Moisture tolerant cationic RAFT polymerization of vinyl ethers

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Experimental Procedures

Figures and tables

General Reagent Information

Isobutyl vinyl ether (IBVE) (>99%, TCI), ethyl vinyl ether (EVE) (>98%, TCI), 2-chloroethyl vinyl ether (Cl-EVE) (>97%, TCI), 2,3-dihydrofuran (DHF) (>98%, TCI), *tert*-butyl vinyl ether (TBVE) (98%, ACROS Organics), and cyclohexyl vinyl ether (CyVE), (>98%, TCI) were filtered through a plug of activated basic alumina to remove inhibitors prior to use. For experiments that used distilled monomer, IBVE was dried over calcium hydride (CaH_2) overnight, distilled under vacuum, underwent three freeze-pump-thaw cycles, and pumped into a glove box with a N_2 atmosphere for storage. Methyl acrylate (MA) (99%, Sigma Aldrich) was also dried over calcium hydride (CaH_2) overnight, distilled under vacuum, underwent three freeze-pump-thaw cycles, and pumped into a glove box with a N_2 atmosphere for storage. Alumina (activated, basic, Brockman Grade I, 1-20 mm granules, Oakwood Chemical), calcium hydride (92% min, 1–20 mm granules, Alfa Aesar), 2-hydroxylethyl acrylate (96%, Sigma Aldrich), ferrocenium tetrafluoroborate (technical grade, Sigma Aldrich), 2,2'-azobisisobutyronitrile (AIBN) (98%, Sigma Aldrich), and methanol (MeOH) (certified ACS, Fisher Chemical) were used as received. Triethylamine (>99.5%, Sigma Aldrich) used in solution for quenching the polymerizations was used as received. Sodium *N,N*-diethyldithiocarbamate trihydrate (98%, Alfa Aesar) was azeotropically dried with toluene. Dichloromethane (DCM) and acetonitrile (MeCN) were used from the solvent system, from which they were purchased from Honeywell and purified by vigorous purging with argon for 2 hours, followed by passing through two packed columns of neutral alumina under argon pressure. 1,2,3,4,5-Pentacarbomethoxycyclopentadiene (PCCP) was synthesized according to a reported literature procedure.[1] The hydrogen bond donor (HBD), tris(3,5-bis(trifluoromethyl)phenyl) thiophosphotriamide, was synthesized according to a literature procedure.[2] Triethylamine used in the synthesis of the HBD was run through a plug of basic alumina before use. The RAFT chain transfer agents (CTA), *S*-1-isobutoxyethyl *N,N*-diethyl dithiocarbamate and *S*-1-isobutoxylethyl *S'*-ethyl trithiocarbonate, and its corresponding salt, sodium *S'*-ethyl trithiocarbonate, were synthesized according to a literature procedure.[3]

General Analytical Information

All polymer analysis was performed using a Tosoh EcoSEC HLC 8320 GPC system with two SuperHM-M columns in series at a flow rate of 0.350 mL/min with tetrahydrofuran (THF) as the eluent. For all homopolymers unless otherwise noted, number-average molecular weights (M_n), weight-average molecular weights (M_w), and dispersities ($Đ$) were determined by light scattering using a Wyatt miniDawn Treos multi-angle light scattering detector and the following *dn/dc* values: 0.0381 (IBVE), 0.0462 (EVE), 0.0795 (Cl-EVE), 0.1116 (DHF), 0.0637 (TBVE)[4], and 0.0923 (CyVE), with units of mL g^{-1}. Refractive index data from GPC with polystyrene standards was commonly used for small polymers around 5 kg/mol and diblock copolymers as their *dn/dc* values were not known. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker 400 MHz or a Bruker 500 MHz instrument at room temperature using $CDCl_3$ as a solvent unless otherwise noted.

Example of general procedure for polymerization with filtered monomer, under ambient atmosphere

A one dram vial equipped with a stir bar was charged with the dithiocarbamate RAFT CTA (0.019 mmol, 4.7 mg, 1 equiv), HBD (0.0014 mmol, 1.1 mg, 0.075 equiv), and PCCP (0.0014 mmol, 0.5 mg, 0.075 equiv) in that respective order. IBVE (5.6 mmol, 0.73 mL, 300 equiv) was filtered through a plug of basic alumina and added to the dram vial. The vial stirred at room temperature on a magnetic stir plate for 3.5 hours. The polymerization was terminated with 40 µL of 5% triethylamine in methanol, after which samples for GPC and ^1H NMR analysis were taken.

Same procedure was utilized for the polymerizations of EVE, Cl-EVE, DHF, TBVE, and CyVE in Table 2 in the main manuscript.

Example of general procedure for polymerization with filtered monomer, under N_2

A one dram vial was flame dried and equipped with a stir bar and septum cap. The dithiocarbamate RAFT CTA (0.007 mmol, 1.8 mg, 1 equiv), HBD (0.0014 mmol, 1.1 mg, 0.2 equiv), and PCCP (0.0014 mmol, 0.5 mg, 0.2 equiv) were weighed out and added to the vial in that respective order. The vial was purged with N_2 for 10 minutes. For trials with solvent, dry DCM was added before monomer under N_2. IBVE (5.6 mmol, 0.73 mL, 800 equiv) was filtered through a plug of basic alumina and added to the dram vial under N_2. The vial stirred at room temperature on a magnetic stir plate for 4 hours. The polymerization was terminated with 40 µL of 5% triethylamine in methanol, after which samples for GPC and ^{1}H NMR analysis were taken.

Same procedure was utilized for the polymerizations of EVE, Cl-EVE, DHF, TBVE, and CyVE from Table S6.

Example of general procedure for polymerization with distilled monomer, under N_2

A one dram vial was flame dried and equipped with a stir bar and septum cap. The dithiocarbamate RAFT CTA (0.014 mmol, 3.5 mg, 1 equiv), HBD (0.0014 mmol, 1.1 mg, 0.1 equiv), and PCCP (0.0014 mmol, 0.5 mg, 0.1 equiv) were weighed out and added to the vial in that respective order. The vial was purged with N_2 for 10 minutes. IBVE (5.6 mmol, 0.73 mL, 400 equiv) that was previously distilled off of calcium hydride was added to the vial under N_2. The vial stirred at room temperature on a magnetic stir plate for 5 hours. The polymerization was terminated with 40 µL of 5% triethylamine in methanol, after which samples for GPC and ^{1}H NMR analysis were taken.

Example calculation for conversion and $M_{\mathrm{n,theo}}$ of polymerizations

In this method, all integrations are relative to the vinyl signal of IBVE at ~6.5 ppm, which was set to 1 proton, as shown in Figure S1. As the PCCP initiates some chains, in addition to the CTA, it is accounted for in the molecular weight calculation. Other monomers were calculated similarly.

$$\text{integration from 0.85 ppm to 0.98 ppm} = 33.63$$

$$\text{integration of polymer} = 33.63 - \text{6H from IBVE} = 27.63$$

$$\text{conversion to polymer} = 27.63 \div 33.63 = 0.82$$

$$M_{\mathrm{n,theo}} = \frac{\text{conversion} \times \text{IBVE equiv} \times \text{MW of IBVE}}{1 + \text{PCCP equiv}} + \text{MW of CTA}$$

$$M_{\mathrm{n,theo}} = \frac{0.82 \times 200 \times 100.16\ \mathrm{g/mol}}{1 + 0.05} + 250\ \mathrm{g/mol} = 15.9\ \mathrm{kg/mol}$$

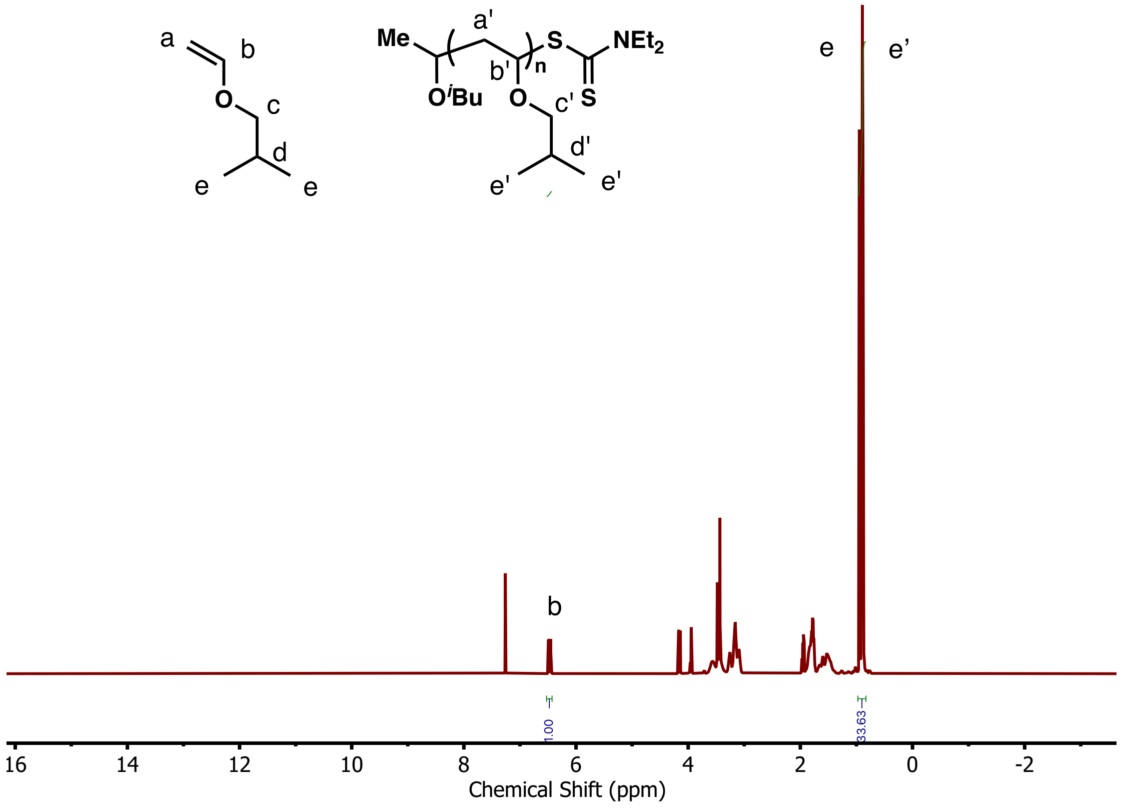


Figure S1. ^{1}H-NMR spectrum of crude polymerization mixture of IBVE.

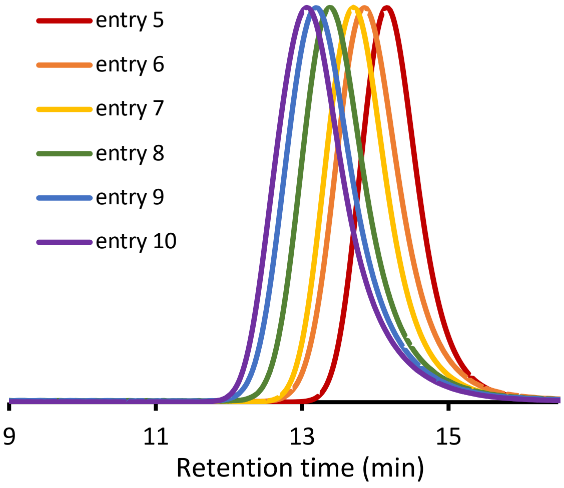


Figure S2. GPC traces of data from Table 1, entries 5-10.

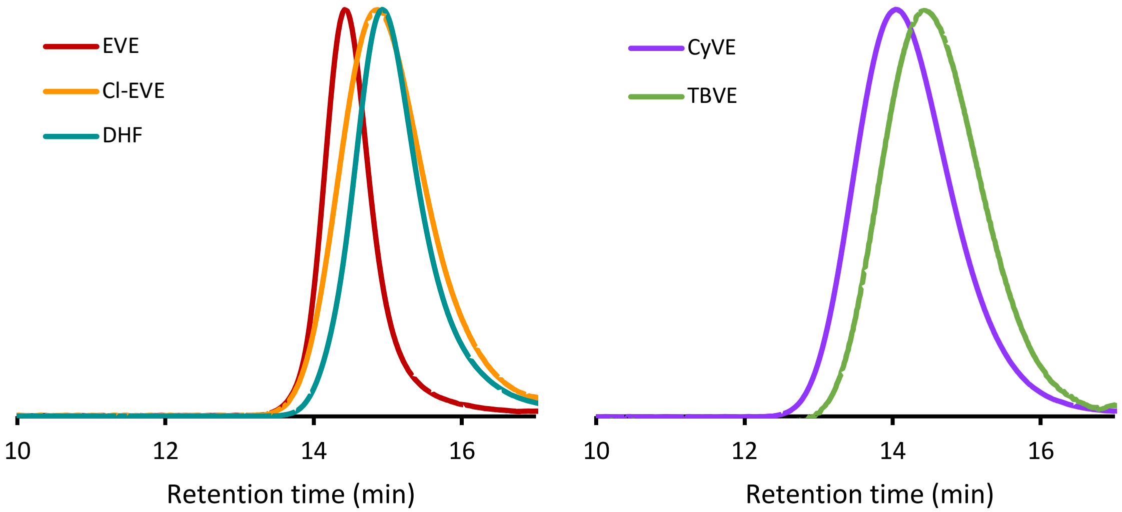


Figure S3. GPC traces of different monomers from Table 2, performed under air.

Table S1. Optimization of PCCP and HBD equivalents without solvent.

Entry[a]	IBVE equiv	PCCP equiv	HBD equiv	Time (h)	$M_{n,theo}$ (kg mol^{-1})	$M_{n,exp}$ (kg mol^{-1})	$Đ$
1	400	0.05	0.05	24	33.6	27.1	1.32
2	400	0.1	0.1	4	27.1	27.5	1.22
3	400	0.1	0.2	2.5	28.8	30.9	1.20
4	400	0.1	0.3	2	29.1	30.1	1.20
5	400	0.1	0.4	1.5	32.8	29.4	1.22
6	400	0.2	0.2	2	25.4	25.6	1.31
7	800	0.1	0.1	24	56.4	32.7	1.42
8	800	0.2	0.2	4	53.1	40.2	1.32
9	800	0.2	0.4	2.5	53.4	44.4	1.33
10	800	0.2	0.6	2	51.8	45.8	1.27
11	800	0.2	0.8	1.5	56.9	41.2	1.36
12	800	0.4	0.4	2	48.7	40.2	1.32

[a] IBVE (5.6 mmol, filtered through basic alumina) was added to CTA (1 equiv), PCCP, and HBD and stirred under a nitrogen atmosphere at room temperature.

Table S2. Effects of DCM as solvent, targeting a molecular weight of ~30 kg/mol.

Entry	PCCP equiv	HBD equiv	Dry DCM (mL)	Time (h)	$M_{n,theo}$ (kg mol^{-1})	$M_{n,exp}$ (kg mol^{-1})	$Đ$
1	0.1	0.1	0.73	6	32.8	29.4	1.23
2	0.1	0.1	0.36	5	20.3	17.1	1.32
3	0.1	0.1	0.18	5.5	29.3	26.0	1.30
4	0.1	0.2	0.07	3.5	31.7	31.7	1.20
5	0.1	0.3	0.07	3	32.8	33.3	1.20
6	0.1	0.4	0.07	2	33.9	32.4	1.28
7	0.2	0.2	0.73	3.5	33.2	25.4	1.31
8	0.2	0.2	0.36	3.5	32.1	26.4	1.34
9	0.2	0.2	0.18	3.5	30.9	28.4	1.23

[a] IBVE (400 equiv, 5.6 mmol, filtered through basic alumina) and dry DCM was added to CTA (1 equiv), PCCP, and HBD and stirred under a nitrogen atmosphere at room temperature.

Table S3. Effects of DCM as solvent, targeting a molecular weight of ~60 kg/mol.

Entry	PCCP equiv	HBD equiv	Dry DCM (mL)	Time (h)	$M_{n,theo}$ (kg mol^{-1})	$M_{n,exp}$ (kg mol^{-1})	$Đ$
1	0.2	0.2	0.73	2.75	44.2	30.8	1.30
2	0.2	0.2	0.36	6	57.4	35.0	1.41
3	0.2	0.2	0.18	5.5	50.6	38.2	1.32
4	0.2	0.4	0.07	3.5	59.8	44.5	1.36
5	0.2	0.6	0.07	3	58.7	45.3	1.31
6	0.2	0.8	0.07	2	60.5	41.0	1.46
7	0.4	0.4	0.73	4.5	55.9	37.2	1.32
8	0.4	0.4	0.36	3.5	55.9	35.1	1.42
9	0.4	0.4	0.18	3	54.0	43.4	1.31

[a] IBVE (800 equiv, 5.6 mmol, filtered through basic alumina) and dry DCM was added to CTA (1 equiv), PCCP, and HBD and stirred under a nitrogen atmosphere at room temperature.

Table S4. Effects of an increase in PCCP and HBD equivalents when targeting high molecular weights.

Entry	PCCP equiv	HBD equiv	Time (h)	$M_{\mathrm{n,theo}}$ (kg mol^{-1})	$M_{\mathrm{n,exp}}$ (kg mol^{-1})	Đ
1	0.3	0.3	3	74.6	49.8	1.43
2	0.3	0.6	2	68.3	49.5	1.57
3	0.3	0.9	1	69.3	49.9	1.39
4	0.6	0.6	1	71.0	43.6	1.42
5	0.9	0.9	0.25	56.1	21.6	2.20
6	1.0	1.0	0.2	50.5	16.8	2.18

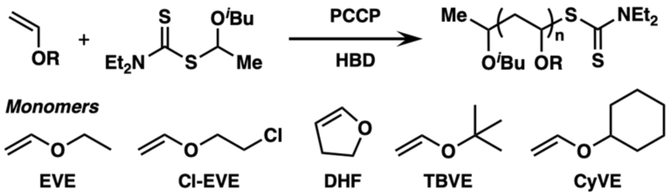
[a] IBVE (1200 equiv, 5.6 mmol, filtered through basic alumina) was added to CTA (1 equiv), PCCP, and HBD and stirred under a nitrogen atmosphere at room temperature.

Table S5. Comparison of different monomer purification techniques and polymerization atmospheres.

Entry	IBVE:PCCP:HBD	Monomer purification	Atmosphere	Time (h)	$M_{\mathrm{n,theo}}$ (kg mol^{-1})	$M_{\mathrm{n,exp}}$ (kg mol^{-1})	Đ
1a	100:0.025:0.025	distilled	N_2	4	6.7	8.0	1.16
1b	100:0.025:0.025	filtered	N_2	4	7.1	8.9	1.11
1c	100:0.025:0.025	filtered	air	4	6.9	9.3	1.12
2a	200:0.05:0.05	distilled	N_2	5	15.7	17.2	1.17
2b	200:0.05:0.05	filtered	N_2	4	14.1	16.0	1.17
2c	200:0.05:0.05	filtered	air	3.5	15.9	18.6	1.11
3a	400:0.1:0.1	distilled	N_2	5	24.9	24.0	1.35
3b	400:0.1:0.1	filtered	N_2	4	27.1	27.5	1.22
3c	400:0.1:0.1	filtered	air	3.5	29.0	26.7	1.26
4a	800:0.2:0.2	distilled	N_2	4	51.5	45.1	1.29
4b	800:0.2:0.2	filtered	N_2	4	53.1	40.2	1.32
4c	800:0.2:0.2	filtered	air	3.5	51.7	46.6	1.27
5a	1200:0.3:0.3	distilled	N_2	5	71.4	51.4	1.42
5b	1200:0.3:0.3	filtered	N_2	3	74.6	49.8	1.43
5c	1200:0.3:0.3	filtered	air	3.5	68.6	47.8	1.38

[a] IBVE (5.6 mmol, purification method indicated) was added to CTA (1 equiv), PCCP, and HBD and stirred under the indicated atmosphere at room temperature.

Table S6. Polymerization of different monomers, performed under N_2.



Entry[a]	Monomer	HBD equiv	Time (h)	M_n theo (kg/mol)	M_n exp (kg/mol)	Đ
1	EVE	0.15	22	13.4	10.9	1.13
2	Cl-EVE	0.30	24	15.3	12.1	1.35
3[b]	DHF	0.05	23	13.2	12.1	1.21
4[b]	TBVE	0.05	29	16.4	10.5	1.73
5[b,c]	CyVE	0.05	2.5	24.1	20.6	1.54

[a]Vinyl ether (200 equiv, 5.6 mmol, filtered through basic alumina), CTA (1 equiv, 0.028 mmol), PCCP (0.05 equiv, 0.0014 mmol), and HBD were stirred under nitrogen atmosphere at room temperature unless otherwise noted. [b]Performed with 1:2 of DCM:VE by volume. [c]Performed at 0 °C.

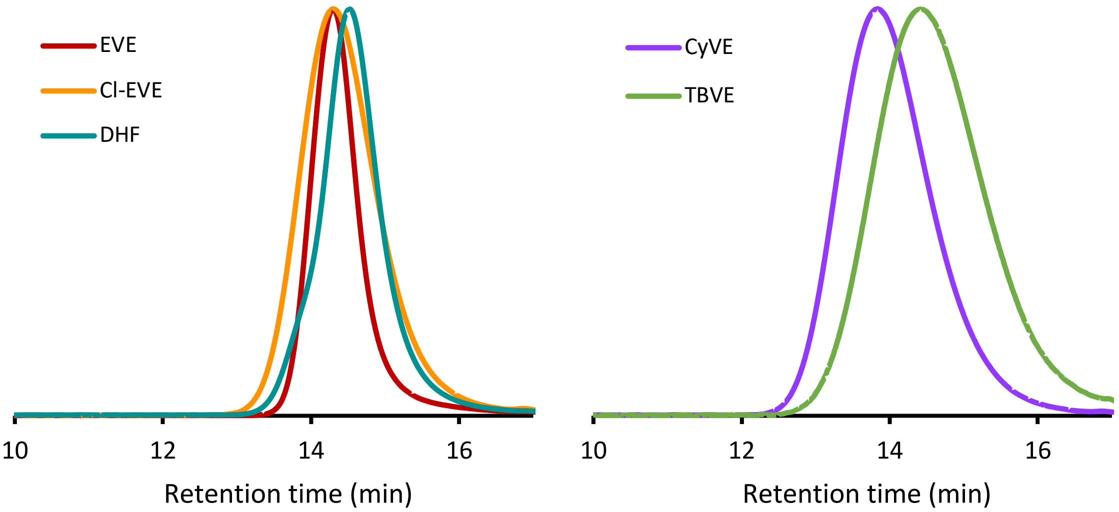


Figure S4. GPC traces of different monomers from Table S6, performed under N_2.

Procedure for kinetic analysis, up to 85% conversion

A one dram vial was flame dried and equipped with a stir bar and septum cap. The dithiocarbamate RAFT CTA (0.028 mmol, 7.0 mg, 1 equiv), HBD (0.0028 mmol, 2.1 mg, 0.1 equiv), and PCCP (0.0028 mmol, 1.0 mg, 0.1 equiv) were weighed out and added to the vial in that respective order. The vial was purged with N_2 for 10 minutes. IBVE (distilled, 5.6 mmol, 0.73 mL, 200 equiv) was added to the vial under N_2. The vial stirred at room temperature on a magnetic stir plate for 2 hours. During that time, aliquots were taken at 10, 20, 30, 40, 60, 90, and 120 minutes. The needle used for sampling was first purged 3 times in a flame dried, nitrogen filled vial. The aliquot was then taken under a positive pressure of N_2 and quenched with a solution of 5% NEt_3 in MeOH and $CDCl_3$ to obtain samples for GPC and ^{1}H NMR analysis.

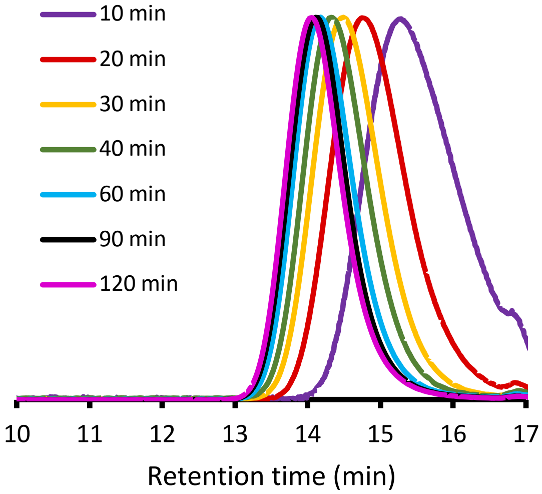


Figure S5. GPC traces of aliquots for kinetic analysis in Figure 2.

Procedure for kinetic analysis with DCM, up to 95% conversion

A one dram vial was flame dried and equipped with a stir bar and septum cap. The dithiocarbamate RAFT CTA (0.028 mmol, 7.0 mg, 1 equiv), HBD (0.0028 mmol, 2.1 mg, 0.1 equiv), and PCCP (0.0028 mmol, 1.0 mg, 0.1 equiv) were weighed out and added to the vial in that respective order. The vial was purged with N_2 for 10 minutes. DCM (dry, 0.18 mL, 1:4 DCM:IBVE by volume) and IBVE (distilled, 5.6 mmol, 0.73 mL, 200 equiv) was added to the vial under N_2. The vial stirred at room temperature on a magnetic stir plate for 5 hours. During that time, aliquots were taken at 10, 20, 30, 50, 70, 90, 120, 180, 240, and 300 minutes. The needle used for sampling was first purged 3 times in a flame dried, nitrogen filled vial. The aliquot was then taken under a positive pressure of N_2 and quenched with a solution of 5% NEt_3 in MeOH and $CDCl_3$ to obtain samples for GPC and ^{1}H NMR analysis.

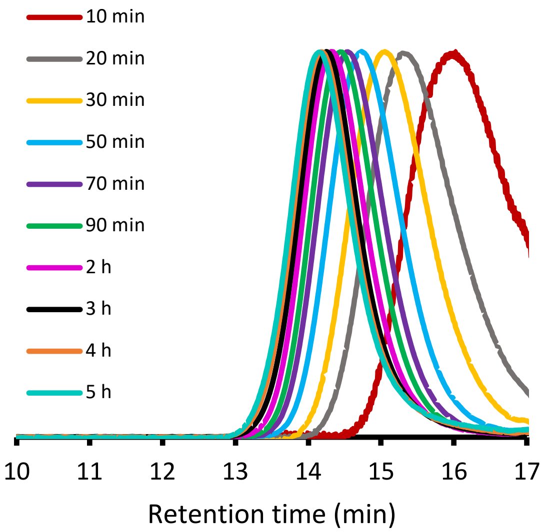


Figure S6. GPC traces of aliquots for kinetic analysis with DCM.

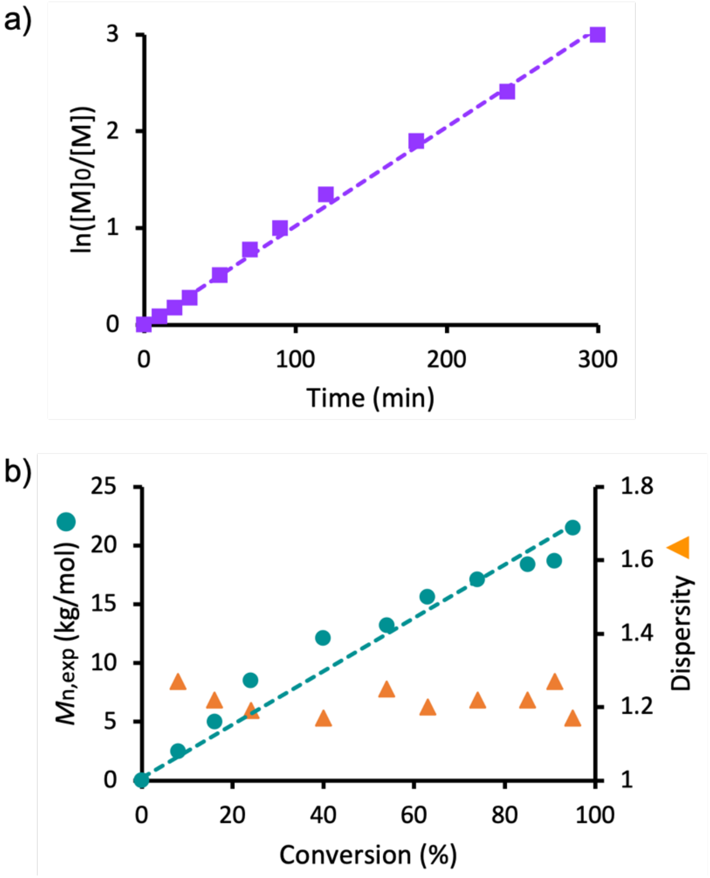


Figure S7. Kinetic analysis with DCM showing a) first order kinetics from the semilogarithmic plot and b) increase in M_n^{exp} as conversion increases.

Procedure for chain extension after isolation by precipitation of the first block, under ambient conditions

A one dram vial was equipped with a stir bar and cap. The dithiocarbamate RAFT CTA (0.11 mmol, 28 mg, 1 equiv), HBD (0.0014 mmol, 1.1 mg, 0.013 equiv), and PCCP (0.0014 mmol, 0.5 mg, 0.013 equiv) were weighed out and added to the vial in that respective order. IBVE (filtered thru basic alumina, 5.6 mmol, 0.73 mL, 50 equiv) was added to the vial. The vial stirred at room temperature on a magnetic stir plate for 6 hours. The polymerization was terminated with 0.72 mL of a sodium *N,N*-diethyldithiocarbamate solution (1 mg of salt per 1 mL of solvent mixture (1:1 MeCN:DCM)). The theoretical molecular weight of the crude polymer was determined by conversion with ^{1}H-NMR to be 2.9 kg/mol. The $M_{n,exp}$ and $Đ$ of the crude polymer was determined to be 3.2 kg/mol and 1.19 by GPC analysis with refractive index, respectively. The polymer was then precipitated in cold MeOH twice and dried under high vacuum overnight. The $M_{n,exp}$ and $Đ$ of the purified polymer used in the next step were determined through refractive index detection by GPC to be 4.3 kg/mol and 1.12, respectively. This gave a degree of polymerization of 40. Chain end analysis was done on the purified PIBVE by ^{1}H-NMR. The proton at ~6 ppm has been shown in literature to be that next to the CTA chain end, as pictured in Figure 3 in the main manuscript.[5] By integrating this proton to 1H versus the polymer peaks, the degree of polymerization was found to be 43, giving a matching $M_{n,NMR}$ of 4.5 kg/mol.

After precipitation, the resulting PIBVE was dried under high vacuum overnight in a tared two dram vial. Once dried, the vial was equipped with a stir bar and cap. HBD (0.0038 mmol, 2.8 mg, 0.15 equiv) and PCCP (0.0013 mmol, 0.4 mg, 0.05 equiv) were weighed out and added to the vial already containing the PIBVE macro CTA (0.025 mmol, 105 mg, 1 equiv, 4.3 kg/mol). EVE (filtered thru basic alumina, 3.5 mmol, 0.34 mL, 140 equiv) was added to the vial. After 6 hours of stirring at room temperature, the polymerization was terminated with 0.72 mL of a sodium *N,N*-diethyldithiocarbamate solution (1 mg of salt per 1 mL of solvent mixture (1:1 MeCN:DCM)). The $M_{n,theo}$ (13.3 kg/mol) of the crude polymer was determined by adding the conversion of EVE found with ^{1}H NMR (93%

conversion, 9.0 kg/mol) to the $M_{n,exp}$ of the first PIBVE block (4.3 kg/mol). The $M_{n,exp}$ and $Đ$ of the crude polymer were determined to be 9.4 kg/mol and 1.28 by refractive index. The polymer was then dried under high vacuum for 2 hours. The experimental molecular weight of the purified polymer was determined by comparison of the ^{1}H-NMR integrations of the polymer peaks, like in Figure S10. From the GPC data of the purified PIBVE, a DP of 40 was obtained, giving the PEVE block a DP of 126. As with the example calculation below, this gave a molecular weight of 13.4 kg/mol. The $Đ$ of the purified polymer was determined to be 1.29 by GPC analysis with refractive index. The data can be seen in Figure 3 of the main manuscript.

Procedure for chain extension through sequential monomer addition, under N_2

A one dram vial was flame dried and equipped with a stir bar and septum cap. The dithiocarbamate RAFT CTA (0.11 mmol, 28 mg, 1 equiv), HBD (0.0042 mmol, 3.1 mg, 0.038 equiv), and PCCP (0.0014 mmol, 0.5 mg, 0.013 equiv) were weighed out and added to the vial in that respective order. The vial was purged with N_2 for 10 minutes. IBVE (filtered thru basic alumina, 5.6 mmol, 0.73 mL, 50 equiv) and dry DCM (0.36 mL, 1:2 DCM:IBVE) were added to the vial under N_2. The vial stirred at room temperature on a magnetic stir plate for 7 hours. After this time, an aliquot was taken under N_2 to ensure a high conversion (94%, $M_{n,exp}$ = 4.9 kg/mol) of IBVE before adding the next monomer and to determine the molecular weight and dispersity of the first block by refractive index GPC analysis ($M_{n,exp}$ = 5.2 kg/mol, $Đ$ = 1.15). EVE (filtered thru basic alumina, 7.7 mmol, 0.74 mL, 69 equiv) was added to the vial under N_2. After an additional 21 hours, the polymerization was terminated with 40 µL of 5% triethylamine in MeOH. The $M_{n,theo}$ of the diblock (8.2 kg/mol) was determined by adding the $M_{n,exp}$ of the first block (5.2 kg/mol) to the molecular weight obtained by the conversion given by ^{1}H-NMR (62% conversion to PEVE, 3.0 kg/mol). The molecular weight and $Đ$ determined by refractive index analysis on GPC was 7.2 kg/mol and 1.20, respectively. As the *dn/dc* value was unknown, light scattering could not be used for a more accurate molecular weight, so ^{1}H-NMR was used to find $M_{n,exp}$ by comparing integrations of the polymer peaks. An example calculation and NMR (Figure S10) are in the next procedure. This method gave an $M_{n,exp}$ of 7.9 kg/mol.

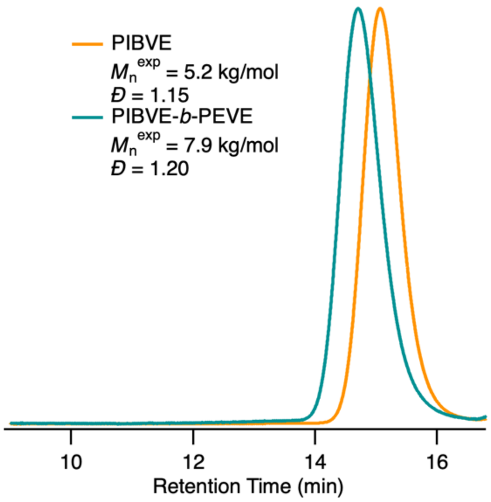
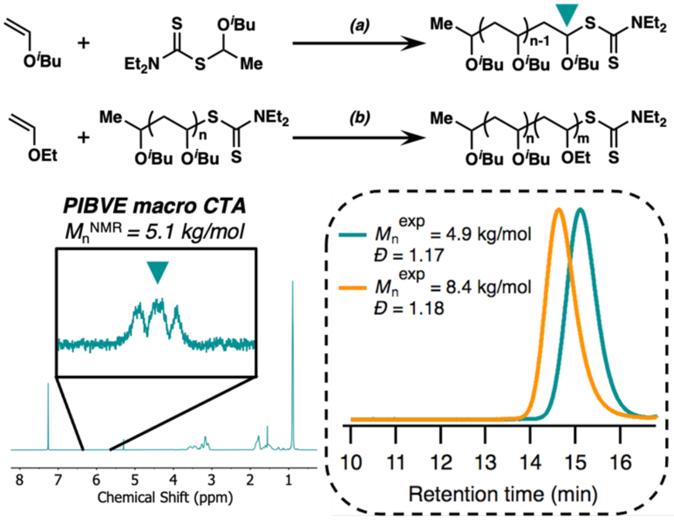


Figure S8. GPC traces of PIBVE and PIBVE-*b*-PEVE after in situ chain extension, under N_2.

Procedure for chain extension after isolation by precipitation of the first block, under N_2

A one dram vial was flame dried and equipped with a stir bar and septum cap. The dithiocarbamate RAFT CTA (0.11 mmol, 28 mg, 1 equiv), HBD (0.0014 mmol, 1.1 mg, 0.013 equiv), and PCCP (0.0014 mmol, 0.5 mg, 0.013 equiv) were weighed out and added to the vial in that respective order. The vial was purged with N_2 for 10 minutes. IBVE (filtered thru basic alumina, 5.6 mmol, 0.73 mL, 50 equiv) was added to the vial under N_2. The vial stirred at room temperature on a magnetic stir plate for 5.5 hours. The polymerization was terminated with 0.72 mL of a sodium *N,N*-diethyldithiocarbamate solution (1 mg of salt per 1 mL of solvent mixture (1:1 MeCN:DCM)). The theoretical molecular weight of the crude polymer was determined by conversion with ^{1}H-NMR to be 4.3 kg/mol. The $M_{n,exp}$ and Đ of the crude polymer was determined to be 4.4 kg/mol and 1.19 by GPC analysis with refractive index, respectively. The polymer was then precipitated in cold MeOH twice and dried under high vacuum overnight. The $M_{n,exp}$ and Đ of the purified polymer used in the next step were determined through refractive index detection by GPC to be 4.9 kg/mol and 1.17, respectively. This gave a degree of polymerization of 46. Chain end analysis was done on the purified PIBVE by ^{1}H-NMR. The proton at ~6 ppm has been shown in literature to be that next to the CTA chain end, as pictured in Figure S9.[5] By integrating this proton to 1H versus the polymer peaks, the degree of polymerization was found to be 48, giving a matching $M_{n,NMR}$ of 5.1 kg/mol.

After precipitation, the resulting PIBVE was dried under high vacuum overnight in a tared two dram vial. Once dried, the vial was equipped with a stir bar and septum cap. HBD (0.0032 mmol, 2.4 mg, 0.038 equiv) and PCCP (0.0011 mmol, 0.4 mg, 0.013 equiv) were weighed out and added to the vial already containing the PIBVE macro CTA (0.085 mmol, 520 mg, 1 equiv, 6.1 kg/mol). The vial was purged with N_2 for 10 minutes. EVE (filtered thru basic alumina, 5.9 mmol, 0.56 mL, 69 equiv) was added to the vial under N_2. After 20 hours of stirring at room temperature, the polymerization was terminated with 0.72 mL of a sodium *N,N*-diethyldithiocarbamate solution (1 mg of salt per 1 mL of solvent mixture (1:1 MeCN:DCM)). The theoretical molecular weight (9.3 kg/mol) of the crude polymer was determined by adding the conversion of EVE found with ^{1}H NMR (90% conversion, 4.4 kg/mol) to the experimental M_n of the first PIBVE block (4.9 kg/mol). The $M_{n,exp}$ and $Đ$ of the crude polymer were determined to be 7.8 kg/mol and 1.20 by refractive index. The polymer was then precipitated in cold MeOH twice and dried under high vacuum overnight. The experimental molecular weight of the purified polymer was determined by comparison of the ^{1}H-NMR integrations of the polymer peaks (Figure S10). From the GPC data of the purified PIBVE, a DP of 46 was obtained, giving the PEVE block a DP of 50. As shown below, this gave a molecular weight of 8.5 kg/mol. The $Đ$ of the purified polymer were determined to be 1.18 by GPC analysis with refractive index. The data can be seen in Figure S9.



(a) IBVE (50 equiv, 5.6 mmol), CTA (1 equiv, 0.11 mmol), PCCP (0.013 equiv, 0.0014 mmol), HBD (0.013 equiv, 0.0014 mmol), N_2, room temp, 5.5 h.
(b) EVE (69 equiv, 4.1 mmol), PIBVE macro CTA (1 equiv, 0.085 mmol), PCCP (0.013 equiv, 0.0011 mmol), HBD (0.038 equiv, 0.0032 mmol), N_2, room temp, 20 h.

Figure S9. Chain end analysis of PIBVE and extension to PIBVE-*b*-PEVE, performed under N_2.

Example calculation for $M_{n,exp}$ of PIBVE-b-PEVE copolymers

$$\text{integration of PIBVE block set to 6, worth 6H}$$

$$\text{integration of PEVE block} = 3.23\text{, worth 3H}$$

$$\text{value of 1H in PEVE} = 3.23 \div 3 = 1.08$$

$$\text{DP of PEVE} = \text{DP of PIBVE} \times 1.08 = 46 \times 1.08 = 50$$

$$M_{\text{n,theo}} = (\text{DP of PEVE} \times \text{MW of EVE}) + M_{n,exp} \text{ of PIBVE macro CTA}$$

$$M_{\text{n,theo}} = (50 \times 72.11\ \text{g/mol}) + 4.9\ \text{g/mol} = 8.5\ \text{kg/mol}$$

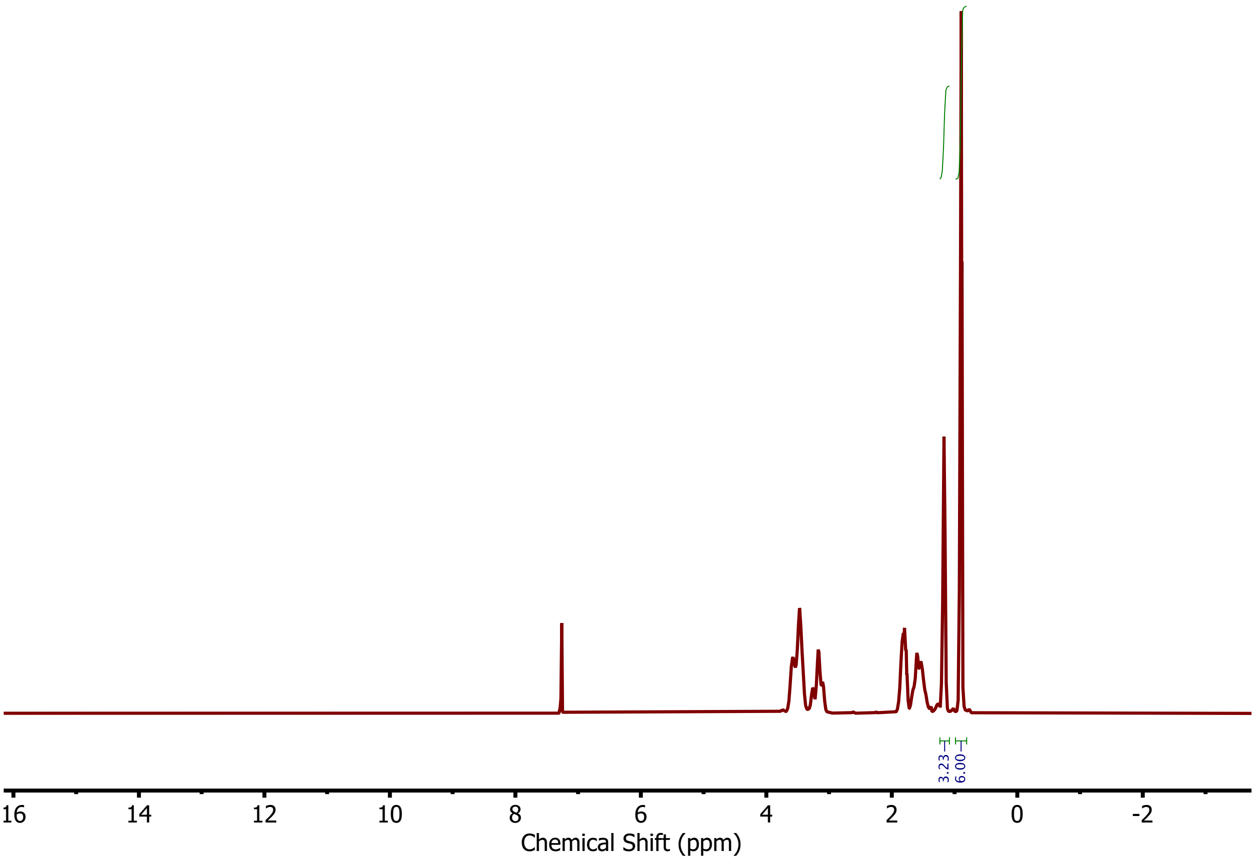


Figure S10. ^{1}H-NMR spectrum of precipitated PIBVE-*b*-PEVE for molecular weight determination.

Procedure for cationic to radical chain extension through sequential monomer addition, with the trithiocarbonate CTA

A one dram vial was flame dried and equipped with a stir bar and septum cap. The trithiocarbonate CTA (0.11 mmol, 27 mg, 1 equiv), HBD (0.0028 mmol, 2.1 mg, 0.025 equiv), and PCCP (0.0014 mmol, 0.5 mg, 0.013 equiv) were weighed out and added to the vial in that respective order. The vial was purged with N_2 for 10 minutes. IBVE (filtered thru basic alumina, 5.6 mmol, 0.73 mL, 50 equiv) was added to the vial under N_2. The vial stirred at room temperature on a magnetic stir plate for 3 hours. After this time, an aliquot was taken and quenched with 5 μL of 5% triethylamine in MeOH. The conversion of IBVE was determined to be 92% by ^{1}H-NMR to give an $M_{n,theo}$ of 4.8 kg/mol. The refractive index data from GPC gave a matching $M_{n,exp}$ of 4.7 kg/mol and a $Đ$ of 1.60. In a separate one dram vial, AIBN (0.014 mmol, 2.3 mg, 0.13 equiv) was purged with N_2 for 10 minutes. MA (distilled, 19 mmol, 1.7 mL, 170 equiv) was added to the vial under N_2 to dissolve the AIBN. The solution was then transferred to the reaction vial and vortexed until evenly mixed. The reaction was heated to 60 °C and stirred for 1.5 hours and then quenched by cooling to room temperature and opening to air. The conversion of MA was determined to be 80% by ^{1}H-NMR to give a theoretical molecular weight of 14.9 kg/mol. The refractive index data from GPC gave an $M_{n,exp}$ of 11.7 kg/mol and a $Đ$ of 1.72. The traces can be found in the main manuscript (Figure 4a).

Procedure for cationic to radical chain extension after isolation by precipitation of the first block, with the trithiocarbonate CTA

A one dram vial was flame dried and equipped with a stir bar and septum cap. The trithiocarbonate CTA (0.11 mmol, 27 mg, 1 equiv), HBD (0.0028 mmol, 2.1 mg, 0.025 equiv), and PCCP (0.0014 mmol, 0.5 mg, 0.013 equiv) were weighed out and added to the vial in that respective order. The vial was purged with N_2 for 10 minutes. IBVE (filtered thru basic alumina, 5.6 mmol, 0.73 mL, 50 equiv) was added to the vial under N_2. The vial was stirred at room temperature for 4 hours. After this time, the reaction was quenched with 0.73 mL of a solution of sodium *S′*-ethyl trithiocarbonate (1 mg of salt per 1 mL of solvent mixture (1:1 MeCN:DCM)). The conversion of IBVE was determined to be 93% by ^{1}H-NMR to give a theoretical molecular weight of 4.8 kg/mol. The refractive index data from GPC for the crude polymer gave a matching experimental M_n of 5.1 kg/mol and a $Đ$ of 1.53. The polymer was precipitated in cold MeOH twice and dried under high vacuum overnight. Chain end analysis of the precipitated polymer by ^{1}H-NMR gave a degree of polymerization of 60, resulting in an $M_{n,NMR}$ of 6.3 kg/mol. The GPC refractive index data of the precipitated polymer gave a $Đ$ of 1.40 and a matching $M_{n,exp}$ of 6.1 kg/mol, giving a DP of 59, which was the value used in calculations in the next step.

The PIBVE macro CTA (0.1 mmol, 610 mg, 1 equiv) was transferred to a two dram vial. A septum cap, stir bar, and AIBN (0.013 mmol, 2.1 mg, 0.13 equiv) were added. The vial was purged with N_2 for 10 minutes. After this time, MA (distilled, 17 mmol, 1.5 mL, 170 equiv) was added to the vial under N_2. The reaction was heated to 60 °C for 1 hour and then quenched by cooling to room temperature. The conversion of MA was determined to be 83% by ^{1}H-NMR to give a theoretical molecular weight of 16.9 kg/mol. The refractive index data from GPC of the crude polymer gave an M_n of 17.8 kg/mol and a $Đ$ of 1.62. The polymer was then precipitated in cold MeOH twice and dried under high vacuum. The theoretical molecular weight of the purified polymer was determined by comparison of the ^{1}H-NMR integrations of the polymer peaks (Figure S11). From the GPC data of the purified PIBVE, a DP of 59 was obtained, giving the PEVE block a DP of 253. As shown below, this gave a molecular weight of 27.9 kg/mol. The trace in Figure S12 is the refractive index data from GPC of the precipitated polymer with an M_n of 24.7 kg/mol and a $Đ$ of 1.44.

Example calculation of $M_{n,exp}$ for PIBVE-b-PMA copolymers

$$\text{integration of PIBVE block set to 6, worth 6H}$$

$$\text{integration of PMA block} = 4.28\text{, worth 1H}$$

$$\text{DP of PMA} = \text{DP of PIBVE} \times 4.28 = 59 \times 4.28 = 253$$

$$M_{\text{n,theo}} = (\text{DP of PEVE} \times \text{MW of EVE}) + M_{n,exp} \text{ of PIBVE macro CTA}$$

$$M_{\text{n,theo}} = (253 \times 86.09\ \text{g/mol}) + 6.1\ \text{kg/mol} = 27.9\ \text{kg/mol}$$

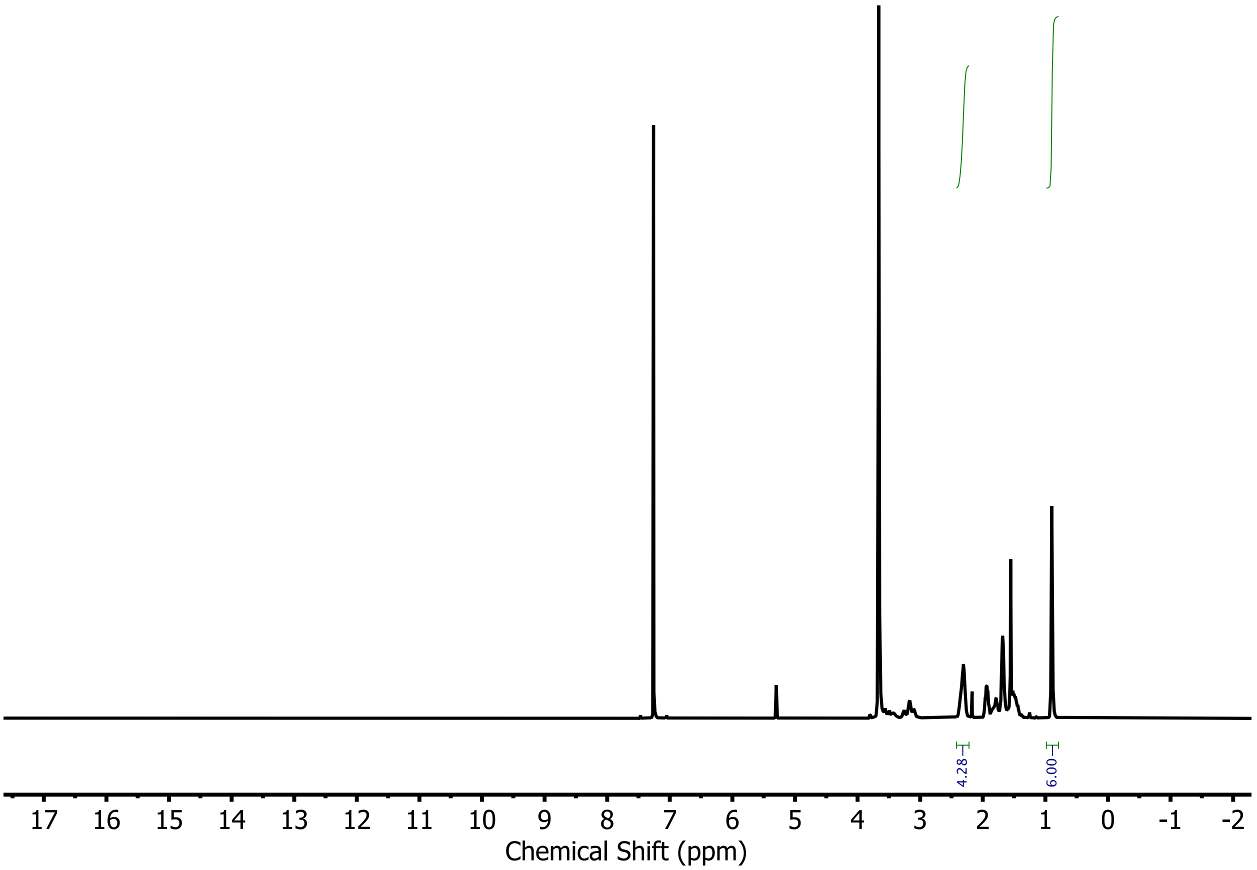


Figure S11. ^{1}H-NMR spectrum of precipitated PIBVE-*b*-PMA for molecular weight determination, with trithiocarbonate CTA.

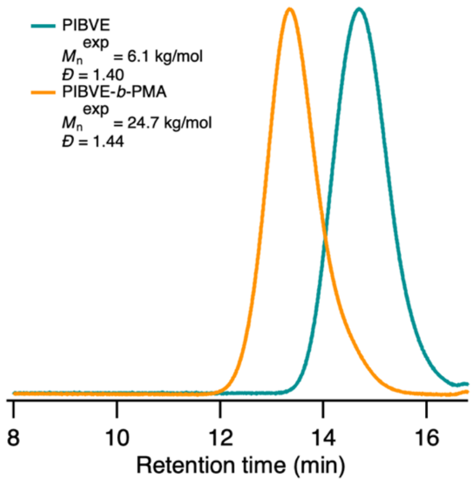


Figure S12. GPC traces of PIBVE and PIBVE-*b*-PMA after precipitation, with trithiocarbonate CTA.

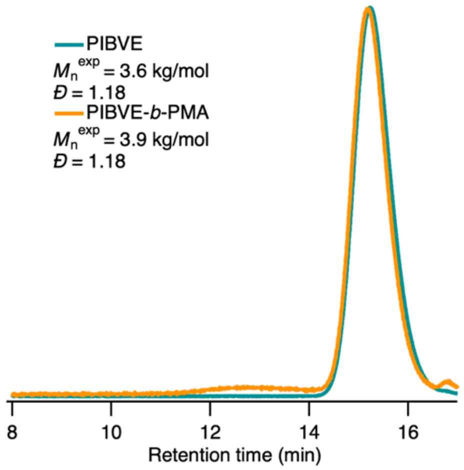


Figure S13. GPC traces of PIBVE and PIBVE-*b*-PMA after precipitation, with dithiocarbamate CTA.

Procedure for polymerizations quenched by 2-hydroxyethyl acrylate

A one dram vial was flame dried and equipped with a stir bar and septum cap. The dithiocarbamate RAFT CTA (0.11 mmol, 28 mg, 1 equiv), HBD (0.0014 mmol, 1.1 mg, 0.013 equiv), and PCCP (0.0014 mmol, 0.5 mg, 0.013 equiv) were weighed out and added to the vial in that respective order. The vial was purged with N_2 for 10 minutes. IBVE (5.6 mmol, 0.73 mL, 50 equiv) was filtered through a plug of basic alumina and added to the dram vial under N_2. Equal volume amounts of dry DCM (0.73 mL) was added to the vial under N_2. The vial stirred at room temperature on a magnetic stir plate for 20 hours. The polymerization was determined to be at 99% conversion by ^{1}H-NMR and have an M_n of 5.1 kg/mol and a Đ of 1.14 by refractive index measurements on the GPC. The polymerization was terminated by adding 3 mL of a solution of $FcBF_4$ in dry DCM (2 mg of $FcBF_4$ per 1 mL of DCM, 0.2 equiv), followed by 2-hydroxyethyl acrylate (filtered through basic alumina first, 0.56 mmol, 64 μL, 5 equiv), under N_2. The reaction was allowed to stir overnight at room temperature, after which it was precipitated twice in cold MeOH. The sample for GPC gave refractive index measurements of 6.1 kg/mol for $M_{n,exp}$ and 1.09 for Đ. The chain end functionalization was observed by ^{1}H NMR analysis (Figure 4b).

Procedure for polymerizations with added water

A one dram vial equipped with a stir bar was charged with the dithiocarbamate RAFT CTA (0.056 mmol, 14.0 mg, 1 equiv), HBD (0.0042 mmol, 3.1 mg, 0.075 equiv), and PCCP (0.0014 mmol, 0.5 mg, 0.025 equiv) in that respective order. IBVE (5.6 mmol, 0.73 mL, 100 equiv) was filtered through a plug of basic alumina and added to the dram vial, followed by the indicated amount of deionized water (40-800 equiv, relative to PCCP). The vial stirred at room temperature on a magnetic stir plate for the indicated time. The polymerization was terminated with 40 μL of 5% triethylamine in methanol, after which samples for GPC and ^{1}H NMR analysis were taken.

Conversion was determined by accounting for the side products produced by the acid-catalyzed decomposition of IBVE by H_2O, which proceeds as below. One equivalent of IBVE is decomposed by acid and H_2O to give isobutanol and acetaldehyde. Isobutanol goes on to react with another equivalent of IBVE to form the acetal shown below.

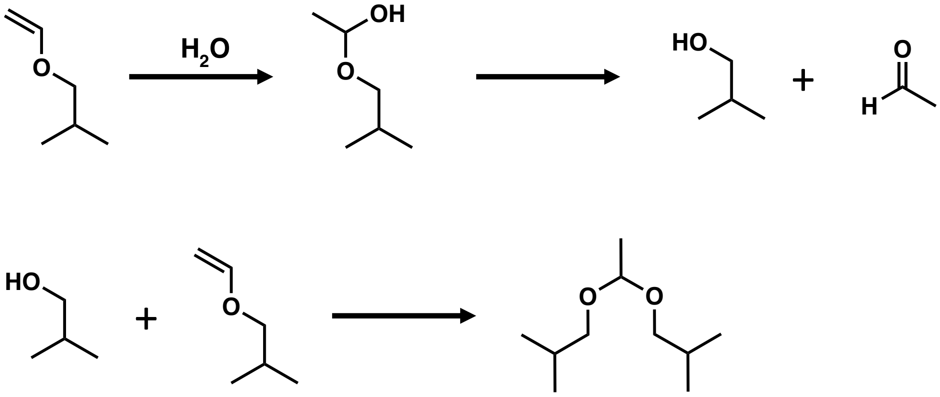


Figure S14. Side products resulting from the decomposition of IBVE by water.

Assuming that these are the only side products made, by accounting for the decomposition of IBVE to isobutanol and the acetal, the conversion of IBVE to polymer can be found. In all spectra from ^{1}H-NMR analysis, no signals for isobutanol were seen though, indicating it was quantitively converted to acetal. Therefore, only conversion to the acetal and polymer were considered in finding the theoretical molecular weights. An example calculation and spectrum are given below. All integrations are relative to proton *b* on IBVE at ~6.5 ppm, given the value 1H.

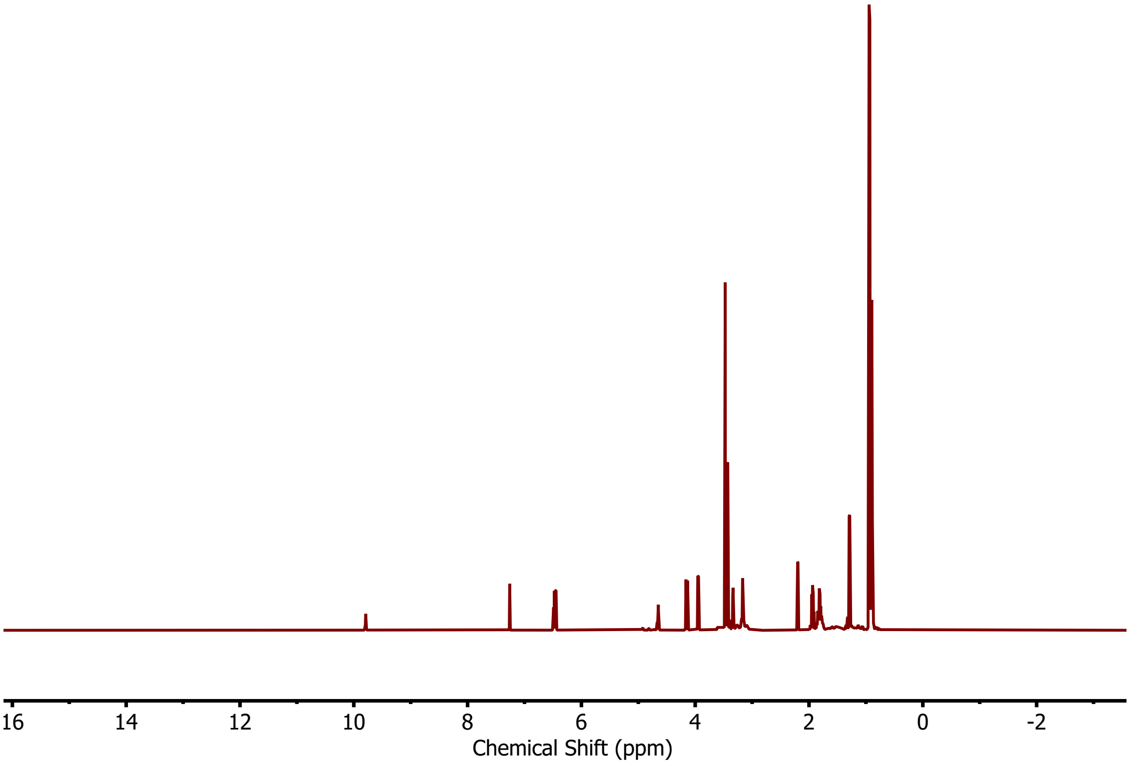


Figure S15. **^{1}H-NMR spectrum of PIBVE polymerized with 600 equiv of water relative to PCCP.**

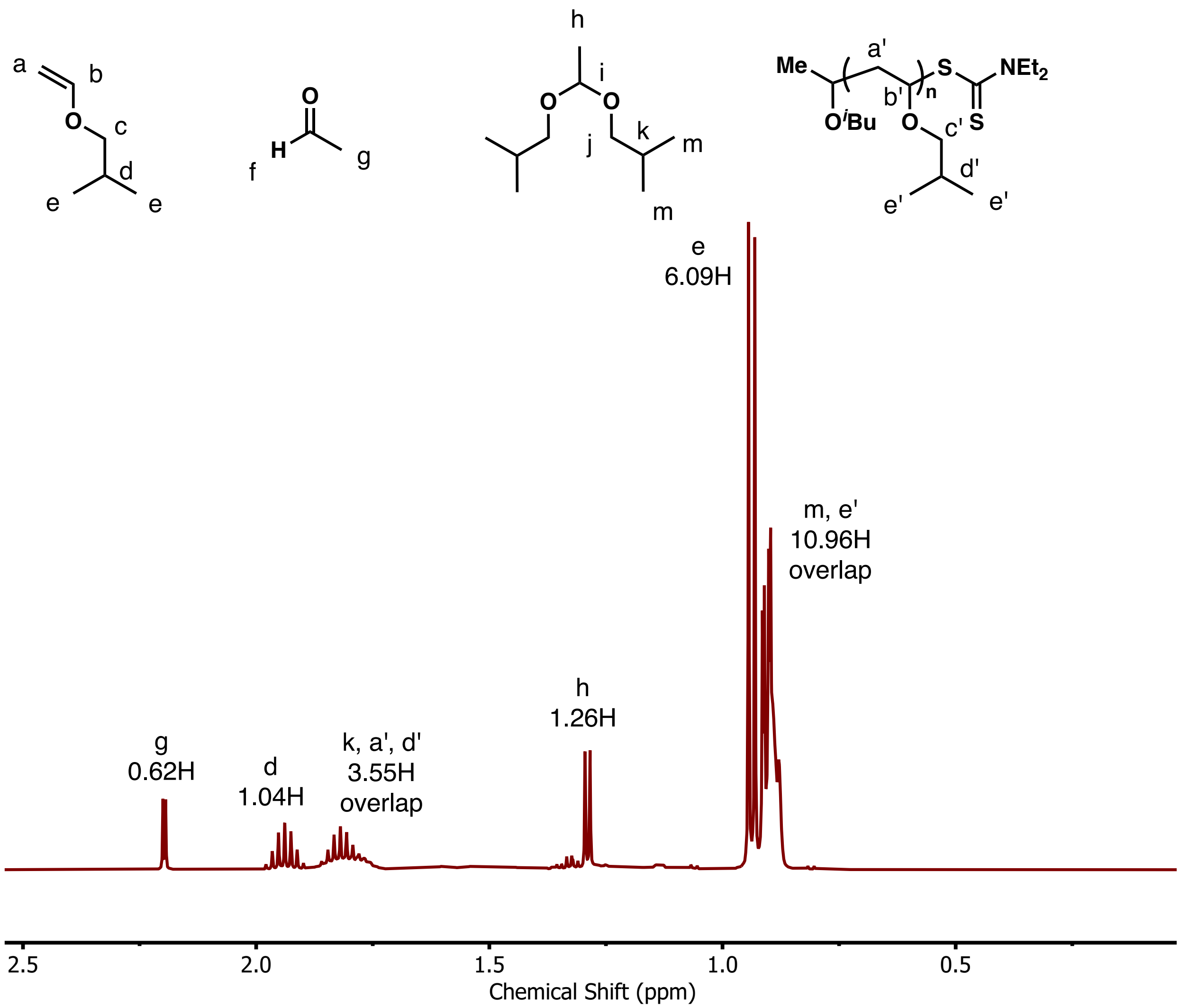


Figure S16. ^{1}**H-NMR spectrum of PIBVE polymerized with 600 equiv of water relative to PCCP, 0 – 2.5 ppm.**

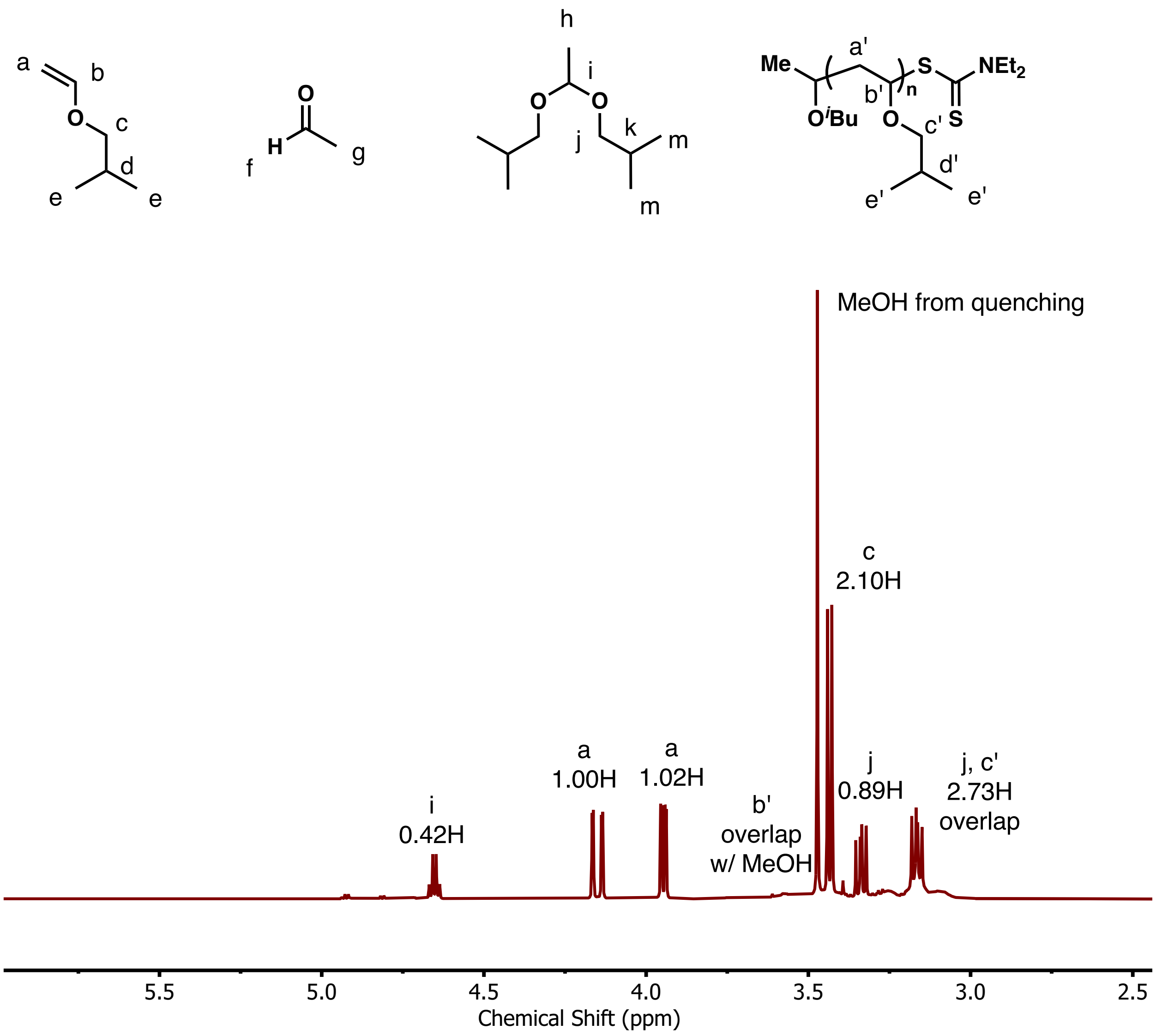


Figure S17. ^{1}**H-NMR spectrum of PIBVE polymerized with 600 equiv of water relative to PCCP, 2.5 – 6 ppm.**

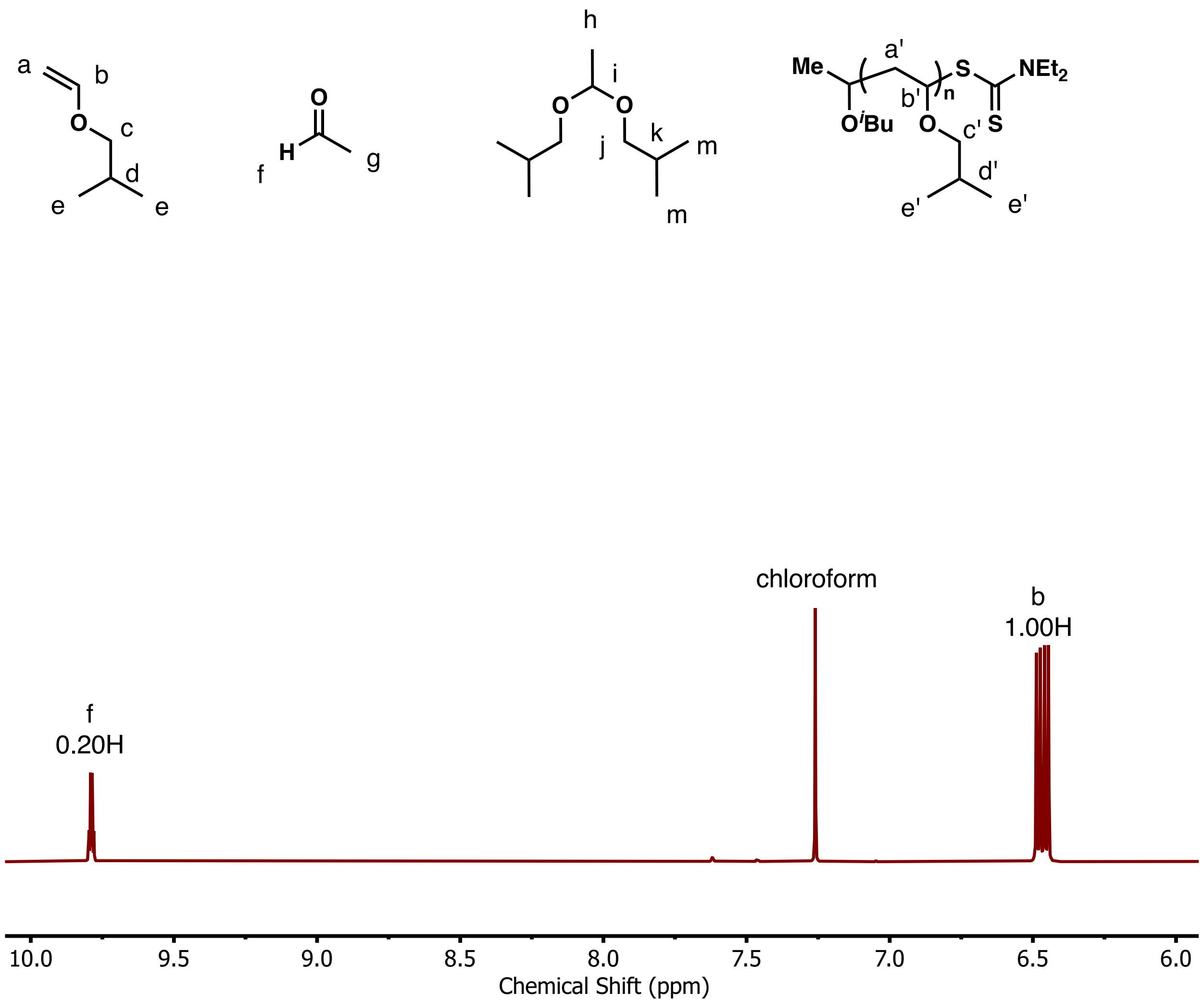


Figure S18. ^{1}**H-NMR spectrum of PIBVE polymerized with 600 equiv of water relative to PCCP, 6 – 10 ppm.**

Example calculation for conversion and $M_{\text{n,theo}}$ of polymerizations with water:

$$\text{integration (int.) from 0.85 ppm to 0.98 ppm} = 17.19$$

$$\text{int. of polymer e}' = 17.19 - (\text{int. of b} \times 6) - (\text{int. of i} \times 12)$$

$$\text{int. of polymer e}' = 17.19 - (1 \times 6) - (0.42 \times 12) = 6.15$$

$$\text{conversion to polymer} = 6.15 \div 17.19 = 0.36$$

$$M_{\text{n,theo}} = \frac{\text{conversion} \times \text{IBVE equiv} \times \text{MW of IBVE}}{1 + \text{PCCP equiv}} + \text{MW of CTA}$$

$$M_{\text{n,theo}} = \frac{0.36 \times 100 \times 100.16\ \text{g/mol}}{1 + 0.025} + 250\ \text{g/mol} = 3.8\ \text{kg/mol}$$

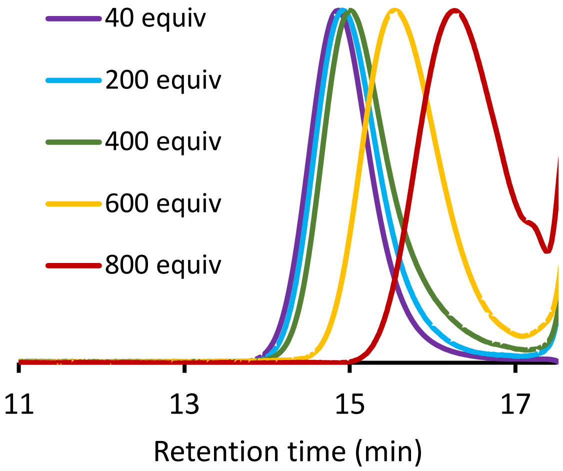


Figure S19. GPC traces of PIBVE with added water, 40-800 equivalents relative to PCCP, from Table 3.

Procedure for kinetics with added water

A one dram vial was flame dried and equipped with a stir bar and septum cap. The dithiocarbamate RAFT CTA (0.056 mmol, 14.0 mg, 1 equiv), HBD (0.0084 mmol, 6.3 mg, 0.15 equiv), and PCCP (0.0028 mmol, 1.0 mg, 0.050 equiv) were weighed out and added to the vial in that respective order. The vial was purged with N_2 for 10 minutes. IBVE (11.2 mmol, 1.46 mL, 200 equiv) was filtered through a plug of basic alumina and added to the dram vial under N_2, followed by deionized water (0.28 mmol, 5 μL, 100 equiv relative to PCCP). The vial stirred at room temperature on a magnetic stir plate for 7 hours. During that time, aliquots were taken. The needle used for sampling was first purged 3 times in a flame dried, nitrogen filled vial. The aliquot was then taken under a positive pressure of N_2 and quenched with a solution of 5% NEt_3 in MeOH and $CDCl_3$ to obtain samples for GPC and ^{1}H NMR analysis.

The control kinetics without water utilized the same procedure but without the addition of deionized water.

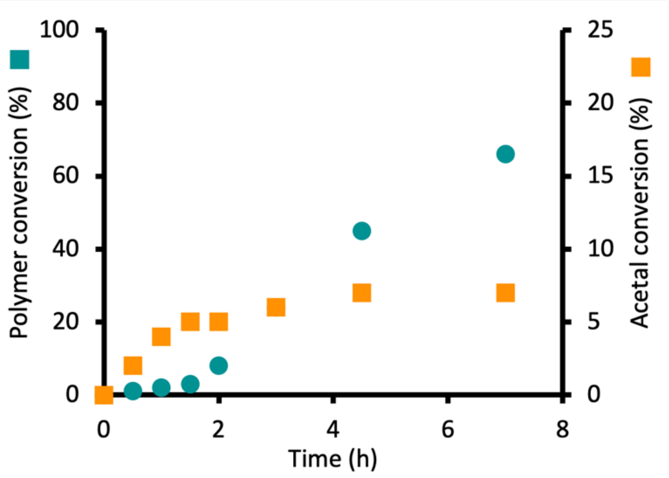


Figure S20. Polymer and acetal conversion for polymerization with 100 equiv of additional water.

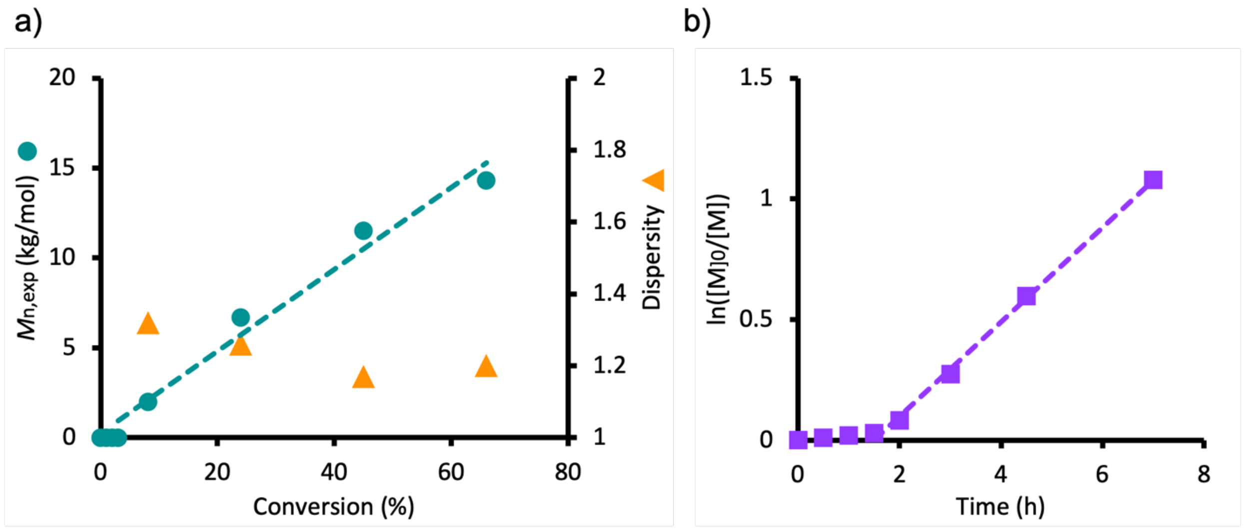


Figure S21. Kinetics of polymerization with 100 equiv of additional water.

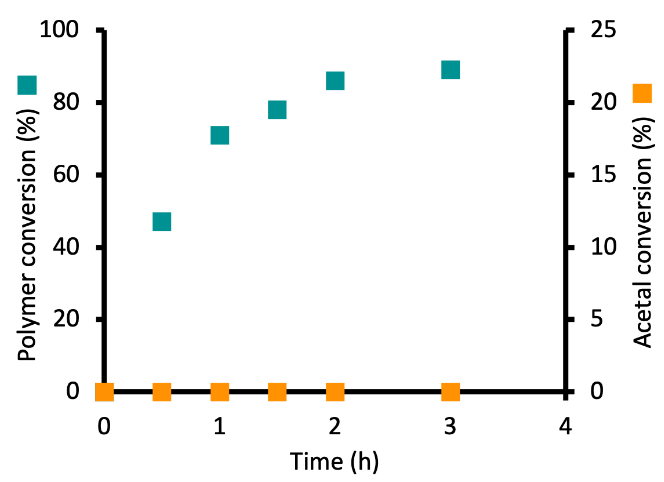


Figure S22. Polymer and acetal conversion for control polymerization without additional water.

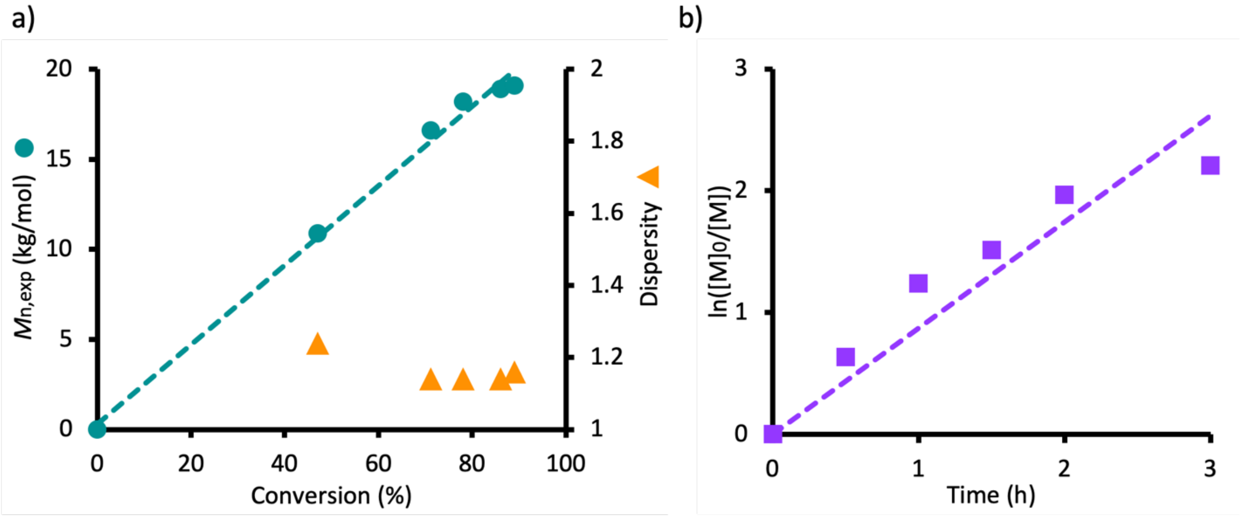


Figure S23. Kinetics of control polymerization without additional water.

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