

**Selective poly(vinyl ether) upcycling via photooxidative degradation with
visible light**

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General Reagent Information

Isobutyl vinyl ether (99 %, Aldrich Chemical Company, Inc.), *tert*-butyl vinyl ether (98 %, Aldrich Chemical Company, Inc.), vinyl acetate (99 %, Aldrich Chemical Company, Inc.), and methyl acrylate (99 %, Aldrich Chemical Company, Inc.) were filtered through a plug of aluminum oxide (activated, basic, Brockman Graded I, Oakwood Chemical) to remove any stabilizers prior to use. FeCl₃ (98 %, anhydrous, Alfa Aesar), FeBr₃ (98 %, Oakwood Chemical), [Ir(dF(Me)ppy)₂(dtbbpy)]PF₆ (95 %, Astatech, Inc.), FcBF₄ (Aldrich Chemical Company, Inc.), isobutanol (99 %, Fischer Scientific), isobutyraldehyde (Lancaster Synthesis), isobutyric acid (99 %, Lancaster Synthesis), dimethyl acetylene dicarboxylate (98 %, TCI America), dimethyl malonate (98 %, Aldrich Chemical Company, Inc.), benzyl trimethylammonium chloride (97 %, Aldrich Chemical Company, Inc.), tetrabutylammonium bromide (99%, Acros Organics), 3,5-bis(trifluoromethyl)aniline (98 %, Oakwood Chemical), thiophosphoryl chloride (98 %, Aldrich Chemical Company, Inc.), 2,2-azobisisobutyronitrile (AIBN) (98 %, Aldrich Chemical Company, Inc.), 1-dodecanethiol (98% Oakwood Chemical), carbon disulfide (99% Oakwood Chemical), 2-bromopropionic acid (98% Oakwood Chemical), HCl (37 wt% Macron Fine Chemicals), and NaOH (Pellets, Macron Fine Chemicals) were used as received. Acetone (ACS 99.5%, Fisher Scientific), dichloromethane (ACS 99.5%, Fisher Scientific), tetrahydrofuran (ACS AR 99%, Macron Fine Chemicals), methanol (ACS 99.8%, Fisher Scientific), acetonitrile (HPLC 99.7%, Fisher Scientific), deuterated chloroform (99.8%, Cambridge, Isotope, Laboratories Inc.), and deuterated dimethyl sulfoxide (99.9 % Cambridge Isotope Laboratories, Inc.) were used as received. Degradation was carried out under white LED (60 W, 6000 k), or 456 nm (50 W). All photoreactors used in the degradation reactions were made out of PLA filaments and manufactured by a QIDI Tech X-Plus 3D printer.

General Analytical Information

Polymer (and degraded polymer) samples were analyzed using a Tosoh EcoSEC HLC 8320 GPC system with two SuperHM-M columns in series at a flow rate of 0.350 mL/min. Tetrahydrofuran was used as the eluent, and number-average molecular weights (M_n) and dispersities (\mathcal{D}) for the samples were determined via Refractive Index (RI) in THF against polystyrene standards. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker 400 MHz or 500 MHz instrument at room temperature using CDCl₃ as a solvent unless otherwise noted.

Small molecule products were quantified by Gas Chromatography equipped with a flame ionization detector (GC-FID), Shimadzu GC-2030. The standard calibration curves were generated for each compound against mesitylene as an external standard SH-I-5Sil MS column (30 m x 0.25 mm ID x 0.25 μ M df) was used with Helium (Industrial grade) as the carrier gas. The injection volume was 1 μ L with a split ratio of 100:1. The column temperature began with 50 °C for 3 min, increasing the temperature with a ramp rate of 10 °C/min up to 150 °C, then 20 °C/min up to 300 °C, and held at 300 °C for 1 min for PIBVE degradation samples. For the rest of the samples, the column temperature began with 30 °C for 4 min, increasing the temperature with a ramp rate of 10 °C/min up to 100 °C, then 20 °C/min up to 200 °C, and held at 200 °C for 1 min. Infrared spectra were obtained through a Bruker Tensor II IR spectrometer with a diamond Attenuated Total Reflectance (ATR) attachment.

Calculation of Method for Small Molecules

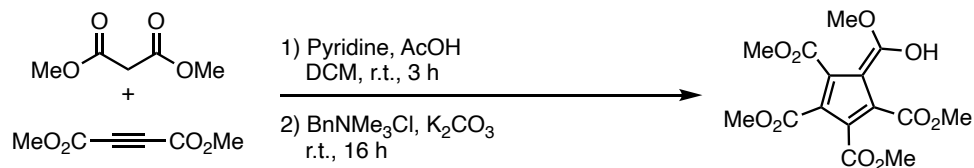
The mole percent of the small molecule products were calculated based on (a) the moles of mesitylene in the experiment, (b) the ratio of the moles of the small molecule to mesitylene from GC, and (c) the moles of monomer units in the polymer in the experiment.

$$\text{mol \%} = \frac{a \times b}{c} \times 100 \%$$

O₂ Gas Safety Precaution

Before dealing with O₂ gas, a user must wear personal protection equipment (lab coat, protection glasses, and gloves). The O₂ gas cylinder was grounded to prevent any static electricity buildup. Before running the reaction, any flammable solvents were properly capped, and combustible materials were removed from the fume hood.

Procedure of 1,2,3,4,5-Pentacarbomethoxycyclopentadiene (PCCP) Synthesis



The following procedure was adapted from the literature.¹ An oven-dried 250 mL round bottom flask was charged with a magnetic stir bar and capped with a rubber septum. The flask was put under vacuum and subsequently purged with N₂. DCM (42 mL), dimethyl acetylene dicarboxylate (4.13 mL, 33.5 mmol, 1 equiv.), and dimethyl malonate (3.835 mL, 33.5 mmol, 1 equiv.) were added via syringe. In a separate 1-dram vial, pyridine (0.14 mL, 1.7 mmol, 0.05 equiv.) and acetic acid (0.13 mL, 2.2 mmol, 0.067 equiv.) were dissolved in DCM (0.5 mL), which was then added slowly to the round bottom flask. The reaction was stirred for 3 hours at room temperature. Benzyl trimethylammonium chloride (BnNMe₃Cl) (0.26 mg, 0.134 mmol, 0.004 equiv.) and saturated K₂CO₃ (42 mL) were added to the reaction mixture. The reaction mixture was then stirred for an additional 16 hours. The reaction mixture was then vacuum filtered to isolate a purple precipitate, which was washed with DCM and allowed to air dry for 30 minutes. The dried solid product was then added to a clean beaker and dissolved in deionized water (42 mL). Once the solution was fully homogeneous, aqueous HCl (37 wt. %) was added until the product precipitated as white crystals. The precipitate was isolated via vacuum filtration and allowed to air dry, then placed under vacuum overnight to further dry. The dried product (yield = 2.2 g; 56 %) was analyzed via ¹H NMR spectroscopy, shown in **Figure S1**. ¹H NMR (CDCl₃, 500 MHz): δ = 4.07 (s, 6 H), 3.93 (s, 6 H), 3.79 (s, 3 H)

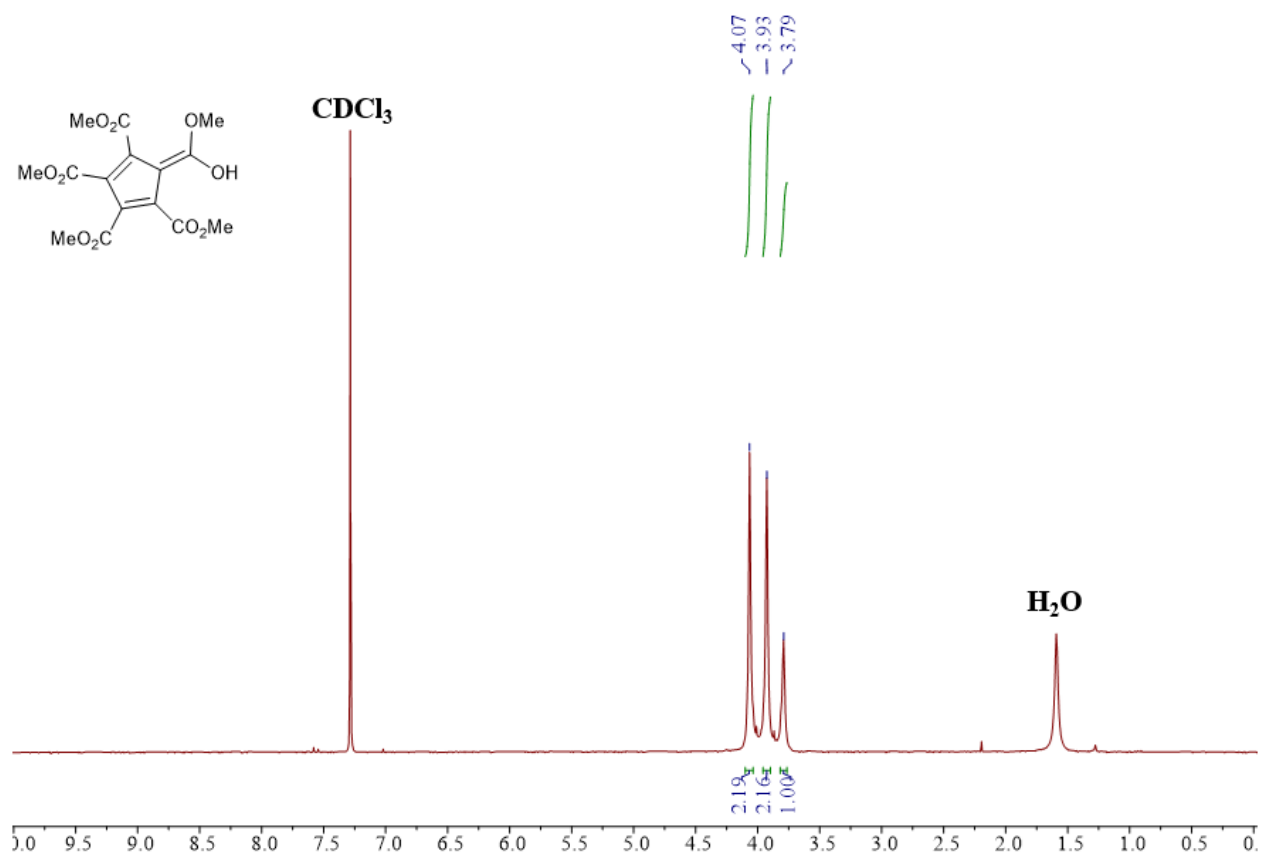
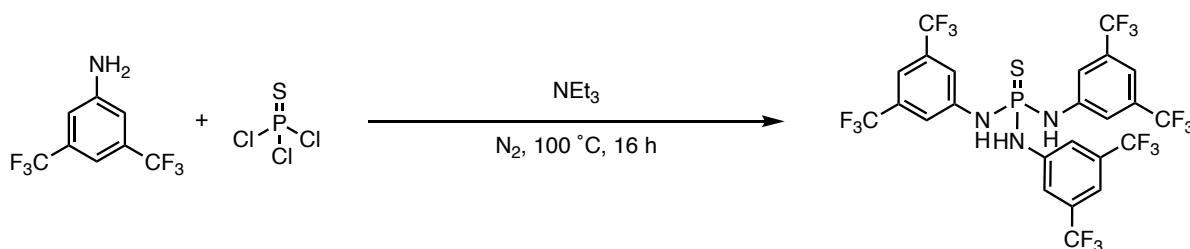


Figure S1: ¹H NMR spectrum (CDCl₃) of PCCP

Procedure of Tris-[3,5-bis(trifluoromethyl)aniline]phosphine Sulfide (HBD) Synthesis



The following procedure was adapted from the literature.² An oven-dried 50 mL round bottom flask was charged with a large magnetic stir bar and 3,5-bis(trifluoromethyl)aniline (2.0 mL, 12.8 mmol, 3.4 equiv.). A rubber septum-capped reflux condenser was attached to the flask and the apparatus was put under vacuum and subsequently purged with N₂. Triethylamine (8 mL, 57.2 mmol, 15 equiv.) was then added via syringe through the septum. The flask was then cooled to 0 °C and thiophosphoryl chloride (0.39 mL, 3.8 mmol, 1 equiv.) was slowly added. The flask was then immediately placed in a preheated oil bath and refluxed for 16 hours at 100 °C under N₂

from a balloon (a white precipitate formed around the edges). The reaction mixture was diluted with saturated NH_4Cl (50 mL) and extracted from DCM (3 x 50 mL). The organic layers were collected and dried upon the addition of Na_2SO_4 . The product was concentrated then purified via column chromatography (5% ethyl acetate/hexanes running solvent; silica stationary phase). The product was further purified via recrystallization from hexane (yield = 300 mg; 21 %). The ^1H NMR spectrum of the purified product (HBD) is shown in **Figure S2**. ^1H NMR (d_6 -DMSO, 500 MHz): $\delta = 9.49$ (d, $J = 10$ Hz, 3 H), 7.77 (s, 6 H), 7.62 (s, 3 H).

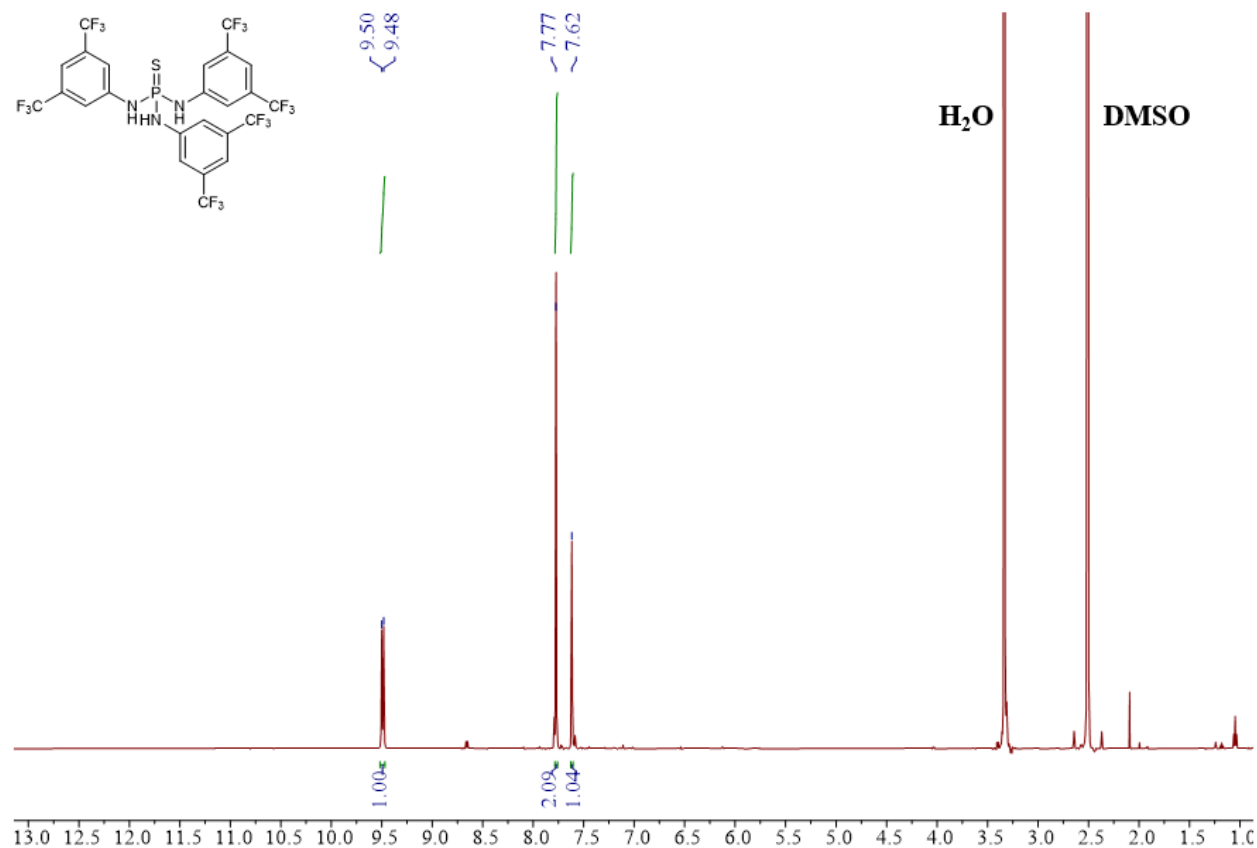
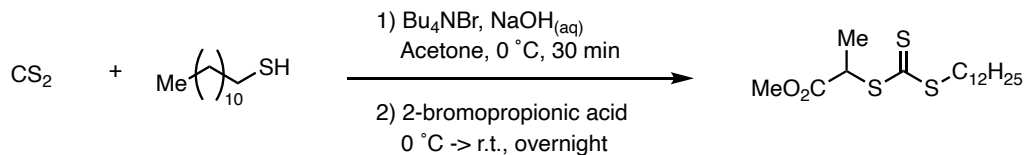


Figure S2: ^1H NMR spectrum (d_6 -DMSO) of HBD

Procedure for 2-(dodecylthiocarbonothio)propionic acid (CTA) Synthesis



The following procedure was adapted from the literature.² A 50 mL round bottom flask was changed with 1-dodecanethiol (1.2 mL, 5.0 mmol, 1 equiv.), acetone (15.5 mL), and

tetrabutylammonium bromide (133 mg, 0.41 mmol, 0.08 equiv.). NaOH solution (2.5 M, 2 mL, 5.0 mmol, 1 equiv.) was slowly added to the reaction mixture. After stirring for 15 min, the flask was placed in an ice bath. Carbon disulfide (302 μ L, 5.0 mmol, 1 equiv.) was slowly added and stirred for 30 min at 0 $^{\circ}$ C. 2-Bromopropionic acid (451 μ L, 5.0 mmol, 1 equiv.) was added and stirred for overnight, allowing the mixture warmed to room temperature. The mixture was cooled to 0 $^{\circ}$ C. HCl (1 M, 7.5 mL) was added to precipitate the solid. The precipitate was filtered through vacuum filtration and washed with a copious amount of water. The powder was dried under vacuum overnight. The dried product (yield = 1.1 g; 61 %) was analyzed via ^1H NMR spectroscopy, shown in **Figure S3**. ^1H NMR (CDCl_3 , 500 MHz): δ = 4.89 (q, J = 7.3 Hz, 1 H), 3.38 (t, J = 7.5 Hz, 2 H), 1.75-1.69 (m, 2 H), 1.65 (d, J = 7.5 Hz, 3 H), 1.44-1.28 (m, 18 H), 0.90 (t, J = 7.0 Hz, 3 H).

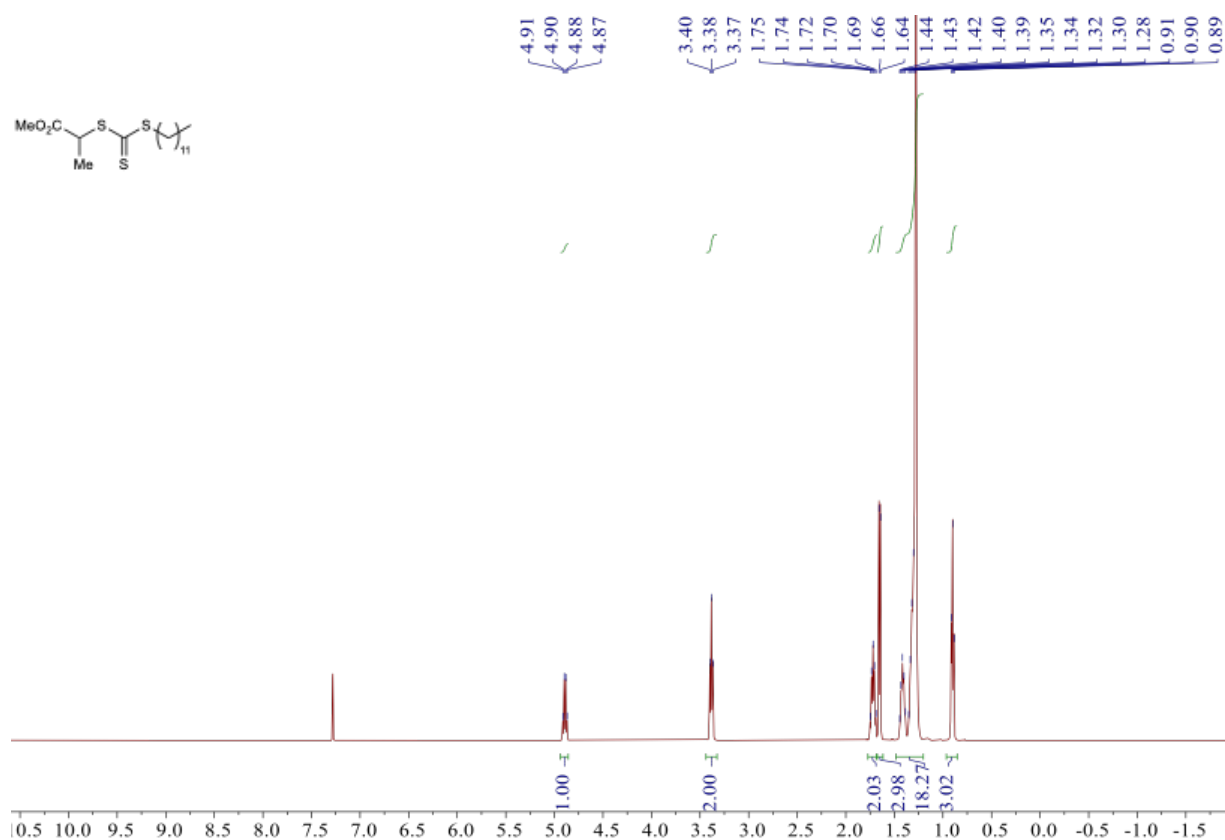
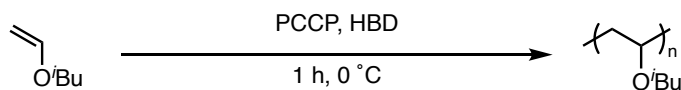


Figure S3: ^1H NMR spectrum (CDCl_3) of CTA

Procedure for Polymer Synthesis

a) Poly(isobutyl vinyl ether) (PIBVE) Synthesis



The following procedure was adapted from the literature.³ A 2-dram vial was charged with PCCP (11.9 mg, 0.03 mmol, 1 equiv.), HBD (24.7 mg, 0.03 mmol, 1 equiv.), and a magnetic stir bar. A separate 2-dram vial was charged with ~2 mL isobutyl vinyl ether (IBVE). Both vials were capped with a teflon-coated septum and allowed to sit in an ice bath to cool to 0 °C. Once equilibrium was reached, cooled IBVE (1.3 mL, 10 mmol, 300 equiv.) was added to the vial containing PCCP, HBD, and a magnetic stir bar (the reaction vial). The reaction vial was capped with a teflon-coated septum and allowed to react for 1 hour at 0 °C (ice bath). The polymerization was terminated upon the addition of 5% triethylamine/methanol (v/v), (95 μ L). The polymer was dissolved in a minimal amount of DCM and precipitated in methanol (30 mL). The precipitated polymer was then concentrated and dried under vacuum overnight. The M_n and D data for the synthesized PIBVE samples are tabulated in **Table S1**, and the GPC traces are shown in **Figure S4**. The ^1H NMR spectrum of polymer is shown in **Figure S5**.

Table S1: Molecular weights of synthesized PIBVE

Entry	Polymer	M_n (kDa) ^a	D ^a
1	PIBVE1	40.7	1.37
2	PIBVE2	27.8	1.08
3	PIBVE3	27.4	1.21
4 ^b	PIBVE4	15.9 (7.6)	1.18 (1.97)
5	PIBVE5	25.2	1.65

^aDetermined by GPC analysis against a polystyrene standard

^bHigh MW peak (Total peak)

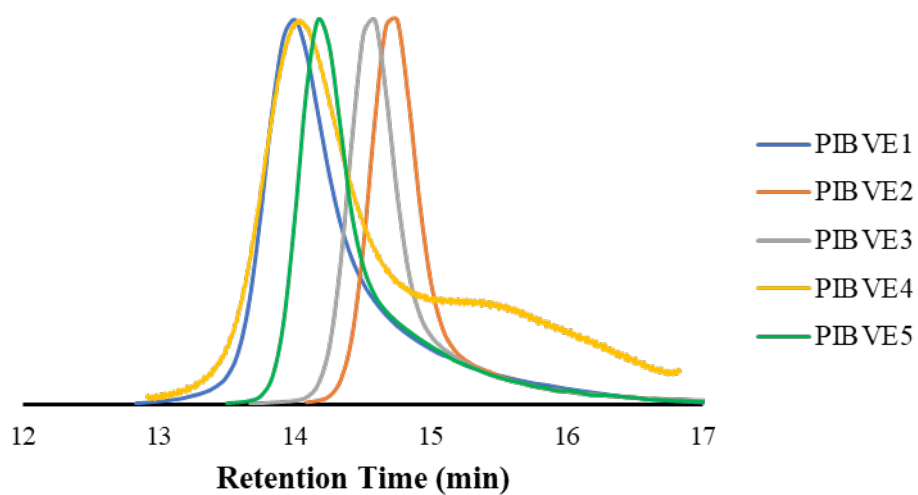


Figure S4: GPC traces of synthesized PIBVE

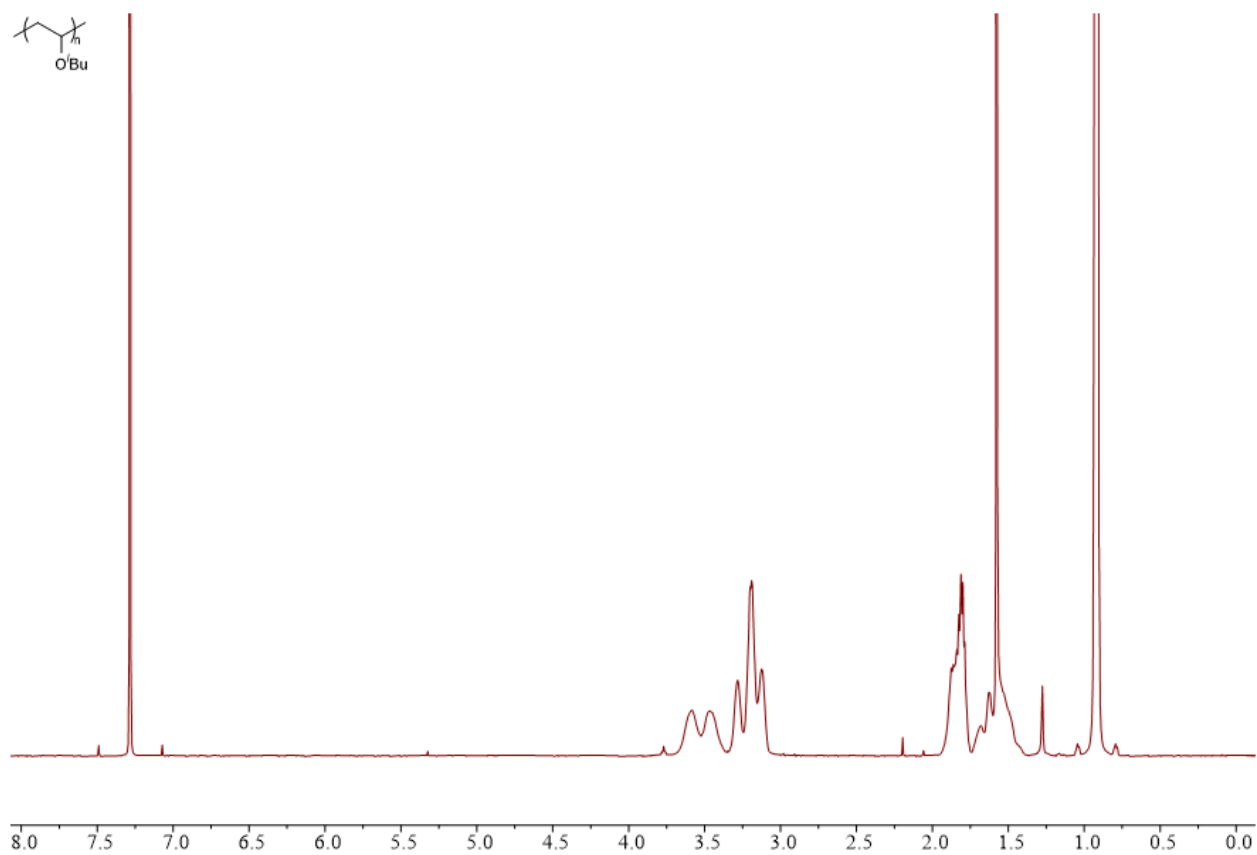


Figure S5: ¹H NMR spectrum (CDCl₃) of dried PIBVE

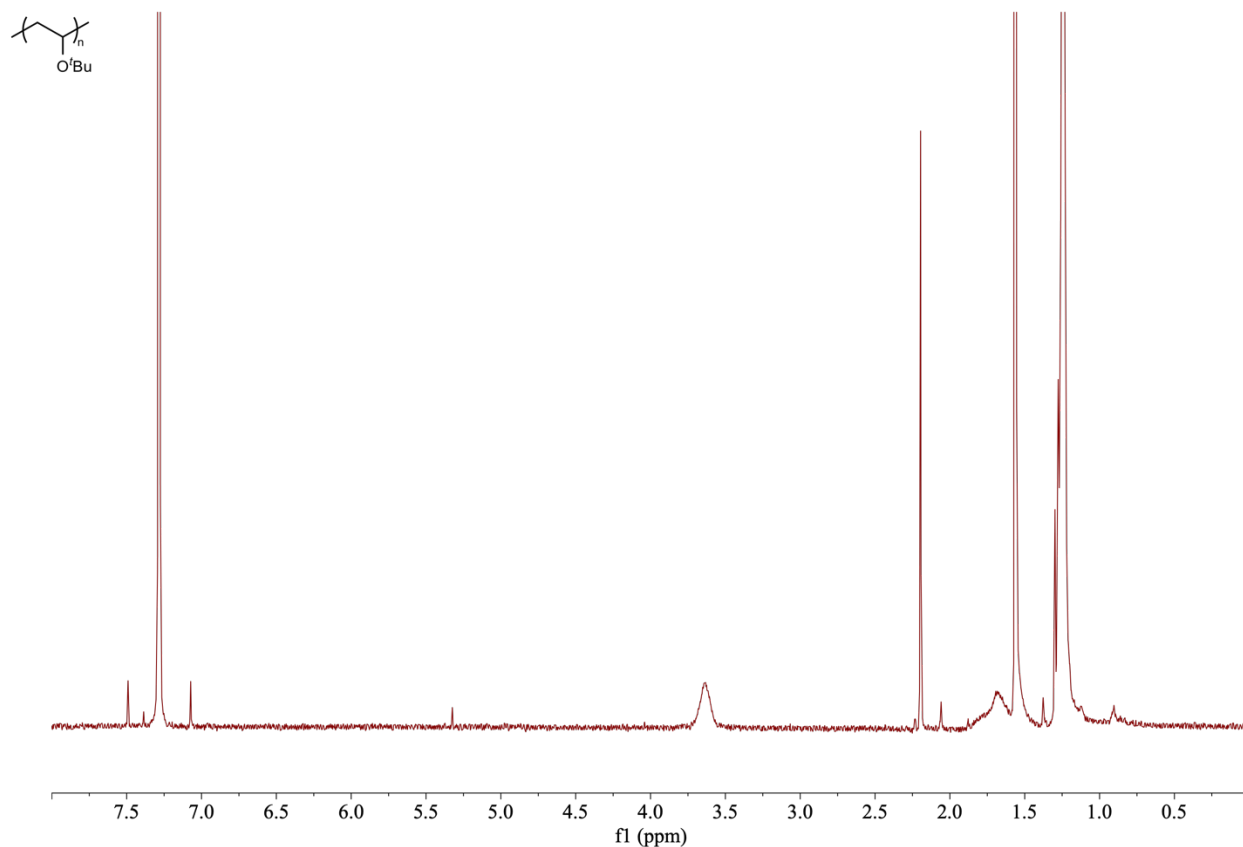
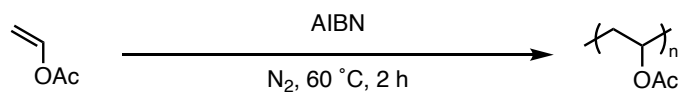


Figure S7: ^1H NMR spectrum (CDCl_3) of dried PTBVE

c) Poly(cyclohexyl vinyl ether) (PCyVE) Synthesis

Poly(cyclohexyl vinyl ether) (PCyVE) was synthesized via a similar procedure for PIBVE and PTBVE. The GPC trace and ^1H NMR spectrum are shown in **Figure S8-S9**. $M_n = 5.0$ kDa and $D = 1.66$.

d) Poly(vinyl acetate) (PVAc) Synthesis



A 2-dram vial was charged with azobisisobutyronitrile (AIBN) (10.8 mg, 0.066 mmol, 1 equiv.) and a magnetic stir bar. The reaction vial was then charged with vinyl acetate (1 mL, 10.8 mmol, 165 equiv.) and capped with a teflon-coated septum. Four cycles of freeze-pump-thaw were performed in order to remove O₂ from the reaction vial. The vial was then purged with N₂, submerged in a preheated oil bath (60 °C), and allowed to react for 2 hours. At the end of the reaction, the reaction mixture had completely gelled. The polymer was dissolved in a minimal amount of THF and precipitated in hexane (30 mL). The polymer was then dissolved in ethyl acetate, transferred to a 20 mL scintillation vial, concentrated, and dried under dynamic vacuum overnight. The GPC trace and ¹H NMR spectrum are shown in **Figure S10-S11**. $M_n = 28.5$ kDa and $D = 3.34$.

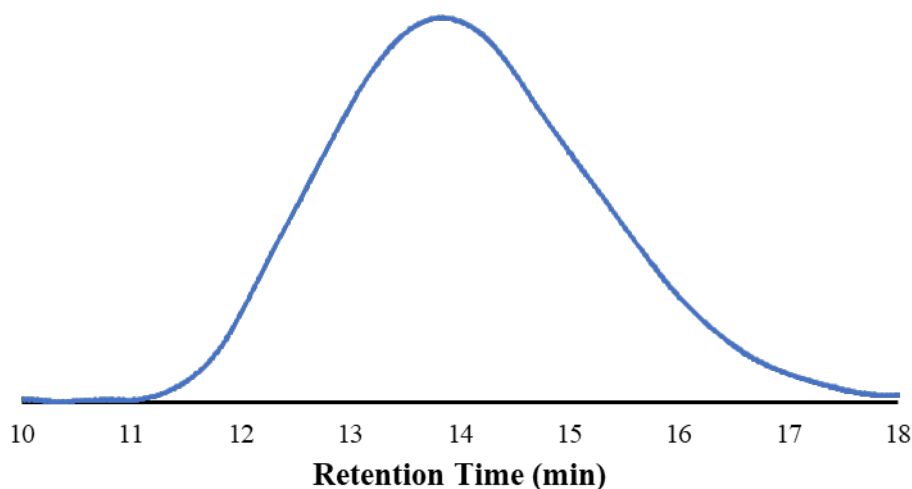


Figure S10: GPC trace of synthesized PVAc

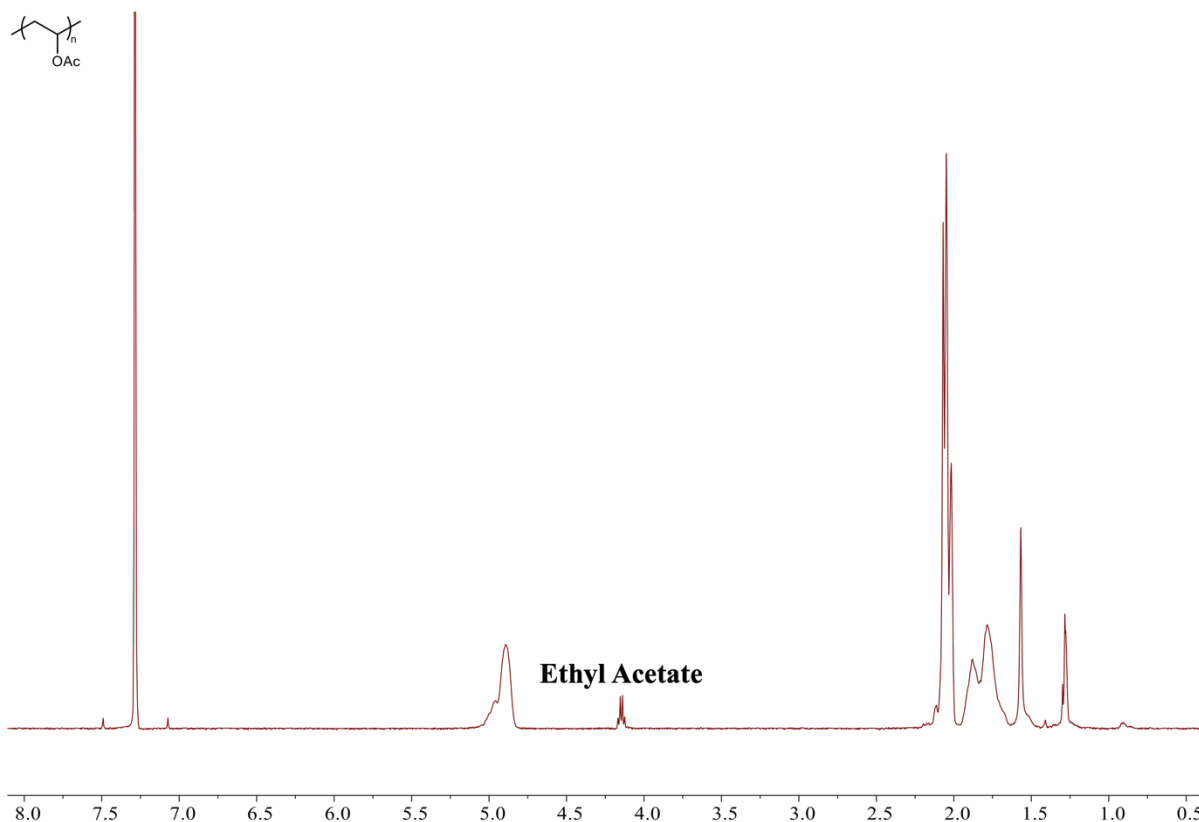
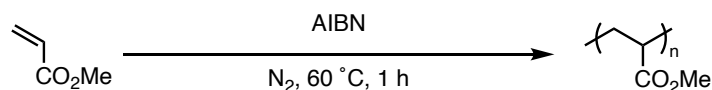


Figure S11: ^1H NMR spectrum (CDCl_3) of dried PVAc

e) Poly(methyl acrylate) (PMA) Synthesis



A 2-dram vial was charged with AIBN (10.8 mg, 0.066 mmol, 1 equiv.) and a magnetic stir bar. Methyl acrylate (1 mL, 10.8 mmol, 165 equiv.) was added to the reaction vial, which was subsequently capped with a teflon-coated septum. Three cycles of freeze-pump-thaw was performed to remove O_2 . The reaction vial was then purged with N_2 and submerged in a preheated oil bath. The reaction was allowed to run for 1 hour at 60°C . At the end of the reaction, the reaction mixture had completely gelled. The polymer was dissolved in a minimal amount of THF and precipitated in hexane (30 mL). The polymer was then transferred to a 20 mL scintillation vial and concentrated on the rotovap and dried under dynamic vacuum overnight. The GPC trace and ^1H NMR spectrum are shown in **Figure S12-S13**. $M_n = 70.7$ kDa and $D = 10.32$.

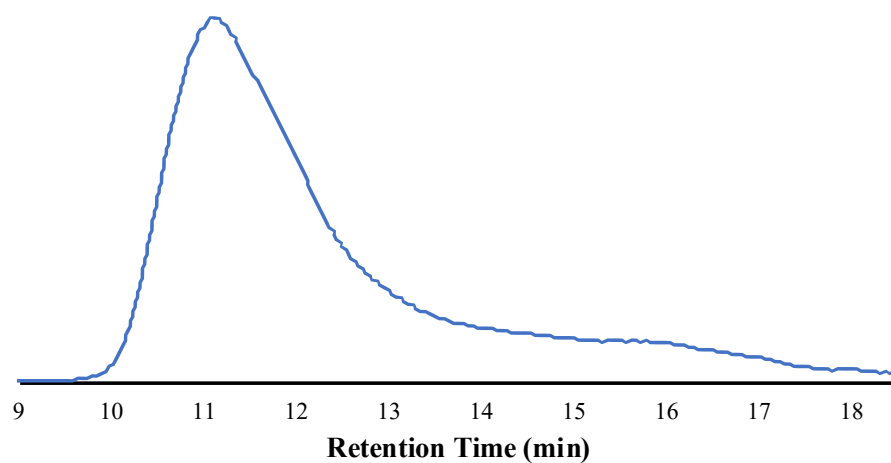


Figure S12: GPC trace of synthesized PMA

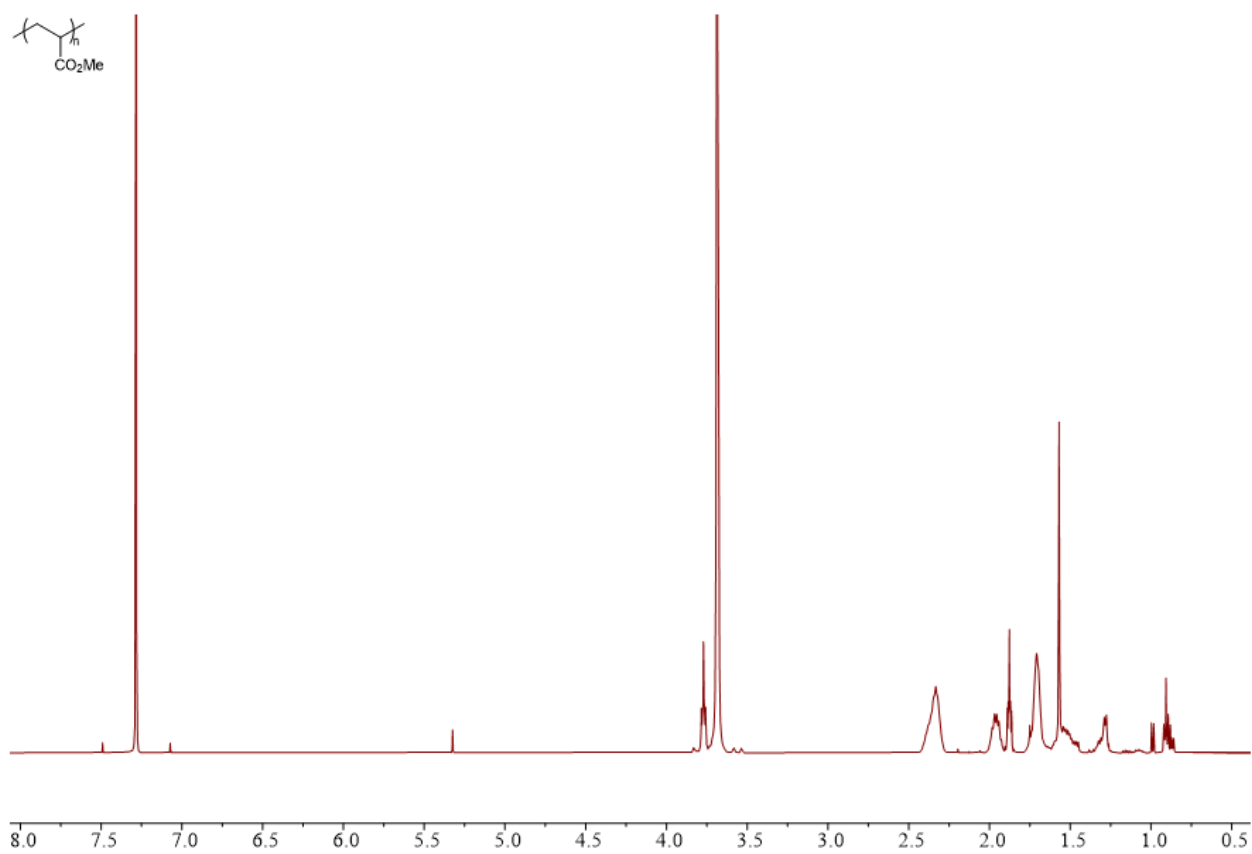
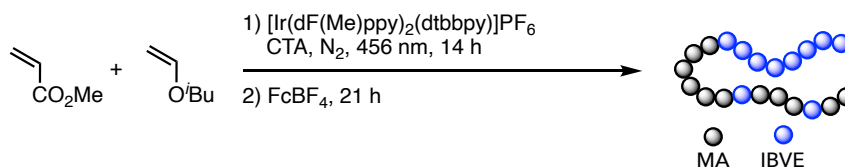


Figure S13: ¹H NMR spectrum (CDCl₃) of dried PMA

f) Poly(MA-co-IBVE) Block Copolymer Synthesis



The following procedure was adapted from the literature.⁴ Inside the glovebox, a 1-dram vial was charged with CTA (8 mg, 0.027 mmol, 1 equiv.) and a magnetic stir bar. A stock solution of $[\text{Ir}(\text{dF}(\text{Me})\text{ppy})_2(\text{dtbbpy})]\text{PF}_6$ (2.6 mg, 0.26 μmol) in DCM (1.3 mL, 0.2 mM) was prepared and 0.13 mL of this stock solution (0.026 μmol , 0.009 equiv.) was added to the reaction vial, along with IBVE (0.52 mL, 6 mmol, 226 equiv.) and MA (0.36 mL, 4 mmol, 150 equiv.). The reaction was capped with a teflon-coated septum, removed from the glovebox, and allowed to react under 456 nm. After 14 hours, the reaction vial was returned back into the glovebox. A small aliquot was taken for GPC and ^1H NMR analysis (^1H NMR analysis revealed IBVE monomers randomly substituted within the PMA block). A stock solution of ferrocenium tetrafluoroborate (FcBF_4) (3 mg, 0.0144 mmol) in of DCM (0.45 mL, 24 mM) was prepared, and this stock solution (0.045 mL, 0.001 mmol, 0.04 equiv.) was added to the reaction vial along with additional IBVE (0.26 mL, 3 mmol, 113 equiv.). The vial was then recapped with a teflon-coated septum, removed from the glovebox, and stirred for 21 hours at room temperature. The reaction was terminated upon the addition of 5% triethylamine/methanol (80 μL). The reaction mixture had completely gelled. The polymer was dissolved in a minimal amount of DCM and precipitated in methanol (30 mL). The polymer was then transferred to a new 2-dram vial, concentrated, and allowed to dry overnight under dynamic vacuum. The GPC trace and ^1H NMR spectrum are shown in **Figure S14-S15**. (MA block) $M_n = 15.4$ kDa and $D = 1.34$. (copolymer) $M_n = 19.6$ kDa and $D = 2.29$.

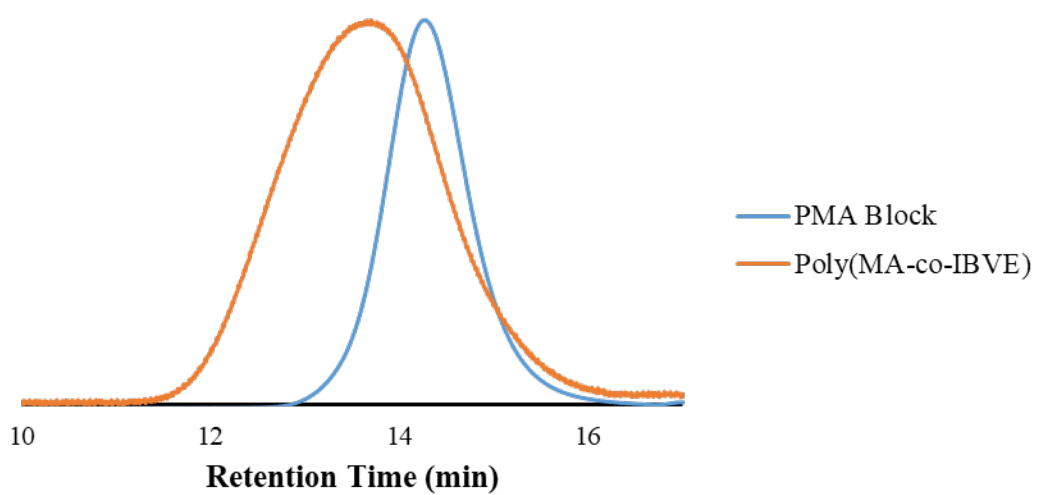


Figure S14: GPC traces of synthesized poly(MA-*co*-IBVE) block copolymer

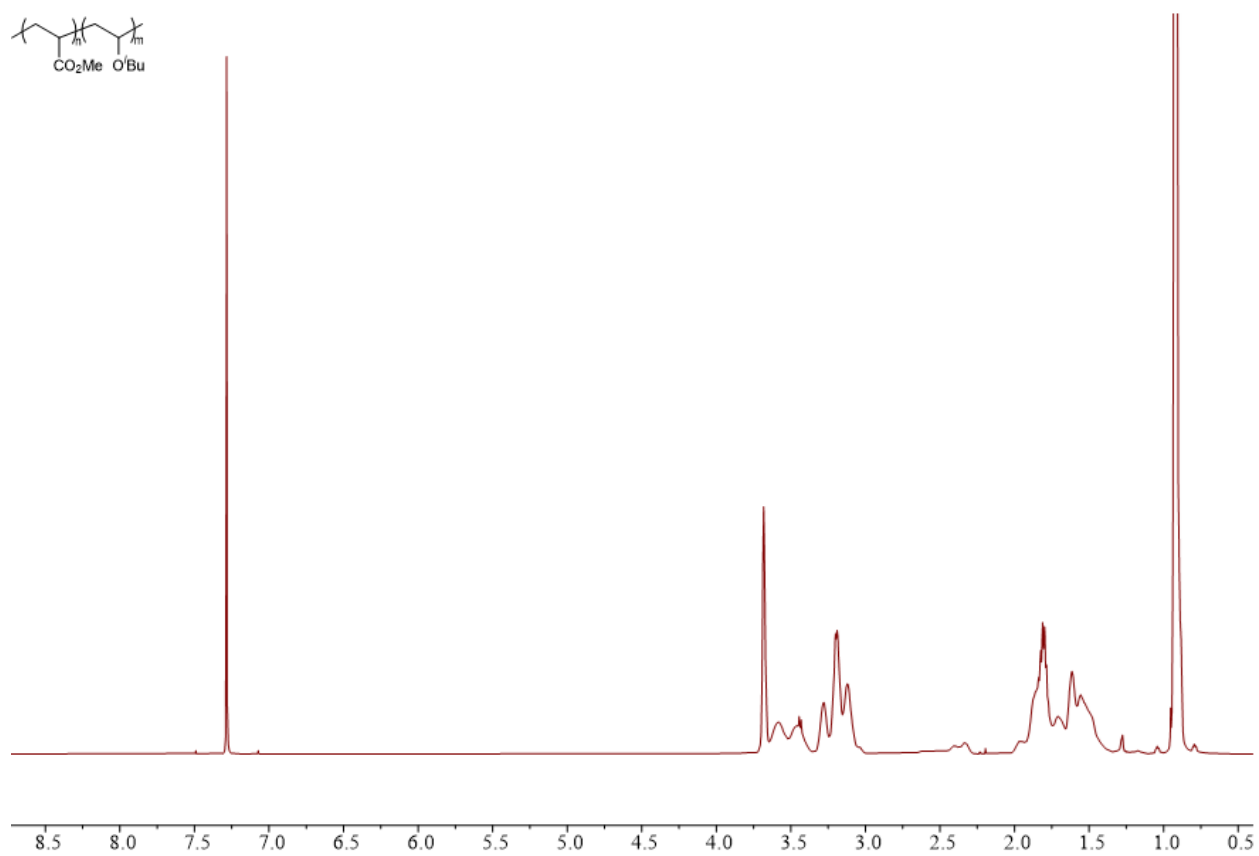
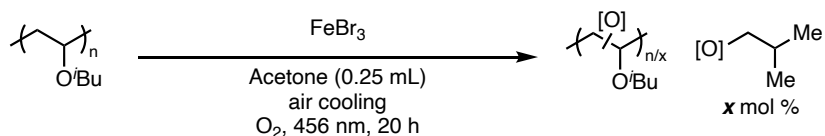


Figure S15: ¹H NMR spectrum (CDCl₃) of dried poly(MA-*co*-IBVE) copolymer

Procedure for PIBVE Degradation

a) FeBr₃ Weight Loading Screen



A 1-dram vial was charged with PIBVE (20 mg) and a magnetic stir bar. A stock solution of FeBr₃ (8 mg, 0.027 mmol) in acetone (1 mL, 27 mM) was prepared. The stock solution and acetone were added to the reaction vial in order to add a desired amount of FeBr₃ (0.34 mol %, 1.67 mol %, or 3.28 mol % in 0.25 mL of acetone). The vial was capped with a teflon-coated septum and the reaction mixtures were bubbled with O₂ for 1 minute. The reaction mixtures were then allowed to react for 20 hours under O₂ and 456 nm light irradiation with air cooling. The *M_n* and *D* data for the degraded oligomers are tabulated in **Table S2**, and the GPC traces and small molecule distribution are shown in **Figure S16-S18**.

Table S2: FeBr₃ weight loading results

Entry	PIBVE	Mol %	<i>M_n</i> (kDa)	<i>D</i>	<i>x</i> mol %
1	PIBVE4	0.34	5.2	2.0	5.2
2	PIBVE1	1.67	2.4	1.6	23.1
3	PIBVE4	3.28	1.9	1.2	17.1

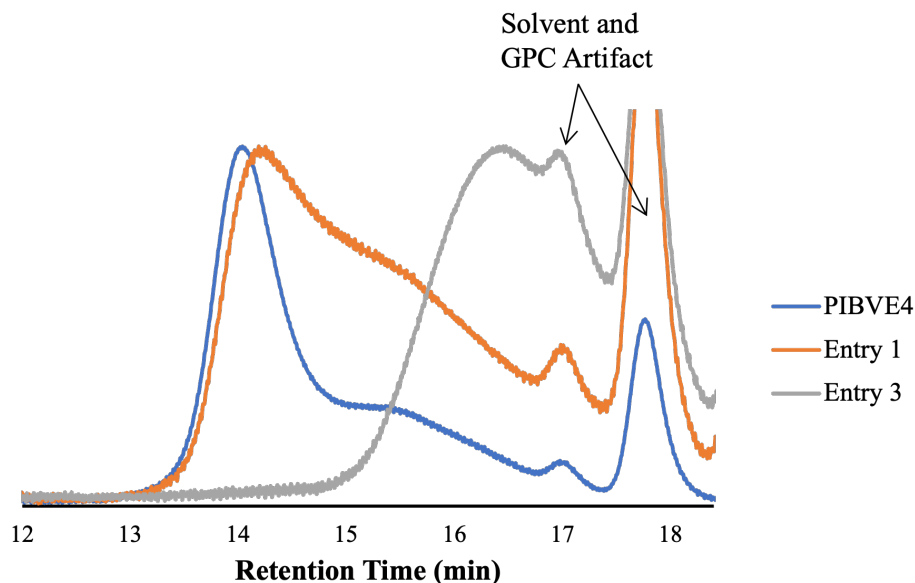


Figure S16: GPC traces of degraded PIBVE oligomer (1 and 10 wt. %)

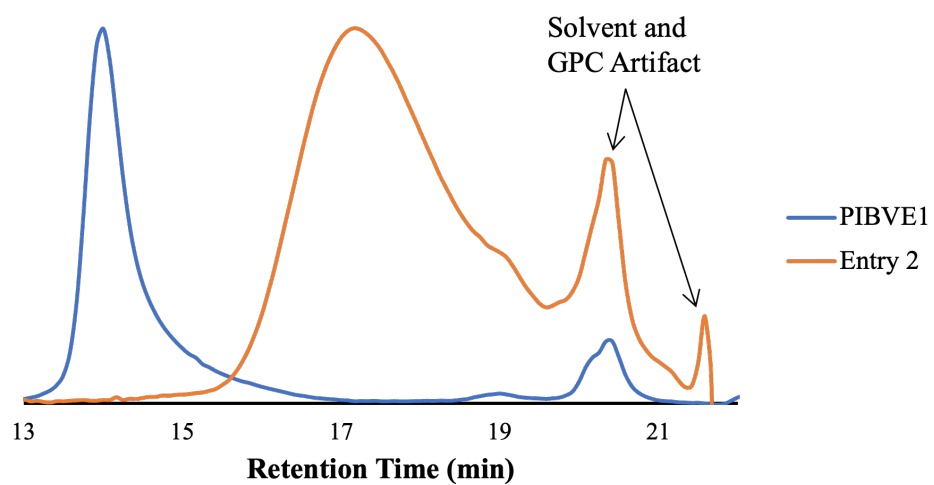


Figure S17: GPC traces of degraded PIBVE oligomer (5 wt. %)

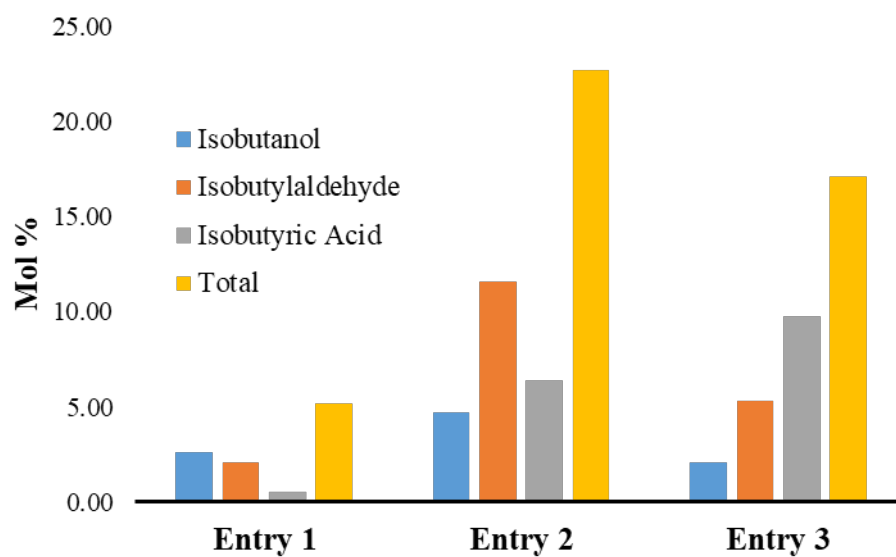
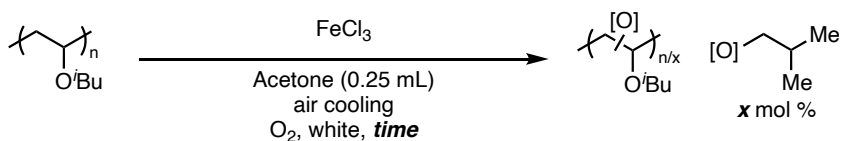


Figure S18: Small molecule distribution – FeBr₃ weight loading from Table S2

b) FeCl₃ Catalyst in Acetone Solvent System



The following procedure was adapted from our previous work.⁵ A 1-dram vial was charged with PIBVE1 (20 mg) and a magnetic stir bar. A 49 mM FeCl_3 stock solution was prepared by dissolving FeCl_3 (8 mg, 0.049 mmol) in acetone (1 mL) and a 0.25 mL aliquot was transferred to the reaction vial. The vial was capped with a teflon-coated septum and the reaction mixture was bubbled with O_2 from a balloon for 1 minute. The reaction vial was then allowed to react for *time* hours under O_2 and white light irradiation with air cooling. The GPC traces and small molecule distribution are shown in **Figure S19-S20**, and the ^1H NMR spectrum (in CDCl_3) of the degradation mixture is shown in **Figure S21** (see **Fig. 1**, entries **1 & 2** in the manuscript for the oligomer M_n and D data). M_n and D were not determined for the 20 h trial because the oligomer GPC trace was not detected. Small molecule quantity = 25.4 mol %.

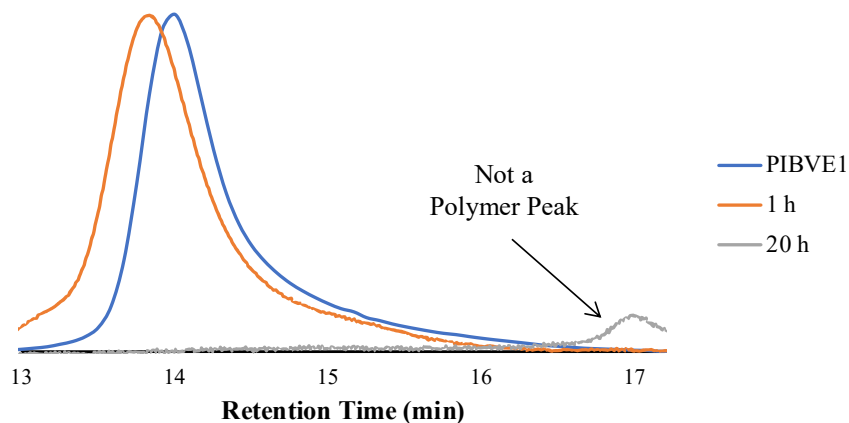


Figure S19: GPC traces of degraded PIBVE oligomer (FeCl_3 in acetone)

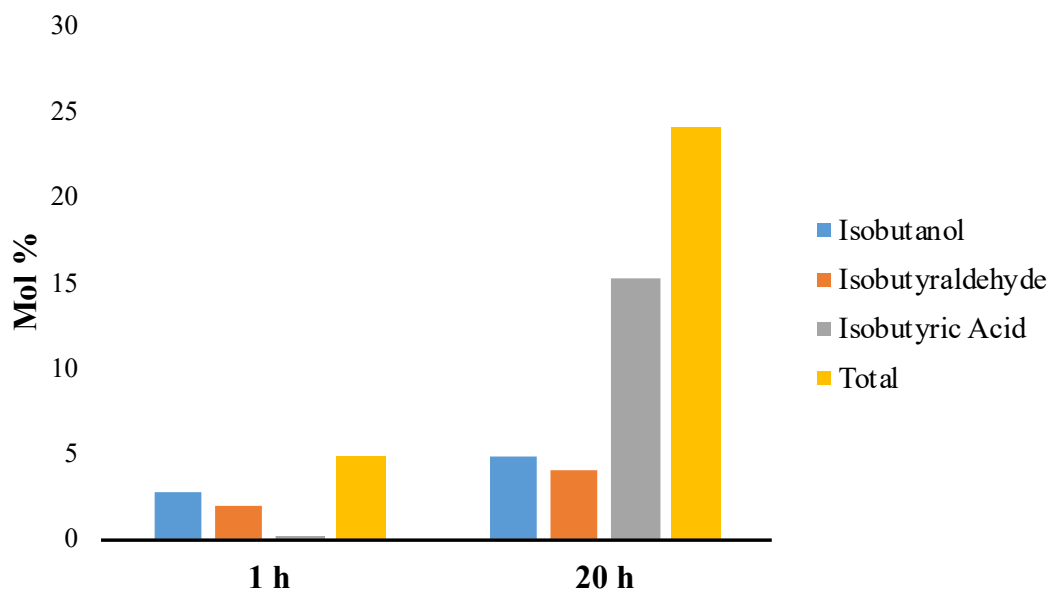


Figure S20: Small molecule distribution – FeCl₃

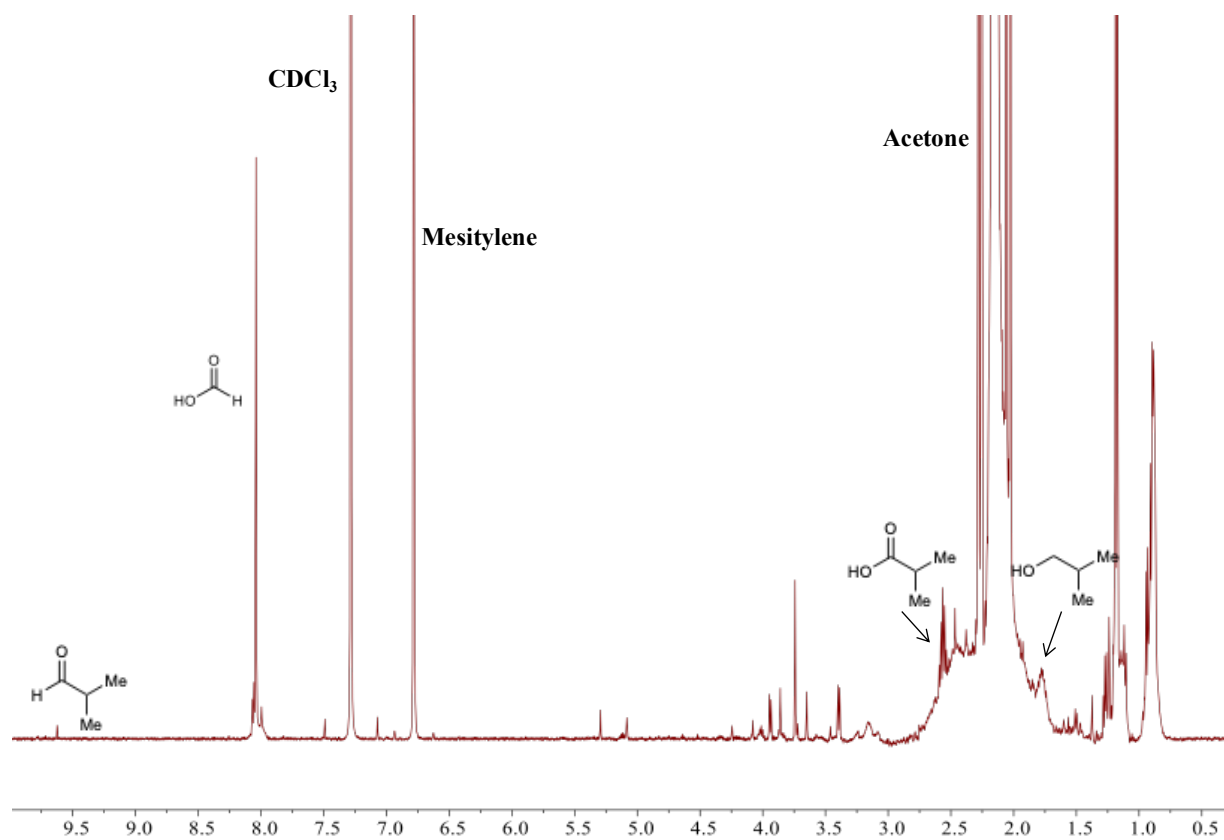
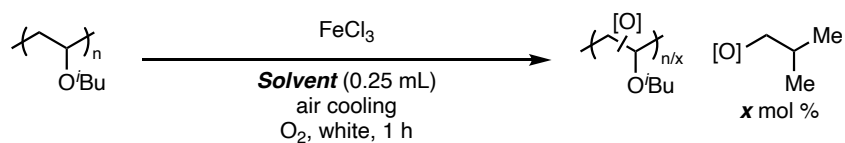


Figure S21: ¹H NMR spectrum (CDCl₃) of FeCl₃-catalyzed degradation mixture (20 h)

c) Benzene Loading for FeCl₃-Catalyzed Degradation



1-dram vials were charged with PIBVE2 (20 mg) and a magnetic stir bar. A 49 mM FeCl₃ stock solution was prepared by dissolving FeCl₃ (8 mg, 0.049 mmol) in *solvent* (1 mL), and 0.25 mL of these stock solutions were transferred to the reaction vials. The vials were capped with a teflon-coated septum and the reaction mixtures were bubbled with O₂ from a balloon for 1 minute. The reaction vials were then allowed to react for 1 hour under O₂ and white light irradiation with air cooling. The M_n and \bar{D} data for the degraded oligomers are tabulated in **Table S3**, and the GPC traces and small molecule distribution are shown in **Figure S22-S23**.

Table S3: FeCl₃ benzene loading results

Entry	<i>Solvent</i>	M_n (kDa)	\bar{D}	x mol %
1	1:1 Ace/Bz	3.6	1.56	48.6
2	4:1 Ace/Bz	4.5	1.70	47.1
3	Benzene	9.1	1.39	4.0

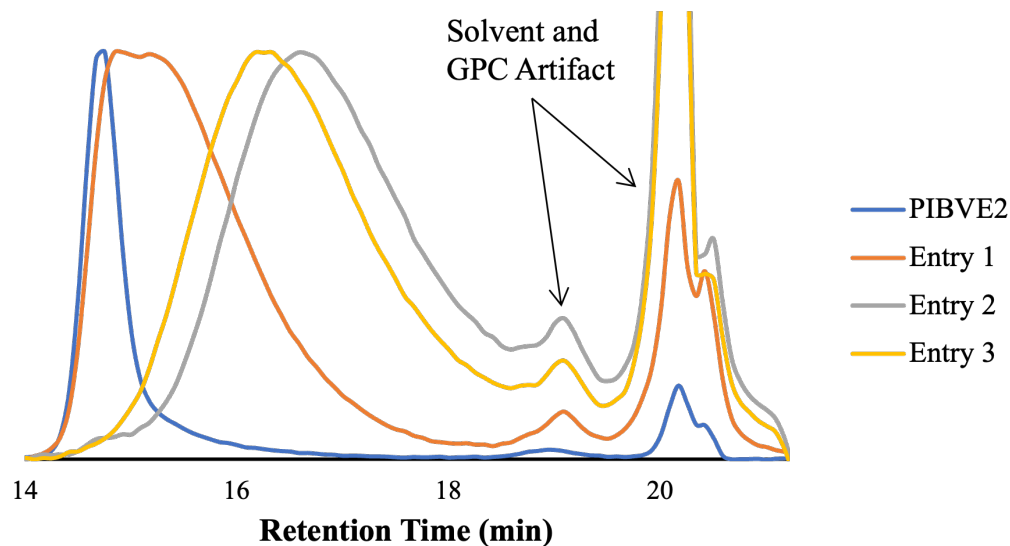


Figure S22: GPC traces of degraded PIBVE oligomer (FeCl₃ benzene loading)

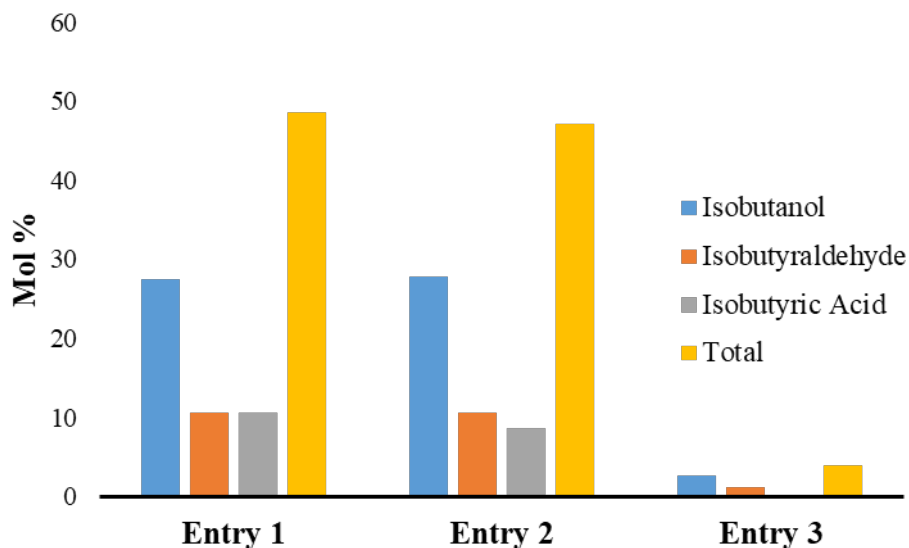
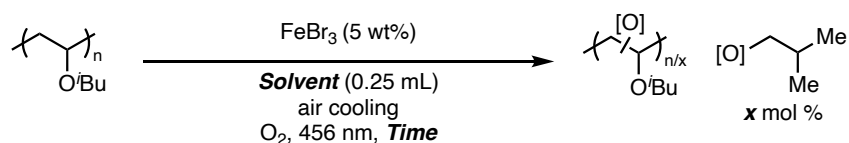


Figure S23: Small molecule distribution –FeCl₃ benzene loading

d) Benzene Effect on FeBr₃-Catalyzed Degradation



1-dram vials were charged with PIBVE4 or PIBVE3 (20 mg) and a magnetic stir bar. Stock solutions of FeBr₃ (2 mg, 0.0068 mmol) in *solvent* (0.5 mL, 13.5 mM) were prepared and 0.25 mL of these stock solutions were transferred to the reaction vials. The vials were capped with a teflon-coated septum and the reaction mixtures were bubbled with O₂ from a balloon for 1 minute. The reaction vials were then allowed to react for 1 or 6 hours under O₂ and 456 nm light irradiation with air cooling. The M_n and \bar{D} data for the degraded oligomers are tabulated in **Table S4**, and the GPC traces and small molecule distribution are shown in **Figure S24-S26**.

Table S4: Benzene effect on FeBr₃ results

Entry	PIBVE	Time (h)	<i>Solvent</i>	M_n (kDa)	\bar{D}	x mol %
1	PIBVE4	1	Acetone	4.2	1.66	8.3
2	PIBVE3	1	1:1 Ace/Bz	10.5	1.43	1.9
3	PIBVE4	6	Acetone	2.9	1.46	20.6
4	PIBVE3	6	1:1 Ace/Bz	4.9	1.66	6.0

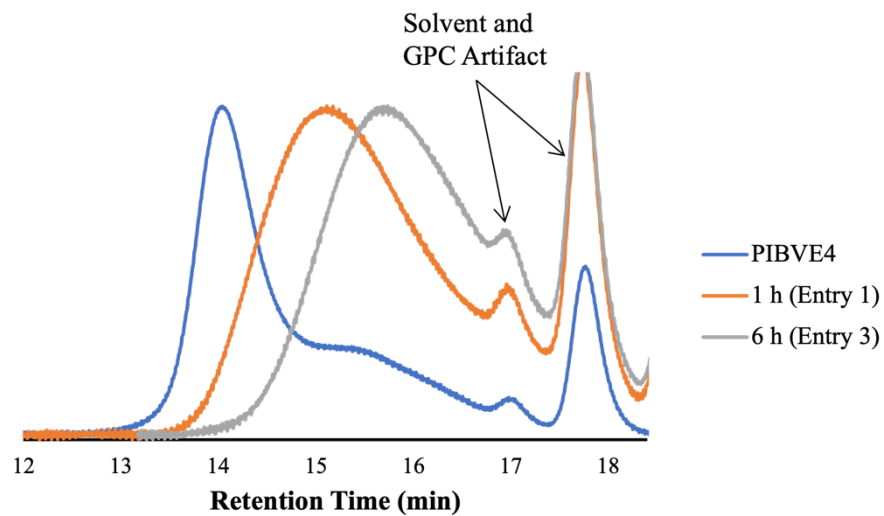


Figure S24: GPC traces of degraded PIBVE oligomer in acetone – FeBr_3 catalyst

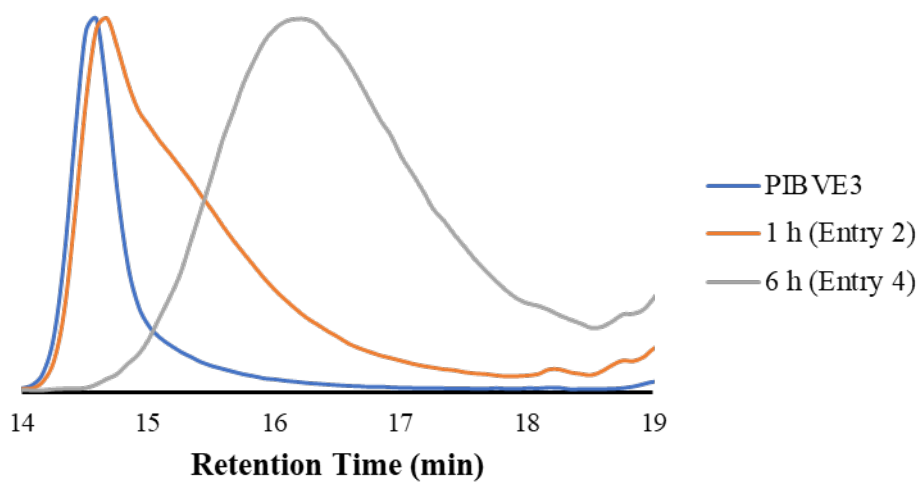
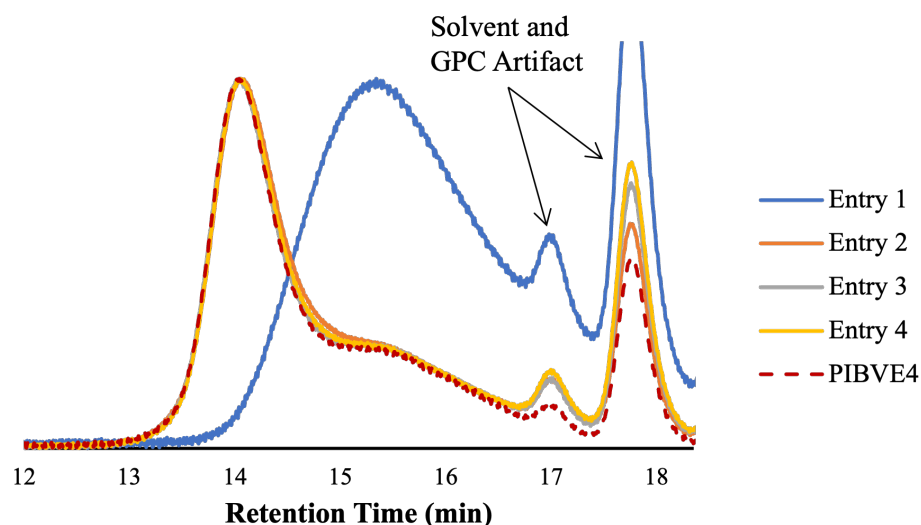


Figure S25: GPC traces of degraded PIBVE oligomer in 1:1 acetone/benzene – FeBr_3

Table S5: FeCl₃-catalyzed degradation control experiments results

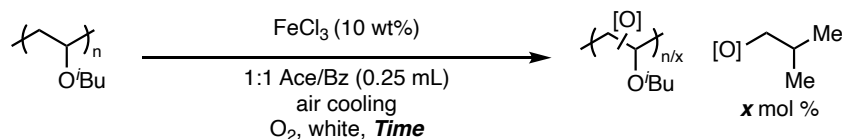
Entry	Deviation	M_n (kDa)	\bar{D}
1	--	3.6	1.61
2 ^a	N ₂	16.8	1.14
3	No FeCl ₃	16.7	1.15
4	No light	16.2	1.16

^aThree cycles of freeze-pump-thaw were performed to remove O₂ from the reaction vial.

**Figure S27:** GPC traces of degraded PIBVE oligomer (FeCl₃ controls)

Procedure for PIBVE Degradation Kinetics

a) FeCl₃-Catalyzed Degradation Kinetics in 1:1 Acetone/Benzene



A 1-dram vial was charged with PIBVE3 (20 mg) and a magnetic stir bar. A stock solution of FeCl₃ (8 mg, 0.049 mmol) in 1:1 acetone/benzene (v/v) (1.0 mL, 49 mM) was prepared, and 0.25 mL of this stock solution was added to the vial. The vials were then capped with a teflon-coated septum and the reaction mixtures were bubbled with O₂ from a balloon for 1 minute. The reaction mixture was then allowed to react for a desired amount of *time* under O₂ and white light irradiation with air cooling. The M_n and \bar{D} data for the degraded oligomers are tabulated in **Table**

S6. The M_n of the degraded oligomers are plotted over time in **Figure S28**, and the small molecule generation is plotted over time in **Figure S29**.

Table S6: FeCl₃-catalyzed PIBVE degradation kinetics results

Entry	Time (h)	M_n (kDa)	\bar{D}	x mol %
1	0	27.4	1.21	0
2	1	3.6	1.68	53.1
3	2	2.2	1.49	57.3
4	3	2.0	1.36	43.1
5	4	1.8	1.59	35.0
6	5	1.5	1.10	33.7
7	6	1.4	1.07	30.2

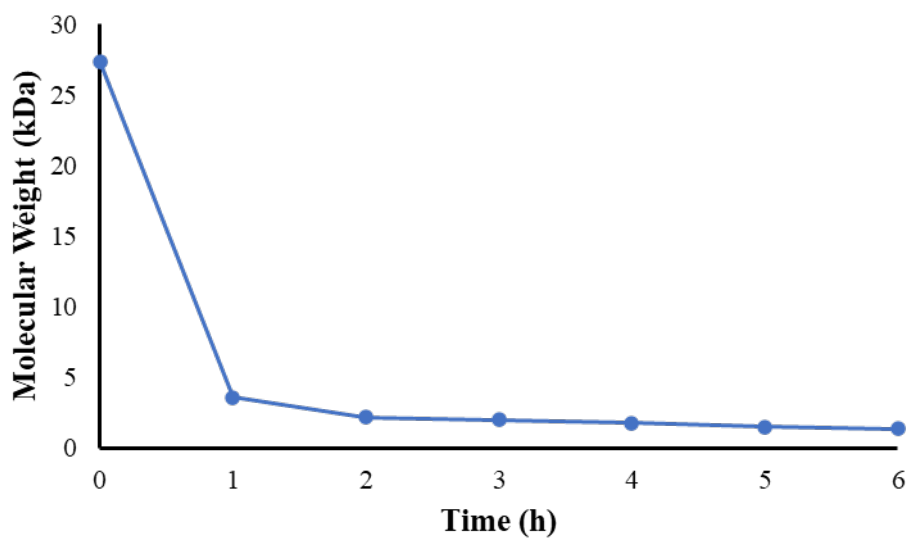


Figure S28: M_n of degraded PIBVE oligomers over time (FeCl₃ kinetics).

Table S7: FeBr₃-catalyzed PIBVE degradation kinetics results

Entry	Time (h)	M_n (kDa)	\bar{D}	x mol %
1	0	15.9	1.18	0
2	1	4.2	1.66	8.3
3	2	3.8	1.65	15.0
4	3	3.4	1.53	15.5
5	4	3.3	1.59	18.2
6	5	3.0	1.56	19.5
7	6	2.9	1.46	20.6

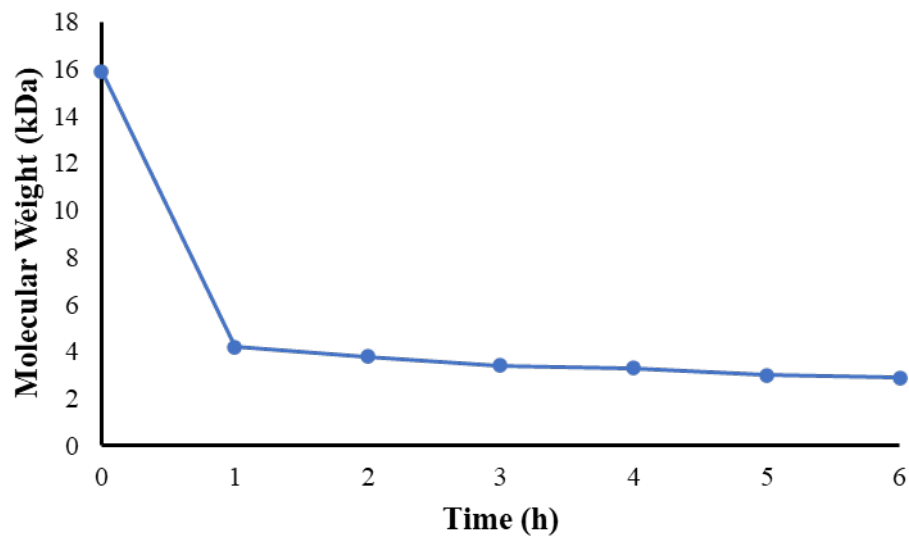


Figure S30: M_n of degraded PIBVE oligomers over time (FeBr₃ kinetics)

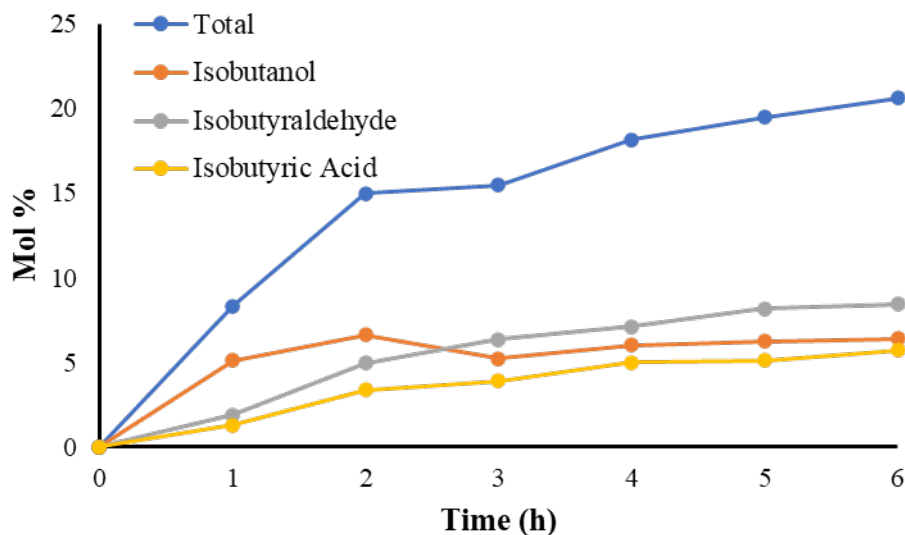
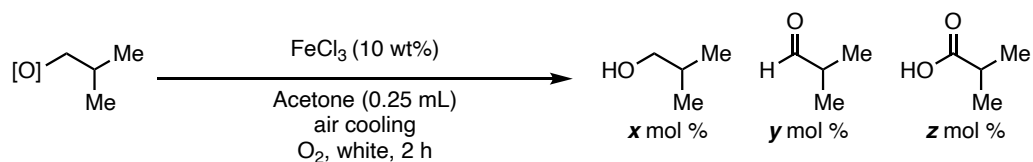


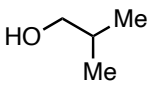
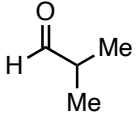
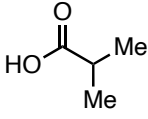
Figure S31: Small molecule generation over time (FeBr₃ kinetics)

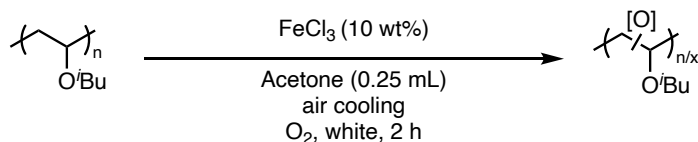
Procedure for Small Molecule Degradation Studies



A 1-dram vial was charged with pure isobutanol, isobutyraldehyde or isobutyric acid (50 μL). A stock solution of FeCl₃ (8 mg, 0.049 mmol) in acetone (1.0 mL, 49 mM) was prepared and 0.25 mL of this stock solution was added to each vial. The vials were capped with a teflon-coated septum and the reaction mixtures were bubbled with O₂ for 1 minute. The reaction mixture was then allowed to react for 2 hours under O₂ and white light irradiation with air cooling. The conversion was tabulated in Table S8.

Table S8: Small molecule degradation results

Small Molecule	x mol %	y mol %	z mol %	Total mol %
	59.5	9.0	7.4	75.9
	0	10.5	46.9	57.4
	0	0	86.5	86.5

Procedure for FT-IR Experiment with Partially Degraded Oligomer

A 1-dram vial were charged with PIBVE5 (20 mg) and a magnetic stir bar. A stock solution of FeCl_3 (8 mg, 0.049 mmol) in acetone (1.0 mL, 49 mM) was prepared and 0.25 mL of this stock solution was added to the vial. The vial was then capped with a teflon-coated septum and the reaction mixture was bubbled with O_2 from a balloon for 1 minute. The reaction mixture was then allowed to react for 2 hours under O_2 and white light irradiation with air cooling. Once the reactions had finished, the degradation mixtures were precipitated in ~1 mL acetonitrile to isolate the degraded oligomers. The acetonitrile was decanted and dried in vacuum. The oligomers were then analyzed via FT-IR spectroscopy (**Figure S32**).

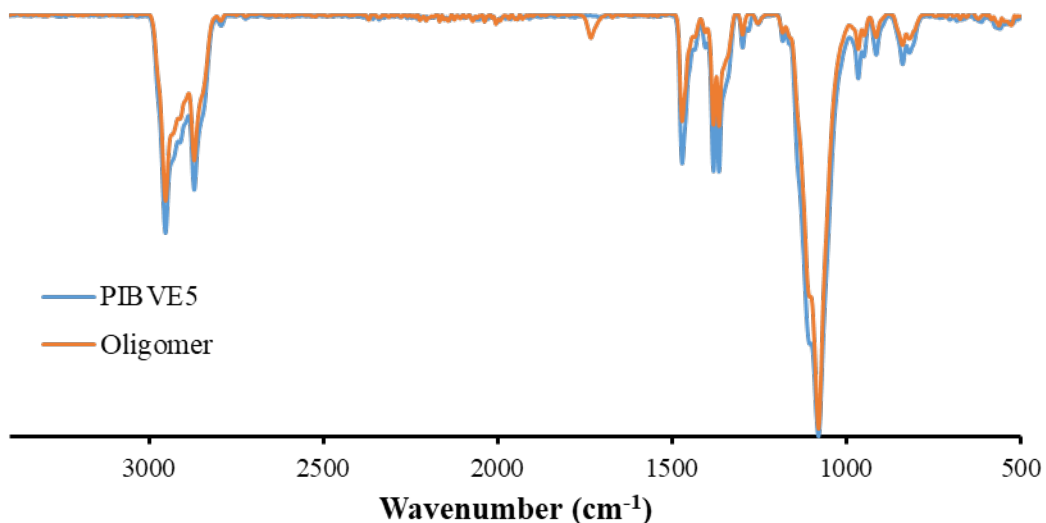
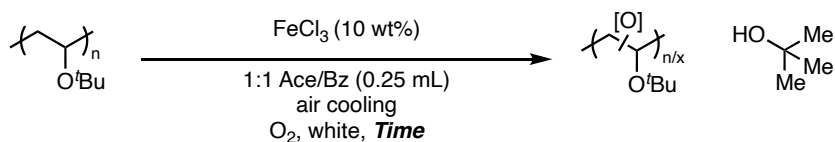


Figure S32: FT-IR spectrum of PIBVE and partially degraded oligomer

Procedure for PTBVE Degradation Study – FeCl₃



A 1-dram vials was charged with PTBVE (20 mg) and a magnetic stir bar. A stock solution of FeCl₃ (8 mg, 0.049 mmol) in 1:1 acetone/benzene (v/v) (1.0 mL, 49 mM) was prepared, and 0.25 mL of this stock solution was added to the vial. The vial was capped with a teflon-coated septum and the reaction mixtures were bubbled with O₂ from a balloon for 1 minute. The reaction mixture was then allowed to react for a desired amount of *time* under O₂ and white light irradiation with air cooling. See **Figure 4b** in the manuscript for the degradation and small molecule generation data.

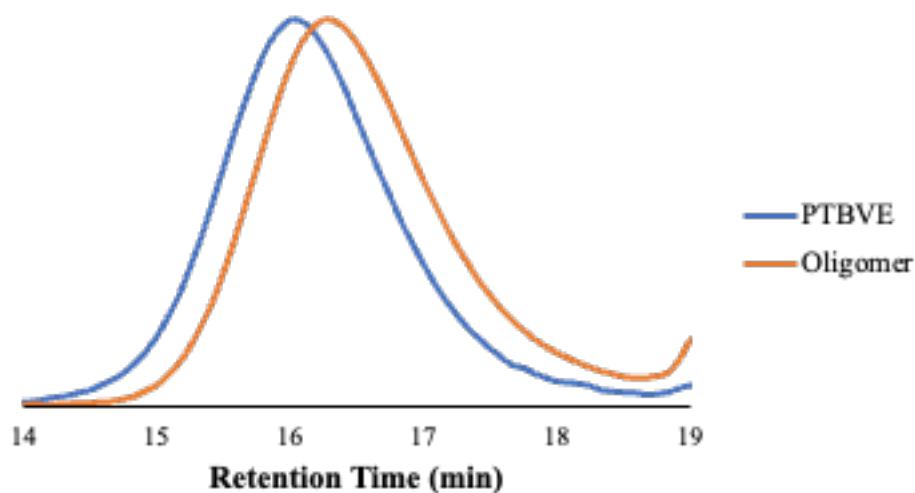
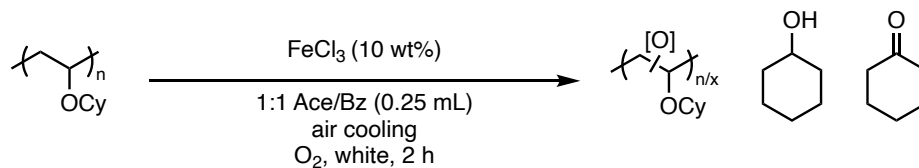


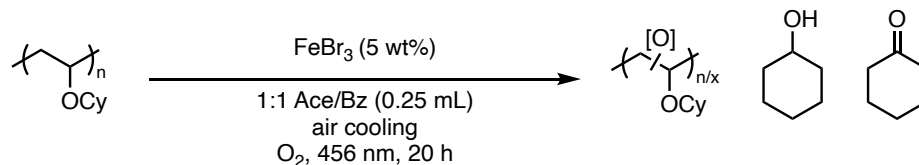
Figure S34: GPC trace of degraded PTBVE – FeBr₃

Procedure for Expanded PVE Substrate Degradation Study

a) Poly(cyclohexyl vinyl ether) Degradation



(FeCl₃ system) A 1-dram vial was charged with PCyVE (20 mg) and a magnetic stir bar. A stock solution of FeCl₃ (8 mg, 0.049 mmol) in 1:1 acetone/benzene (v/v) (1.0 mL, 49 mM) was prepared, and 0.25 mL of this stock solution was added to the vial. The vials were capped with a teflon-coated septum and the reaction mixtures were bubbled with O₂ from a balloon for 1 minute. The reaction vials were then allowed to react for 2 h under O₂ and white light irradiation with air cooling. The GPC traces are shown in **Figure S35**. See **Figure 4a** in the manuscript for the degradation and small molecule generation data.



(FeBr₃ system) A 1-dram vial was charged with PCyVE (20 mg) and a magnetic stir bar. A stock solution of FeBr₃ (2 mg, 0.0068 mmol) in 1:1 acetone/benzene (v/v) (0.5 mL, 13.5 mM) was prepared, and 0.25 mL of this stock solution was added to the vial. (Despite less efficient than pure acetone, 1:1 acetone/benzene was used with FeBr₃ because the polymer was not soluble in pure acetone). The vials were capped with a teflon-coated septum and the reaction mixtures were bubbled with O₂ from a balloon for 1 minute. The reaction vials were then allowed to react for 20 h under O₂ under 456 nm light with air cooling. The GPC traces are shown in **Figure S35**. See **Figure 4a** in the manuscript for the degradation and small molecule generation data.

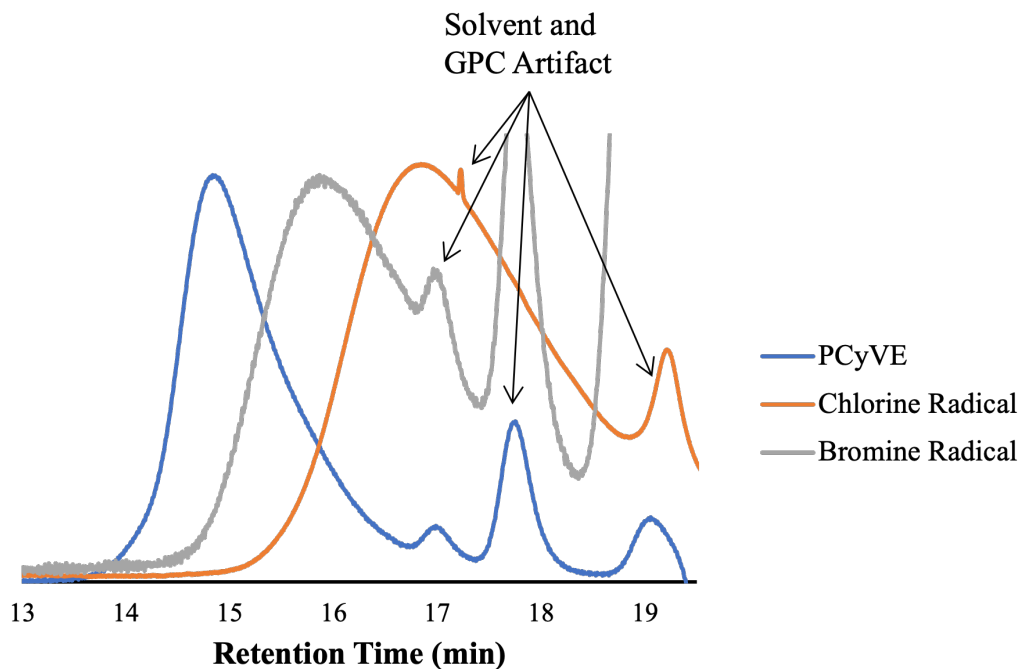
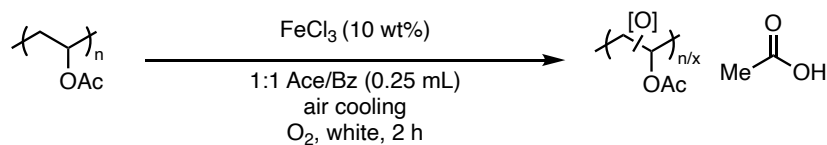
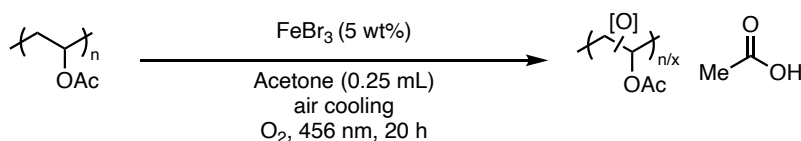


Figure S35: GPC traces of degraded PCyVE

b) Poly(vinyl acetate) Degradation



(FeCl₃ system) A 1-dram vial was charged with PVAc (20 mg) and a magnetic stir bar. A stock solution of FeCl₃ (8 mg, 0.049 mmol) in 1:1 acetone/benzene (v/v) (1.0 mL, 49 mM) was prepared, and 0.25 mL of this stock solution was added to the vial. The vials were capped with a teflon-coated septum and the reaction mixtures were bubbled with O₂ from a balloon for 1 minute. The reaction vials were then allowed to react for 2 h under O₂ and white light irradiation with air cooling. The GPC traces are shown in **Figure S36**. See **Figure 4c** in the manuscript for the degradation and small molecule generation data.



(FeBr₃ system) A 1-dram vial was charged with PCyVE (20 mg) and a magnetic stir bar. A stock solution of FeBr₃ (2 mg, 0.0068 mmol) in acetone (0.5 mL, 13.5 mM) was prepared, and 0.25 mL of this stock solution was added to the vial. The vials were capped with a teflon-coated septum and the reaction mixtures were bubbled with O₂ from a balloon for 1 minute. The reaction vials were then allowed to react for 20 h under O₂ under 456 nm light with air cooling. The GPC traces are shown in **Figure S36**. See **Figure 4c** in the manuscript for the degradation and small molecule generation data.

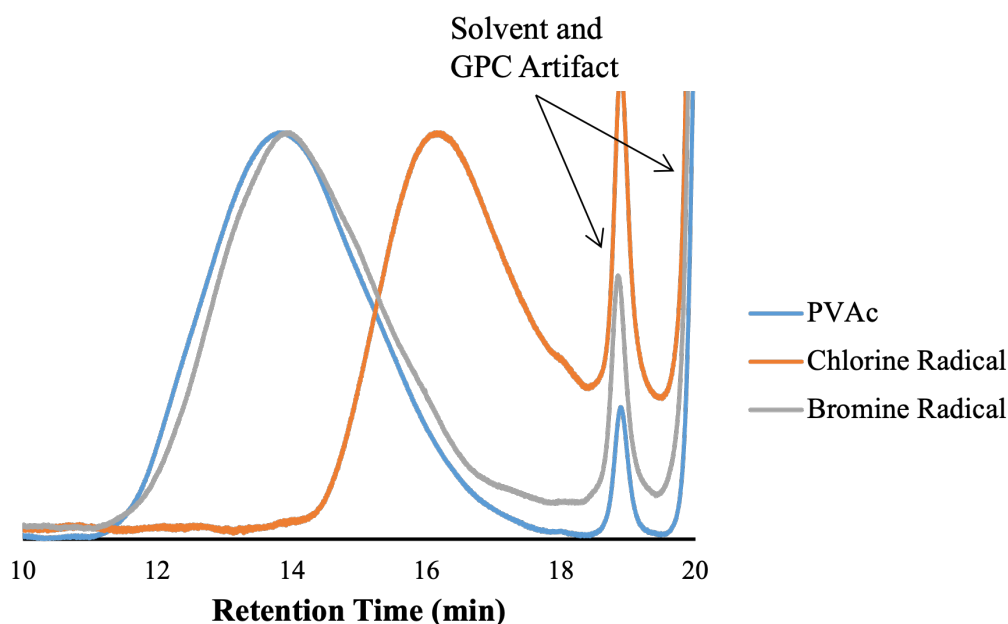
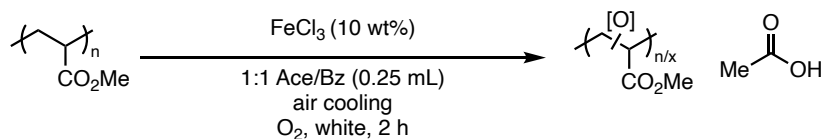
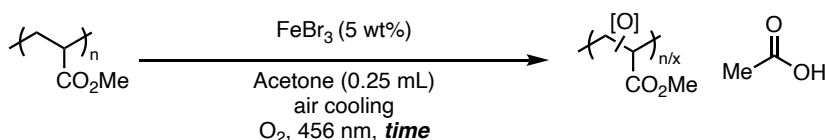


Figure S36: GPC traces of degraded PVAc

c) Poly(methyl acrylate) Degradation



(FeCl₃ system) A 1-dram vial was charged with PMA (20 mg) and a magnetic stir bar. A stock solution of FeCl₃ (8 mg, 0.049 mmol) in 1:1 acetone/benzene (v/v) (1.0 mL, 49 mM) was prepared, and 0.25 mL of this stock solution was added to the vial. The vials were capped with a teflon-coated septum and the reaction mixtures were bubbled with O₂ from a balloon for 1 minute. The reaction vials were then allowed to react for 2 h under O₂ and white light irradiation with air cooling. The GPC traces are shown in **Figure S35**. See **Figure 4d** in the manuscript for the degradation and small molecule generation data.



(FeBr₃ system) A 1-dram vial was charged with PMA (20 mg) and a magnetic stir bar. A stock solution of FeBr₃ (2 mg, 0.0068 mmol) in acetone (0.5 mL, 13.5 mM) was prepared, and 0.25 mL of this stock solution was added to the vial. The vial was capped with a teflon-coated septum and the reaction mixtures were bubbled with O₂ from a balloon for 1 minute. The reaction vial was then allowed to react for *time* under O₂ under 456 nm light with air cooling. The GPC traces are shown in **Figure S37**. See **Figure 4d** in the manuscript for the degradation and small molecule generation data.

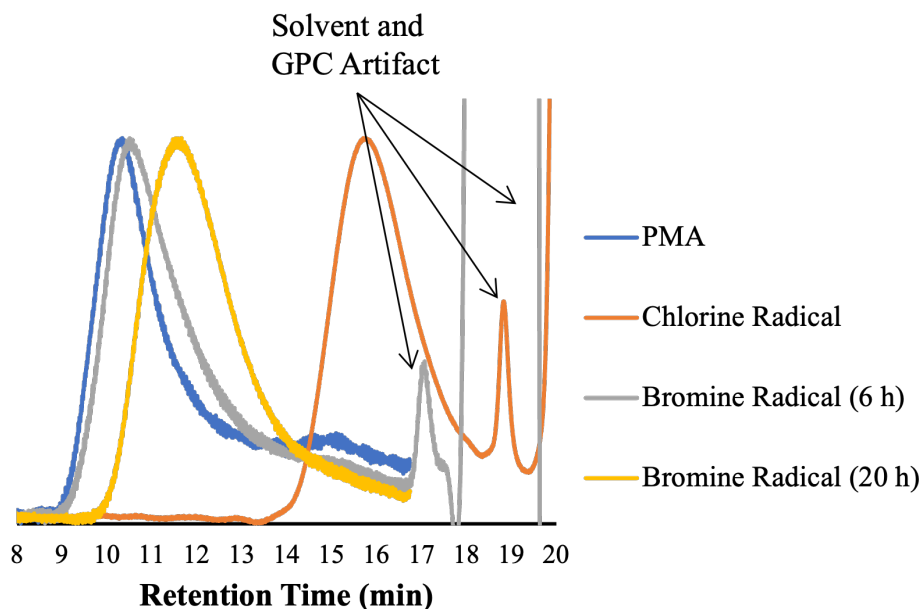
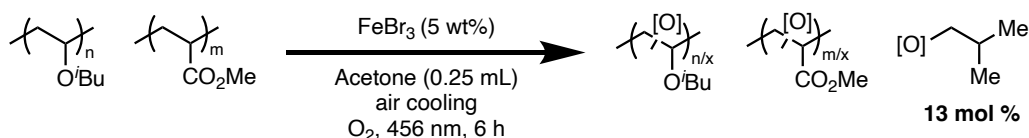


Figure S37: GPC traces of degraded PMA

Entry	Time (h)	M_n (kDa)	\bar{D}	Mol %
1	6	68.0	8.47	0
2	20	27.6	8.66	0

Table S9: FeBr₃-catalyzed PMA degradation results

d) PIBVE and PMA Mixed Polymer Degradation



A 1-dram vial was charged with PIBVE1 (10 mg), PMA (10 mg), and a magnetic stir bar. A stock solution of FeBr₃ (2 mg, 0.0068 mmol) in acetone (0.5 mL, 13.5 mM) was prepared, and 0.25 mL of this stock solution was added to the vial. The vials were capped with a teflon-coated septum and the reaction mixture was bubbled with O₂ from a balloon for 1 minute. The reaction vial was then allowed to react for 6 hours under O₂ under 456 nm light with air cooling. The GPC traces are shown in **Figure S38**. See **Figure 5** in the manuscript for the degradation results (small molecule generation = 13 mol %: isobutanol, isobutyraldehyde, and isobutyric acid).

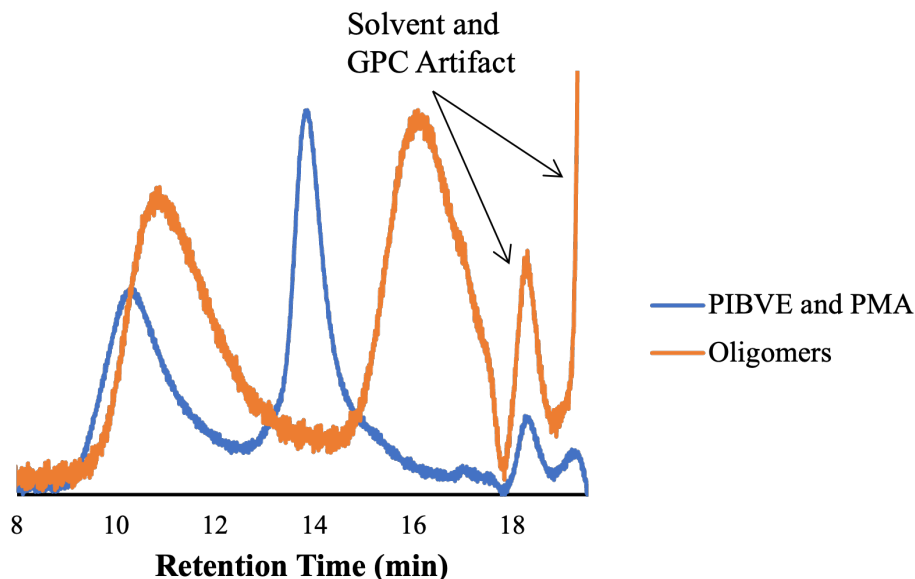
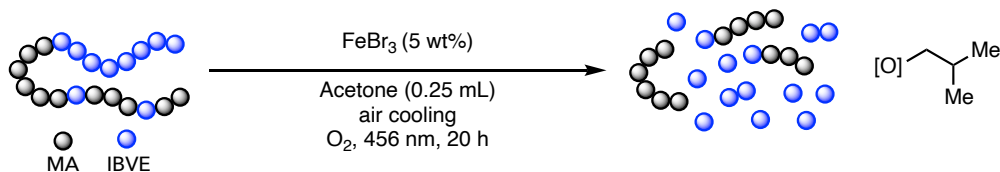


Figure S38: GPC trace of degraded PIBVE and PMA polymer mixture

e) Poly(MA-*co*-IBVE) Block Copolymer Degradation



A 1-dram vial was charged with poly(MA-*co*-IBVE) (20 mg) and a magnetic stir bar. A stock solution of FeBr₃ (2 mg, 0.0068 mmol) in acetone (0.5 mL, 13.5 mM) was prepared, and 0.25 mL of this stock solution was added to the vial. The vial was capped with a teflon-coated septum and the reaction mixture was bubbled with O₂ from a balloon for 1 minute. The reaction vial was then allowed to react for *time* under O₂ under 456 nm light with air cooling. The GPC traces are shown in **Figure S39**. See **Figure 5** in the manuscript for the degradation and small molecule generation data.

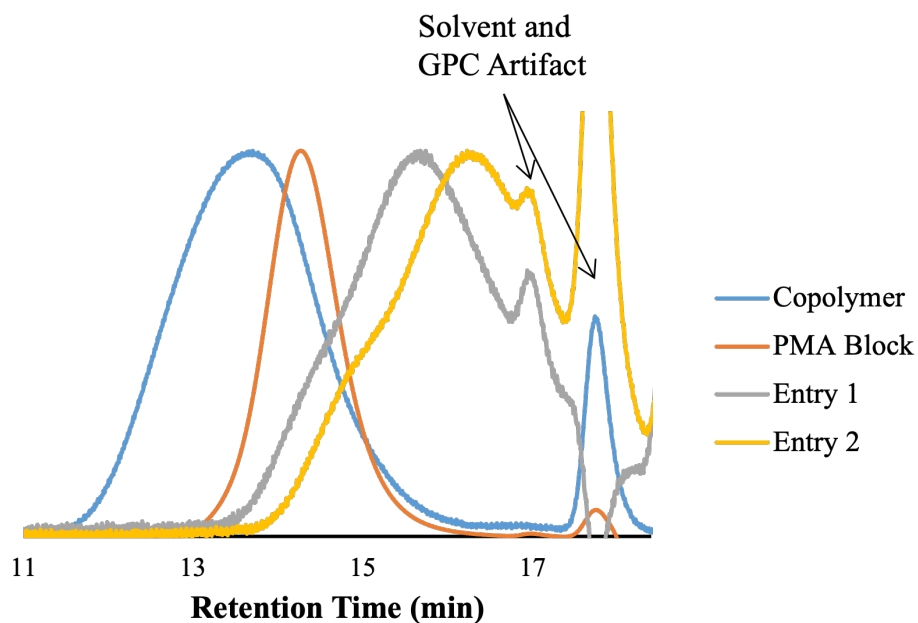


Figure S39: GPC trace of degraded poly(MA-*co*-IBVE) block copolymer

Entry	Time (h)	M_n (kDa)	\mathcal{D}	Mol %
1	6	3.3	1.84	11.8
2 ^a	20	8.7 (2.2)	1.15 (1.20)	15.0

^aHigher M_n peak (lower M_n peak)

Table S10: FeBr₃-catalyzed copolymer degradation results

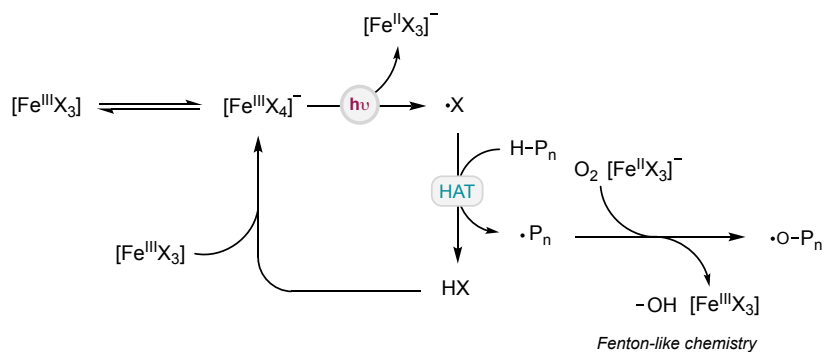


Figure S40: FeX₃ catalytic cycle for photooxidative degradation⁶

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- 4) B. M. Peterson, V. Kottisch, M. J. Supej, B. P. Fors, *ACS Cent. Sci.*, 2018, **4**, 1228–1234.
- 5) S. Oh, E. E. Stache, *J. Am. Chem. Soc.*, 2022, **144**, 5745–5749.
- 6) S. Oh, E. E. Stache, *ACS Catal.*, 2023, **13**, 10968-10975.