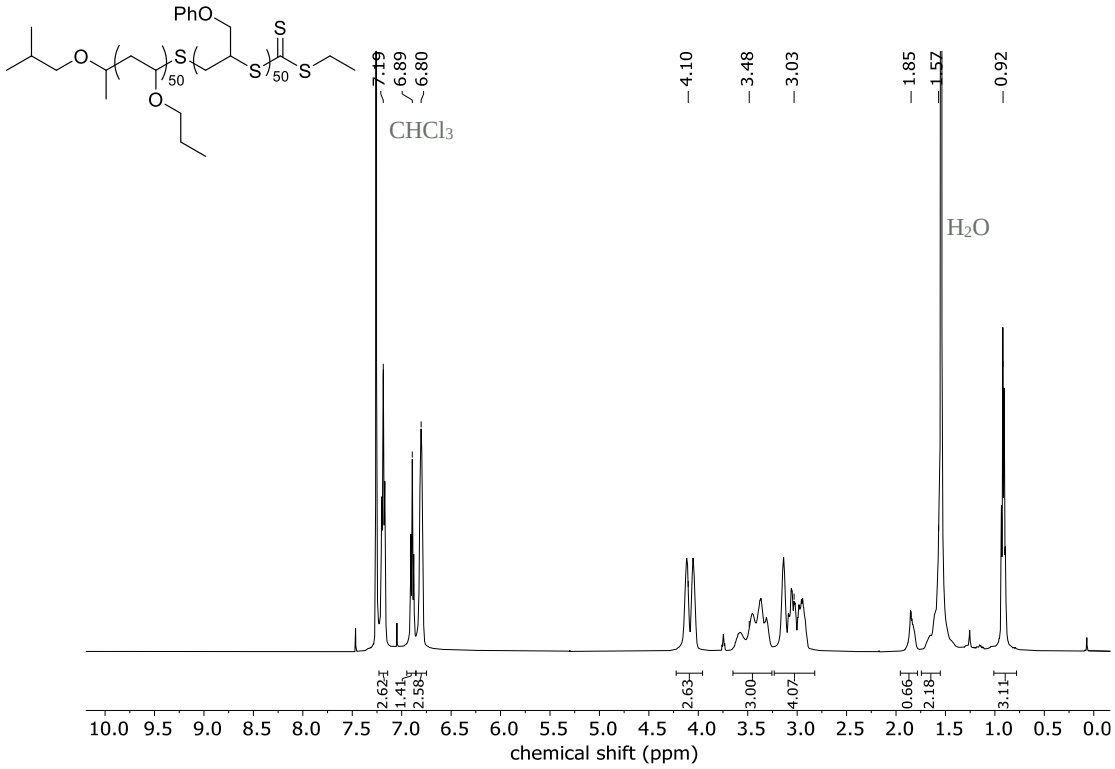
EVE **PVE** **NBVE**

This synthesis was adapted from a previous literature procedure.[2] Inside a nitrogen-filled glovebox, pVE was dissolved in a 1 dram screw-top vial to make a stock solution in DMAc (20 mM). To a separate 1-dram screw-top vial, a stir bar was added, followed by 200 μL of the p(VE) stock solution (4 μmol, 1 eq). To this vial, POPS (33.3 mg, 200 μmol, 50 eq) was added by weight. Lastly, 66 μL of a solution of PPh_4Cl (20 mM, 1.32 μmol, 0.33 eq) was added to the vial to reach a final pVE concentration of 15 mM. The vial was stirred at 60 °C for 6 hours before being removed from the glovebox and quenched with the addition of a small amount of DCM (~100 μL), followed by precipitation (8:2 H_2O:MeOH for p(EVE) or 1:1 H_2O:MeOH for p(PVE) and p(NBVE)). The purified BCP was dried in a vacuum oven overnight at 60 °C.

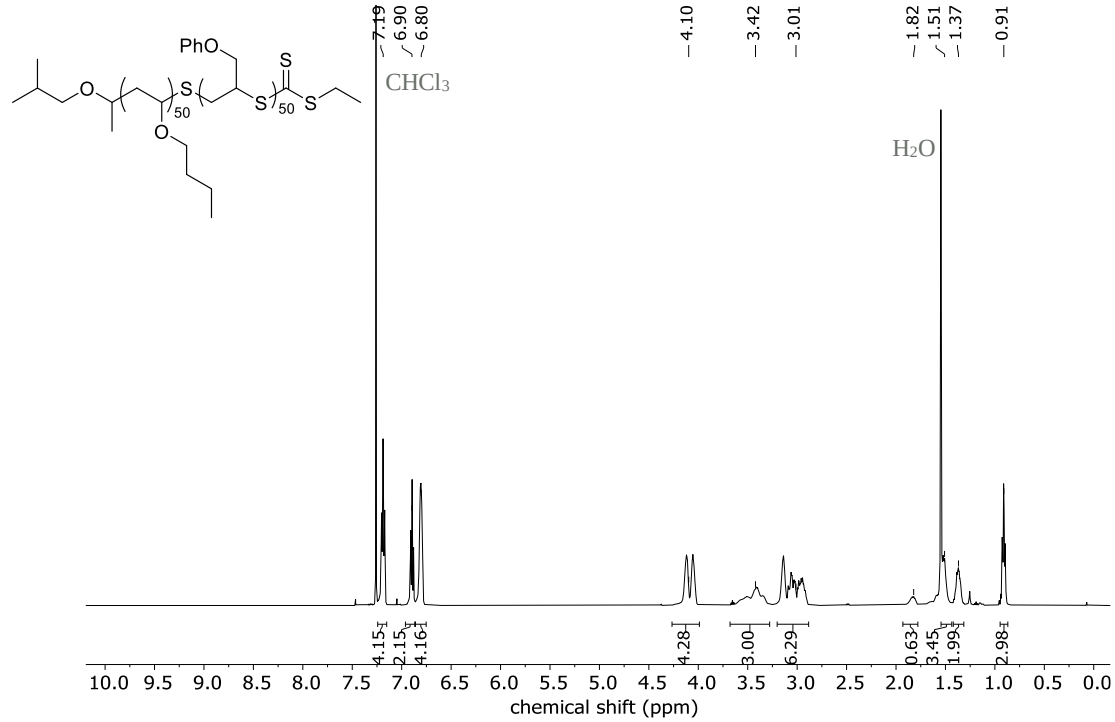
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of $p(EVE)_{50}$-*b*-$p(POPS)_{50}$.



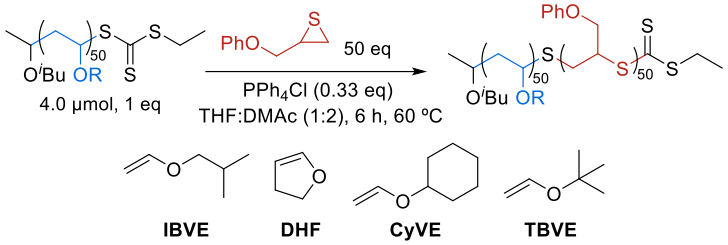
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of p(PVE)$_{50}$-*b*-p(POPS)$_{50}$.



^{1}H NMR (500 MHz, $CDCl_3$) spectrum of p(NBVE)$_{50}$-*b*-p(POPS)$_{50}$.

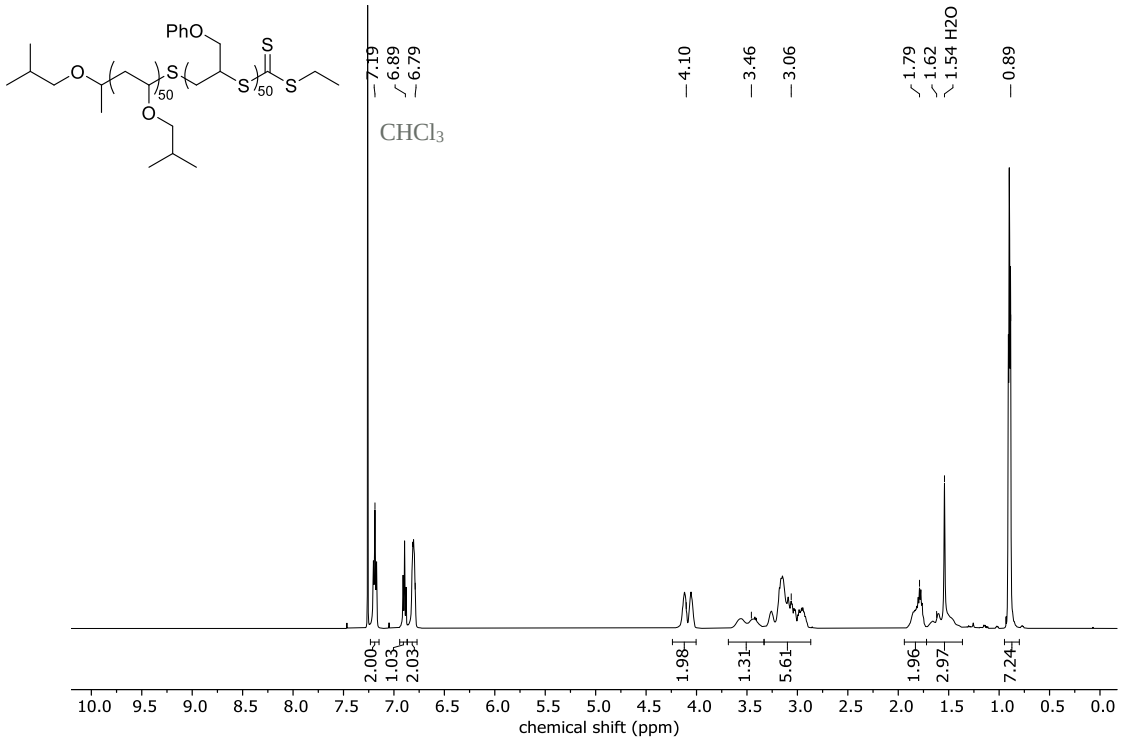


D. General procedure for TAGT chain-extension of less-soluble pVEs

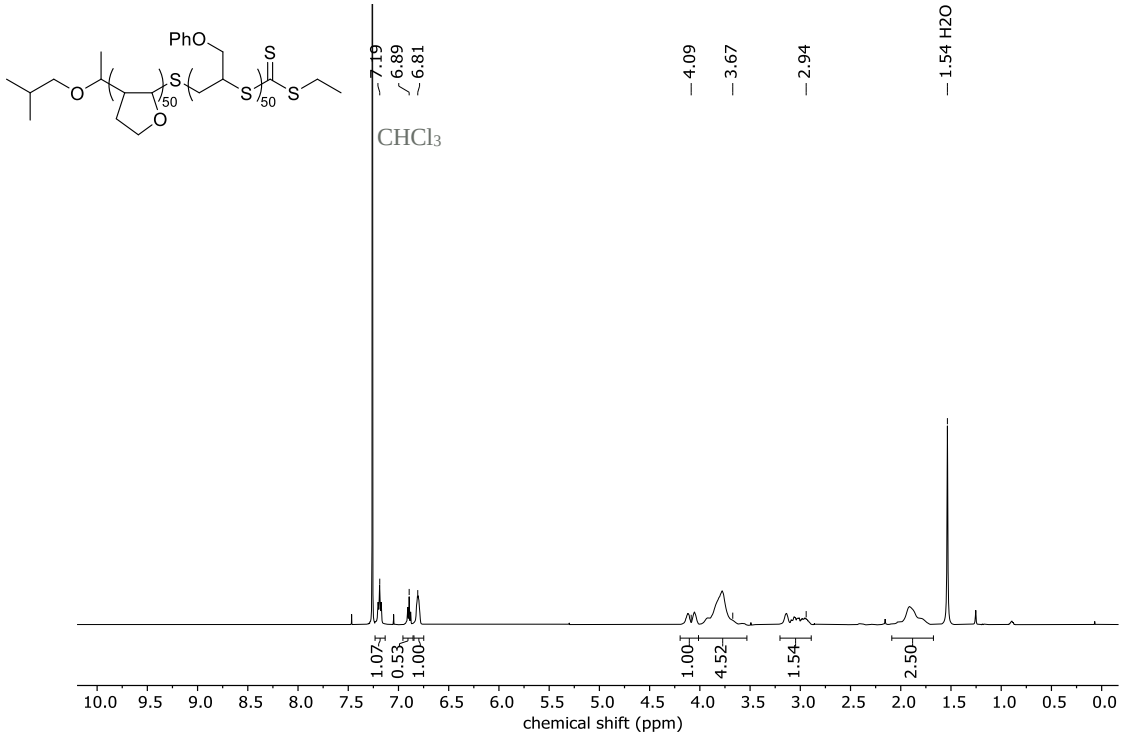


This synthesis was adapted from a previous literature procedure.[2] Inside a nitrogen-filled glovebox pVE was dissolved in a 1 dram screw-top vial to make a stock solution in THF (20 mM). To a separate 1 dram screw-top vial, a stir bar was added, followed by 200 µL of the pVE stock solution (4 µmol, 1 eq). To this vial, POPS (33.3 mg, 200 µmol, 50 eq) was added. This reaction mixture was diluted with THF (64 µL) and DMAc (470 uL). Lastly, 66 µL of a solution of PPh_4Cl (20 mM, 1.32 µmol, 0.33 eq) was added to the vial to reach a final concentration of 5 mM with a 1:2 THF:DMAc ratio. The vial was stirred at 60 °C for 6 hours before being removed from the glovebox and quenched with the addition of a small amount of DCM (~100 µL), followed by precipitation in cold MeOH. The purified BCP was dried in a vacuum oven overnight at 60 °C.

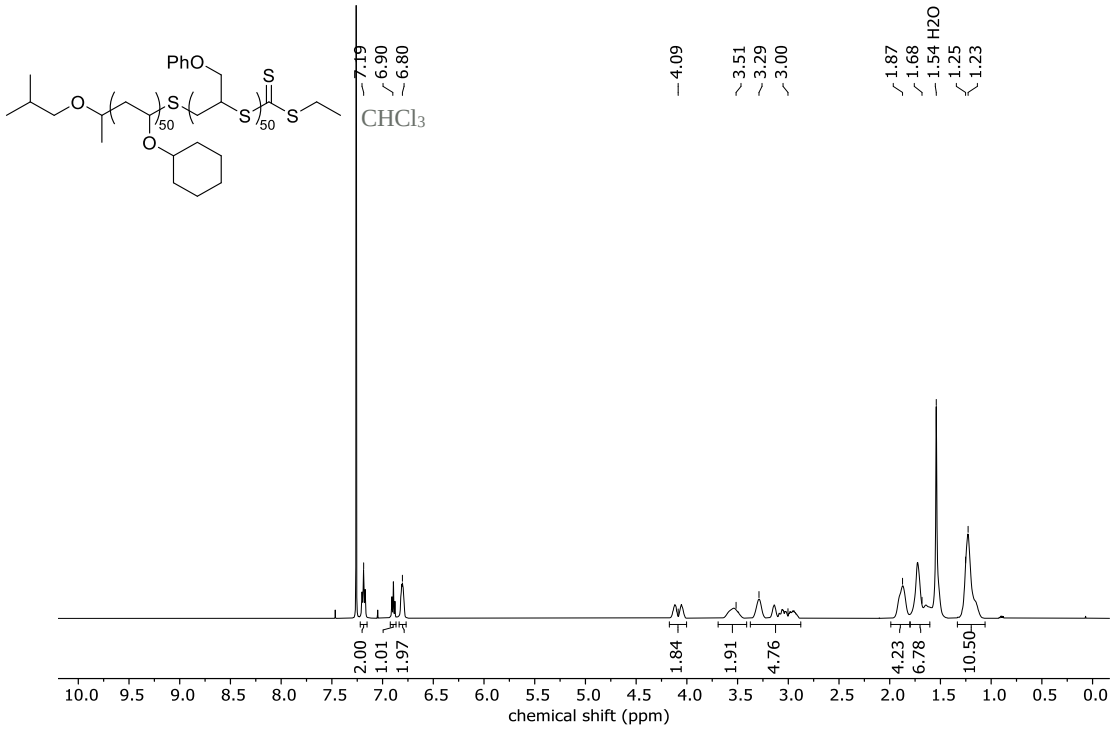
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of p(IBVE)$_{50}$-*b*-p(POPS)$_{50}$.



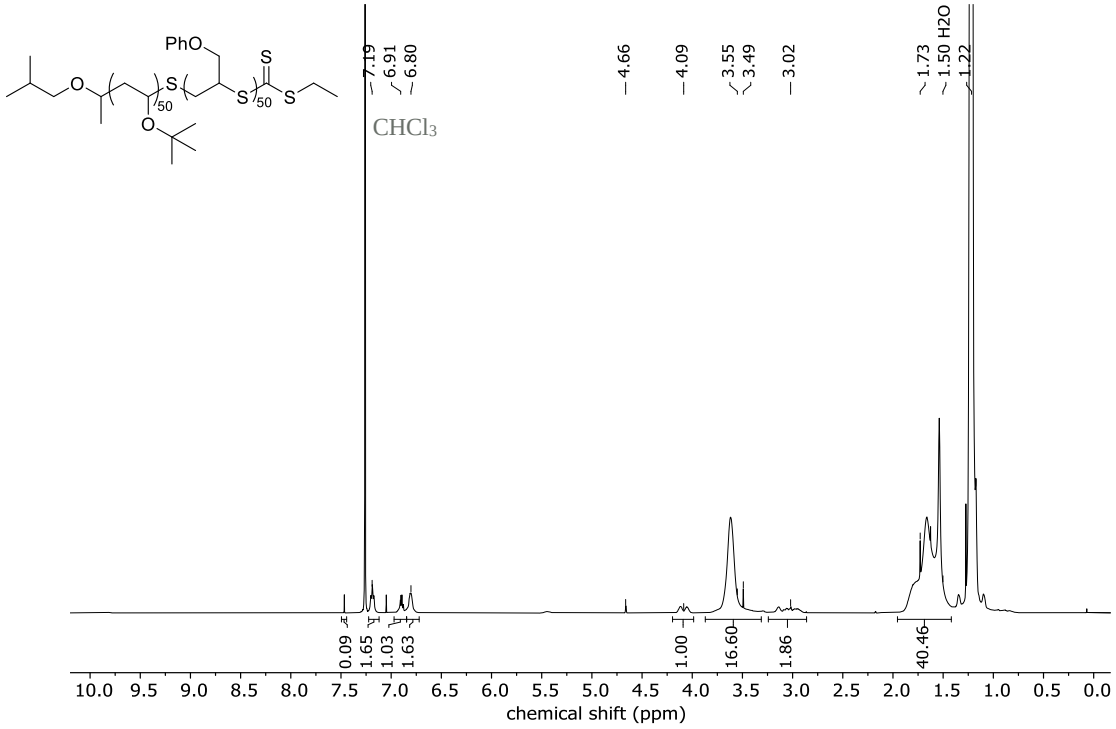
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of p(DHF)$_{50}$-*b*-p(POPS)$_{50}$.



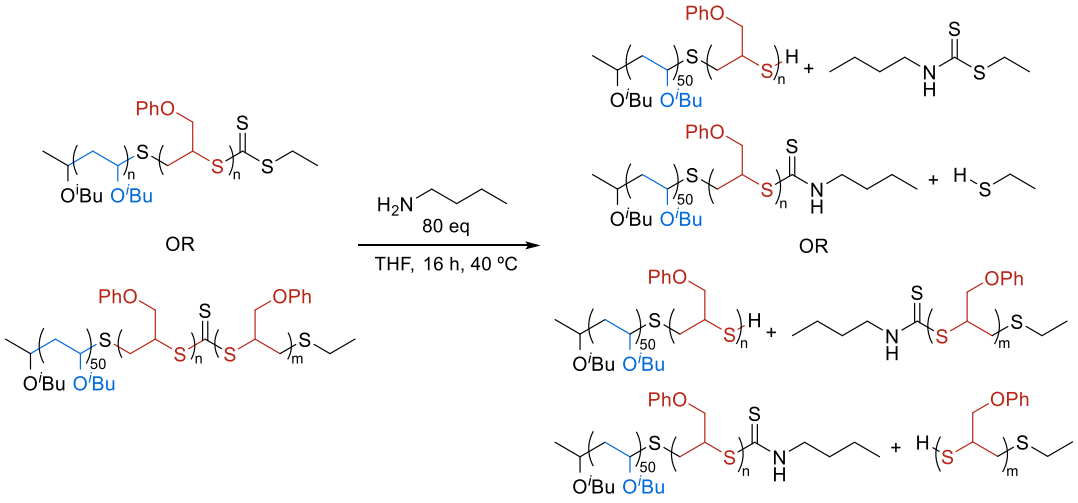
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of p(CyVE)$_{50}$-*b*-p(POPS)$_{50}$.



^{1}H NMR (500 MHz, $CDCl_3$) spectrum of p(TBVE)$_{50}$-*b*-p(POPS)$_{50}$.



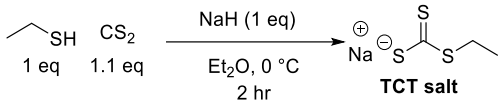
E. General procedure for aminolysis of BCPs



To a 1 dram screw-top vial equipped with a stir bar, p(IBVE)$_{50}$-*b*-p(POPS)$_{50}$ BCP (1.24 µmol, 1 eq) was added and dissolved using anhydrous THF (1 mL, 1.24 mM). To this solution, propylamine (10 µL, 80 eq) was added. The reaction mixture was stirred overnight at 40 °C before being precipitated in cold MeOH and dried in a vacuum oven overnight at 60 °C.

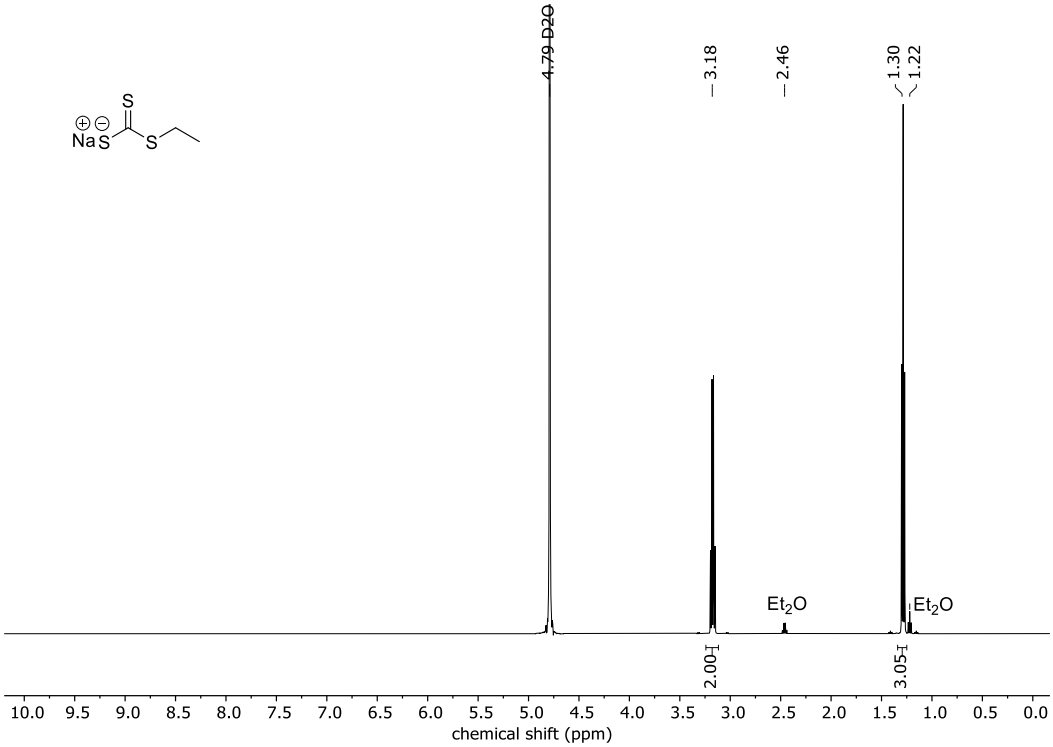
IV. Compound synthesis and characterization

A. Sodium S′-ethyl trithiocarbonate (TCT salt)

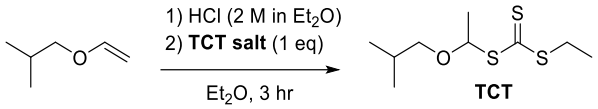


The following procedure is adapted from previous literature.[2] Ethanethiol and carbon disulfide are freshly distilled and stored under an inert atmosphere immediately before use. Inside a nitrogen filled glovebox, to a 25 mL Schlenk flask equipped with a stir bar, Sodium hydride (90%, 333 mg, 12.5 mmol, 1.0 eq) was added. The flask was sealed and brought out of the glovebox and pumped onto a Schlenk line. To the flask, anhydrous Et_2O (5 mL) was added and cooled to 0 ℃. Freshly distilled ethanethiol (926 uL, 12.5 mmol, 1.0 eq) was added in a dropwise manner to the Schlenk flask over 10 minutes. The solution was stirred at room temperature for 10 minutes before being cooled back down to 0 ℃. To the reaction mixture, freshly distilled carbon disulfide (827 uL, 13.8 mmol, 1.1 eq) was added in a dropwise manner over 10 minutes. The reaction mixture was stirred at room temperature for 2 hours. The resulting yellow solid was filtered (open to air) using a Büchner funnel and washed with anhydrous Et_2O. The product was dried under high vacuum overnight before being stored in a desiccator or inside a glovebox to prevent hydrate formation. Further purification is not needed for use in TCT synthesis or quenching of RDCP. **^{1}H NMR** (500 MHz, D_2O): δ 3.18 (q, J = 7.4 Hz, 2H), 1.30 (t, J = 7.4 Hz, 3H).

^{1}H NMR (500 MHz, D_2O) spectrum of **TCT salt**



B. Ethyl 1-(2-methylpropoxy)ethyl carbonotrithioate (TCT1)



The following is adapted from a previously reported procedure.[2] IBVE should be dried and freshly distilled and stored under an inert atmosphere prior to use. Inside of a nitrogen filled glovebox, **TCT salt** (1 g, 6.24 mmol, 1 eq) was added to a 25 mL Schlenk flask equipped with a stir bar. The flask was removed from the glovebox and pumped onto a Schlenk line. In a separate flame-dried 10 mL pear-shaped flask, HCl (2 M in Et_2O, 3.43 mL, 6.86 mmol, 1.2 eq) was added and cooled to −78 °C. To the pear-shaped flask, IBVE (0.814 mL, 6.24 mmol, 1 eq) was added in a dropwise manner. The mixture was stirred at −78 °C for 1 hour before being warmed to 0 °C over 30 minutes. To the Schlenk flask containing **TCT salt**, anhydrous Et_2O (1.66 mL) was added to form a suspension and cooled to 0 °C. Using a canula, the chlorinated IBVE reaction mixture was transferred from the pear-shaped flask into the Schlenk flask in a dropwise manner over 30 minutes. The reaction mixture was stirred at room temperature for 2 hours. Following stirring, the reaction mixture was diluted with anhydrous Et_2O (2.5 mL) and quenched with saturated sodium bicarbonate (2.5 mL). The product was extracted using Et_2O (2 x 20 mL) and the combined organic layers were washed with water (10 mL) and brine (10 mL). The organic fraction was dried over sodium sulfate before being concentrated via rotary evaporation and fully dried via high vacuum for 8 hours. Note: exposure to high vacuum for longer than 8 hours can result in significant product loss due to volatility. The product can be used in polymerizations without further purification. The spectroscopic data for this compound were identical to those in the reported literature.[3]

V. References

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