Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Hydrolytically-Degradable Homo- and Copolymers of a Strained Exocyclic Hemiacetal Ester

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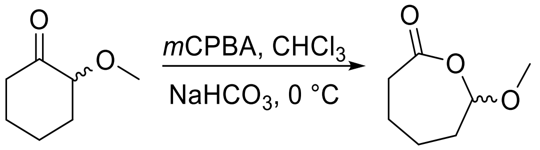
Materials and Analysis.

MOPO synthesis and poly(MOPO) synthesis with organic acids. All chemicals were obtained from Sigma-Aldrich and used as received unless otherwise indicated. Benzyl alcohol was distilled under vacuum and stored over activated 3 Å molecular sieves in a glovebox. When indicated as dry, solvents were either obtained from a JC Meyer solvent drying system or were distilled prior to use according to standard purification methods. $CDCl_3$ used in polymerizations of MOPO with MeOTf and TfOH was distilled from phosphorous pentoxide and stored over activated 3 Å molecular sieves in a glovebox. ^1H and ^{13}C NMR spectra were obtained on a 400 or 500 MHz Bruker Avance III HD. Chemical shifts were referenced to tetramethylsilane (TMS) at 0.00 ppm for ^1H and ^{13}C NMR spectra taken in $CDCl_3$ containing 10 % w/v TMS. Gas chromatography-mass spectrometry (GC-MS) was carried out on an Agilent 6890 GC and Agilent 5973 MS system. The GC-MS column used was a HP-5ms with dimensions 30m x 0.25mm. The standard method for all runs, unless otherwise indicated, consisted of holding the sample at 50 °C for 1.5 min, then ramping to 250 °C at a ramp rate of 20 °C min^{-1}, and holding it at 250 °C for 3.5 min (50to250SPLIT15). Polymerizations were set up in the freezer (−20 °C) of a Unilab MBraun glovebox with a nitrogen atmosphere.

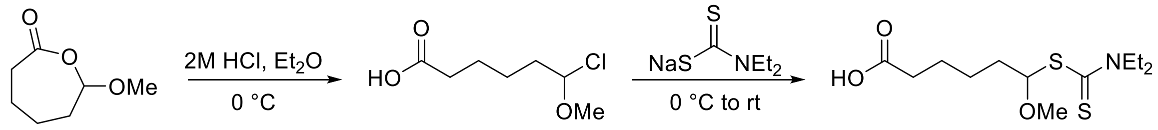
Thermal gravimetric analysis was performed on a TA Instruments Q500 TGA under the conditions specified. Differential scanning calorimetry (DSC) was carried out using a TA Instruments Q2000 at a scanning rate of 5 °C/min. DSC data analysis was performed using TA Instruments TRIOS software using the second heating curve. Molar mass analysis for poly(MOPO) was carried out by injecting samples into an Agilent 1200 series chromatograph (DMF w/ 0.05 M LiBr, 50 °C, flow rate = 1 mL/min, poly(MOPO) $dn/dc = 0.029$) with a Viscotek I-MBMMW-3078 column or *via* conventional calibration analysis relative to polystyrene standards using a Optilab T-rEX RI detector with a Hewlett-Packard series 1100 liquid chromatography system ($CHCl_3$, 35 °C, flow rate = 1 mL/min), equipped with a Hewlett-Packard 1047A RI detector and three PLgel 5 μm MIXED-C columns.

Photomediated Cationic RAFT Homo- and Copolymerizations of MOPO. All polymerizations were set up in an Unilab MBraun glovebox with a nitrogen atmosphere and irradiated with blue diode LED® BLAZE™ lights (450 nm, 2.88 W/ft) under nitrogen atmosphere outside the glovebox. Deionized (DI) water was obtained by reverse osmosis. Hydrochloric acid (HCl, Macron) was used as received and diluted with DI water to make a 3.0 M solution. Chloroform-D ($CDCl_3$, 99.8%, Cambridge Isotope Laboratories, Inc.) was used as received for recording NMR spectra. For polymerizations, $CDCl_3$ used as solvent was dried over calcium hydride (CaH_2, ACROS organics, 93% extra pure, 0 - 2 mm grain size) for 12 h and then distilled under vacuum to a container with activated 3Å molecular sieves. After an additional 12 h drying over activated molecular sieves, the $CDCl_3$ was distilled under vacuum a final time and degassed through three freeze-pump-thaw cycles. Isobutyl vinyl ether (IBVE, 99%, TCI) was dried over CaH_2 for 12 h and distilled under nitrogen and degassed by vigorously sparging with nitrogen for 30 minutes. Dichloromethane (DCM, J.T. Baker) was degassed by sparging with argon for 30 min and then purified by passing through two packed columns of neutral alumina under argon pressure on a JC Meyer solvent system. Ethyl acetate (99.5%, Fisher) was used as received. Tetrabutylammonium perchlorate (TBAP, 98%, TCI) was purified by recrystallization from ethyl acetate three times and dried under reduced pressure at 60 °C for 12 hours prior to use. 2,4,6-Tri-(*p*-methoxyphenyl)pyrylium tetrafluoroborate (**10**) was synthesized according to a known literature procedure.[1] *S*-1-isobutoxyethyl N,N-diethyl dithiocarbamate (**7**) and *S*-1-isobutoxyethyl *S'*-ethyl trithiocarbonate (**8**) were synthesized according to literature procedures.[2] Polymer samples were analyzed using size exclusion chromatography (SEC) operating with THF eluent. A Tosoh EcoSec HLC 8320GPC system with two SuperHM-M columns in series at a flow rate of 0.350 mL/min at 40 °C was used. All number-average molar masses (M_n), weight-average molar masses (M_w), and dispersities ($Đ$) for polymer samples were calculated from refractive index chromatograms against TSKgel polystyrene standards. Polymers samples synthesized at − 15 °C in $CDCl_3$ were analyzed using size exclusion chromatography (SEC) with THF eluent. A Waters ambient temperature system with a flow rate of 1.0 mL/min at 40 °C and a Waters 2412 refractive index detector was used. All number-average molar masses (M_n), weight-aver ge molar masses (M_w), and dispersities ($Đ$) for polymer samples were calculated from refractive index chromatograms against narrow polystyrene standards. Nuclear magnetic resonance (NMR) spectra were recorded on a Mercury 300 MHz, a Varian 400 MHz, a Bruker 500 MHz, or a Varian 600 MHz instrument.

Experimental Procedures.



7-Methoxyoxepan-2-one. 14.8 g *m*CPBA at room temperature (≥77% active oxygen content, 66 mmol, 1.7 eq.) were placed into an Erlenmeyer flask equipped with a stir bar. To the oxidant were added 130 mL of chloroform and the solution stirred over magnesium sulfate ($MgSO_4$) until no further caking was observed. While the *m*CPBA solution was drying over $MgSO_4$, a 250 mL 3-neck round bottom flask equipped with a stir bar, vacuum adapter, internal thermometer, and septum was flame-dried and backfilled with argon. Under positive pressure of argon the septum sealing one of the necks was removed and 4.25 g of sodium bicarbonate (51 mmol, 1.3 eq.) were added into the flask. Then the *m*CPBA solution was carefully decanted through a funnel into the flask and the neck resealed with the septum. The heterogeneous solution was placed in an ice/water bath and cooled under stirring until the internal temperature reached 0 °C. Using a syringe pump, a 6 mL disposable syringe with a Luer lock and an 18-gauge, long metal needle, 4.9 mL of 2-methoxycyclohexanone (5 g, 39 mmol, 1 eq.) were added to the solution over ca. 30 minutes, ensuring that the solution temperature did not exceed 10 °C at any point during the addition. The progress of the reaction was monitored by GC-MS (50to250SPLIT15), looking for disappearance of 2-methoxycyclohexanone at 6.4 min and appearance of MOPO at 8.0 min. Once the starting material was consumed the heterogenous mixture was filtered through a fritted funnel into a sidearm flask. The filtrate was transferred to a separatory funnel containing 100 mL of 10% w/v sodium sulfite to quench residual peracid. The organic layer was separated, washed with 100 mL of a saturated sodium bicarbonate solution, and 50 mL of brine. The combined aqueous layers were extracted with chloroform (2X 250 mL) and the combined organic fractions were dried over $MgSO_4$. At this point the integrity of MOPO was again verified by GC-MS analysis. Solvent was removed *in vacuo* and the residue transferred to a 25 mL 14/20, base-treated round bottom flask equipped with a stir bar. A spatula tip of calcium hydride was added to the round bottom flask and the crude material stirred over the drying agent for 1h. The crude was fractionally distilled in a Kugelrohr with two receiving bulbs (70 °C pot temperature, 500 – 200 mTorr), collecting the first droplets into the bulb furthest from the still pot and MOPO into the second bulb charged with 30 mg of polymer-supported dimethylaminopyridine [poly(DMAP)]. MOPO was collected onto poly(DMAP) as a clear, colorless liquid (3.8 g, 68% yield), was transferred into a 5 mL PTFE vial under inert atmosphere, and pumped into the glovebox immediately. The PTFE container was kept in the −20 °C freezer in the glovebox and purity of MOPO was assessed before each experiment by GCMS (Figure S4) and ^{1}H NMR spectroscopy (Figure S5).



MOPO **Chloromethylether (i)** **Chain transfer agent (9)**

6-Chloro-6-methoxyhexanoic acid **(i)**. In a glovebox 200 mg MOPO on poly(DMAP) were weighed into a vial and dissolved in 1.25 mL Et_2O. The solution was filtered into a clean vial through a 0.2 μm filter to remove poly(DMAP) beads from the solution. The vial was capped with a septum, removed from the glovebox and placed under argon in an ice/water bath. To the MOPO solution were added 0.85 mL 2 M HCl in Et_2O solution dropwise at 0 °C. The solution was warmed to room temperature and full conversion to the chloromethylether verified by ^{1}H NMR spectroscopy (Figure S22).

6-((Diethylcarbamothioyl)thio)-6-methoxyhexanoic acid **(9)**. Sodium N,N-diethyl dithiocarbamate trihydrate was dried by azeotropic distillation with toluene and stored in a vacuum desiccator. For the preparation of the chain transfer agent (CTA) 642 mg of the dried salt were placed in a dry vial and diluted with 10.3 mL Et_2O. The resultant suspension was stirred and cooled to 0 °C, then the previously prepared solution of chloromethylether **(i)** in Et_2O was added dropwise to the salt suspension. The ice bath was removed and the suspension stirred at room temperature for 1.5h. Full conversion to chain transfer agent **9** was verified by ^1H NMR spectroscopy. Ether was evaporated under vacuum and the residual solid dissolved in a minimum amount methylene chloride. The crude was purified by flash column chromatography on silica (2X, 100/1 mass silica/mass sample, first with 8/2 hexanes/EtOAc containing 5% AcOH, then 6.5/3.5 hexanes/EtOAc containing 5% AcOH to eliminate streaking of the acid on silica) yielding 60 mg of pure CTA **9** (15% yield, Figure S23).

Poly(MOPO) Synthesis with TfOH. A stock solution of $[MOPO]_0$ = 4M in $CDCl_3$ over poly(DMAP) was prepared in a Strauss flask in the glovebox. For each reaction, the desired amount of MOPO solution was removed, filtered into a scintillation vial to remove poly(DMAP), and diluted with $CDCl_3$ to a final concentration of $[MOPO]_0$ = 2 M. The vial was capped and returned to the glovebox freezer for 30 min to bring the temperature of the solution to −20 °C. The desired amount of TfOH was added from a stock solution of TfOH in DCM ([TfOH] = 0.043 M) via microsyringe addition directly into the solution. The vial was immediately returned to the freezer and left to react. The polymerizations were quenched using either a stock solution of sodium phenoxide in MeOH or via addition of Amberlyst A21 beads to the polymerization. Poly(MOPO) was precipitated into cold 9/1 hexanes/THF and dried under high vacuum at room temperature.

Photomediated Cationic RAFT Polymerization of MOPO. In a nitrogen filled glovebox, an oven-dried one-dram vial was equipped with a stir bar and charged with MOPO (60 mg, 0.42 mmol, 42 eq). A stock solution of 2,4,6-tri-(*p*-methoxyphenyl)pyrylium tetrafluoroborate (**10**) in DCM (0.05 mL 2.1 mM, 0.1 µmol, 0.02 mol% relative to MOPO) and a stock solution of **7** in DCM (0.01 mL, 1.2 M, 0.010 mmol, 1 eq) were then added. The vial was sealed with a septum cap under an atmosphere of nitrogen, placed next to blue LED strips (~450 nm) outside of the glovebox, and stirred while cooling by blowing compressed air over the reaction vial. Following the desired amount of reaction time, aliquots for NMR and SEC analysis were taken. High conversions (>50 %) were generally reached within 0.6 h. Typical SECs for poly(MOPO) samples synthesized with CTAs **7**, **8**, and **9** are displayed in Figure S24.

For reactions performed in $CDCl_3$, the procedure above was used with $CDCl_3$ in place of DCM. The polymerizations were performed outside of the glovebox with the vial/blue LED strips set-up inside a container filled with a salt water/ice bath at –15 °C. Under these conditions (30:1 MOPO:CTA, CTA **7**), we observed a much slower polymerization rate (15% conversion after 1.8 h) in an uncontrolled fashion compared with polymerizations performed in DCM at rt. Lowering the MOPO:CTA ratio (15:1) results in a similar conversion (12% after 1.8 h) in an uncontrolled fashion. Like the rt/DCM conditions, here a decrease in the M:CTA ratio results in a decrease in the M_n. SEC traces for these two polymers are shown in Figure S25.

Cyclic Voltammogram Studies. Cyclic voltammetric (CV) measurements were performed in a three-compartment glass cell with medium porosity glass frits separating the compartments. An Ag/Ag^+ reference electrode and a Pt wire counter electrode were used, unless otherwise specified. All 3-mm glassy carbon (GC) electrodes were purchased from CH Instruments. Prior to each experiment, electrodes were polished, sequentially, with 1.0 µm, 0.3 µm, and 0.05 µm Alumina in water on polishing paper. Following polishing, electrodes were sonicated in ethanol for 30 seconds and air dried. For the CV of MOPO, a 0.1 M tetrabutylammonium perchlorate (TBAP) electrolyte solution was prepared in DCM. Using this TBAP solution as solvent, a 2.8

mM solution of MOPO was prepared. CVs of the 0.1 M TBAP electrolyte solution were taken until a constant CV trace was obtained (Figure S26), and then a CV was acquired with the 2.8 mM MOPO in a 0.1 M TBAP solution (Figure S27). A final CV of the 0.1 M TBAP electrolyte solution was taken after the MOPO CV (Figure S27).

Fluorescence Quenching Studies. A Varian Cary Eclipse Fluorescence Spectrophotometer was used for the quenching studies. A solution of 2,4,6-tri-(*p*-methoxyphenyl)pyrlium tetrafluoroborate (**10**) was excited at 475 nm and the fluorescence spectra were recorded between 480 and 700 nm. The emission of a 0.21 mM solution of **10** in DCM was measured at varying concentrations of MOPO (0−18 mM). As shown in Figures S28 and S29, fluorescence quenching was not observed in this range.

Photomediated Cationic Copolymerization of MOPO and IBVE. In a nitrogen filled glovebox, an oven-dried one-dram vial was equipped with a stir bar and charged with MOPO (24 mg, 0.17 mmol, 14 eq, 8 mol% in feed ratio) and IBVE (0.26 mL, 1.99 mmol, 173 equiv, 92 mol% in feed ratio). A stock solution of 2,4,6-tri-(*p*-methoxyphenyl)pyrylium tetrafluoroborate (**10**) in DCM (0.2 mL 2.1 mM, 0.4 µmol, 0.02 mol% relative to MOPO) and a stock solution of **7** in DCM (0.01 mL, 1.2 M, 0.010 mmol, 1 eq) were then added. The vial was sealed with a septum cap under an atmosphere of nitrogen, placed next to blue LED strips (~450 nm) outside of the glovebox, and stirred while cooling by blowing compressed air over the reaction vial. Following the desired amount of reaction time, aliquots for NMR and SEC analysis were taken. After 3 h, the polymerization had reached 100% conversion of MOPO and 42% conversion of IBVE. The polymer sample was then dried under vacuum. The ^{1}H and ^{13}C spectrum of poly(MOPO-*co*-IBVE) are shown in Figures S30–S33. 2D NMR (COSY, HSQC, and HMBC) spectra were taken to fully characterize the acylacetoxy resonances and are shown in Figures S34–S36.

Degradation Testing of Poly(MOPO-co-IBVE), Poly(MOPO), and Poly(IBVE). Poly(MOPO) used for degradation testing was synthesized through the general procedure above without any added CTA was used without purification from the crude reaction mixture in DCM, while poly(IBVE) synthesized using a known ferrocenium catalyzed polymerization[3] was used without purification from the crude reaction mixture in DCM. HCl (3 M, 1 mL) was added to both crude reaction mixtures, and the mixtures stirred at rt for 7 h. Following this, an aliquot was taken for SEC and ^{1}H NMR spectral analysis. For poly(IBVE) the SEC aliquot was taken after 92 h. ^{1}H NMR spectra showed no major spectral change for poly(IBVE) (Figure S42) and complete loss of polymer resonances for poly(MOPO) (Figure S40). SEC traces for poly(IBVE) show a small loss of molecular weight after 92 h (Figure S43), while poly(MOPO) shows complete loss of polymer after 7 h (Figure S41). For poly(MOPO-*co*-IBVE), a small amount of polymer that had been dried overnight under vacuum (ca. 5 mg) was diluted with $CDCl_3$ (1 mL) and HCl (3 M, 1 mL) and stirred at room temperature for 7 h. Following this, an aliquot was taken for SEC and NMR spectral analysis. SEC analysis showed loss of molecular weight after stirring in HCl (Figure 6, main text), while NMR spectral analysis showed complete disappearance of the poly(MOPO) resonances in the copolymer (Figure S39).

Supporting Figures (S1 – S43)

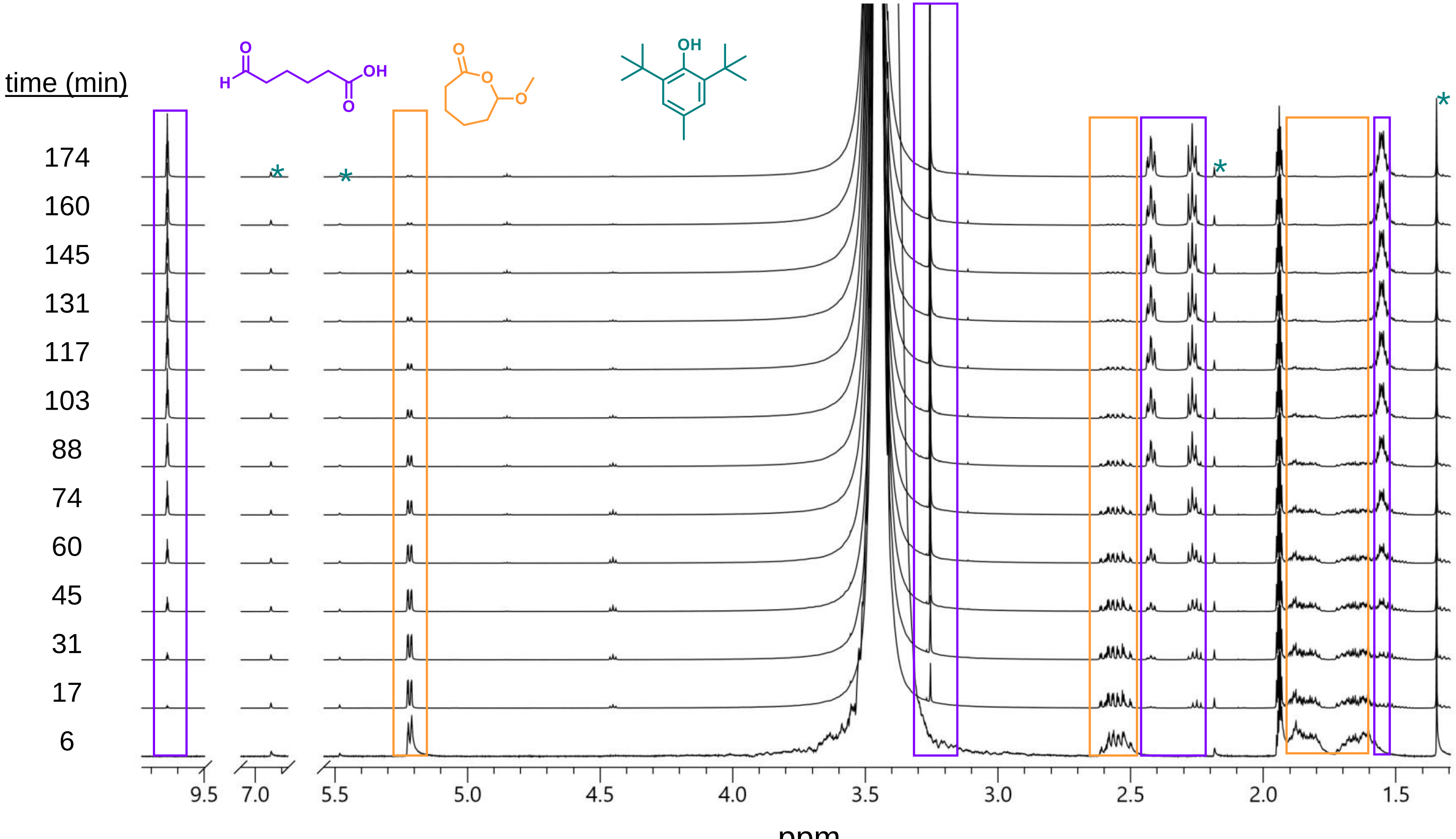


Figure S1. Hydrolysis of MOPO (3.6 mg in 0.45 mL CD_3CN) containing ca. 1% butylated hydroxytoluene treated with 0.1 mL H_2O and monitored by ^1H NMR spectroscopy over time.

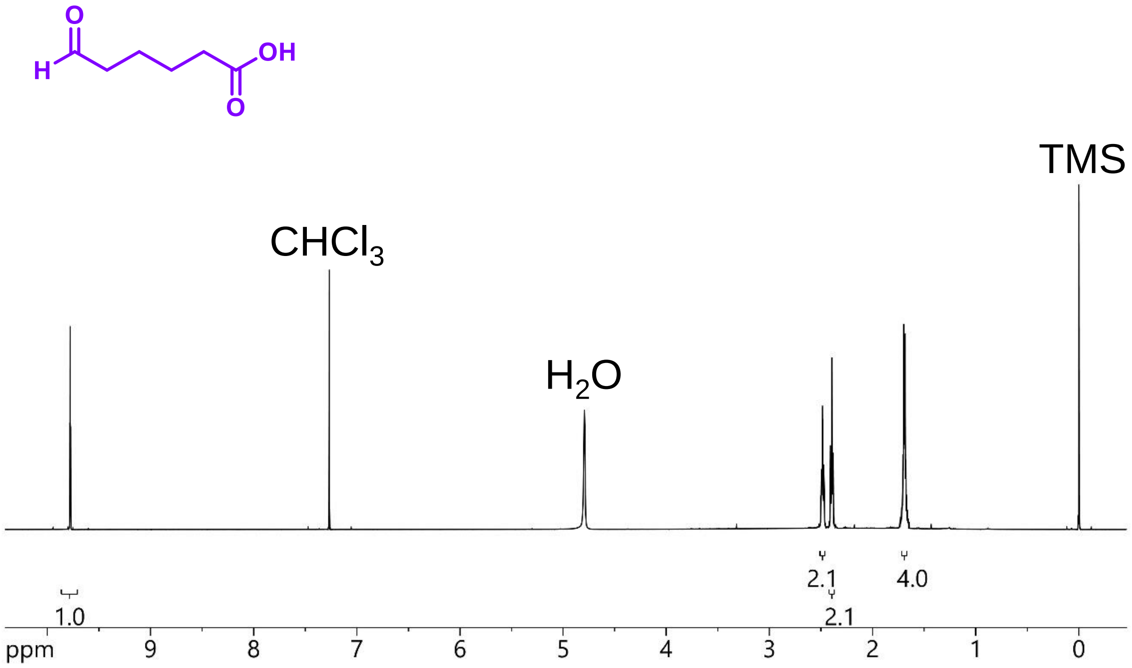


Figure S2. ^{1}H NMR spectrum (CDCl$_3$) of the MOPO hydrolysis product obtained in acetonitrile/water, extracted into CDCl$_3$. The observed signals are in good agreement with those previously reported for 6-oxohexanoic acid.[4]

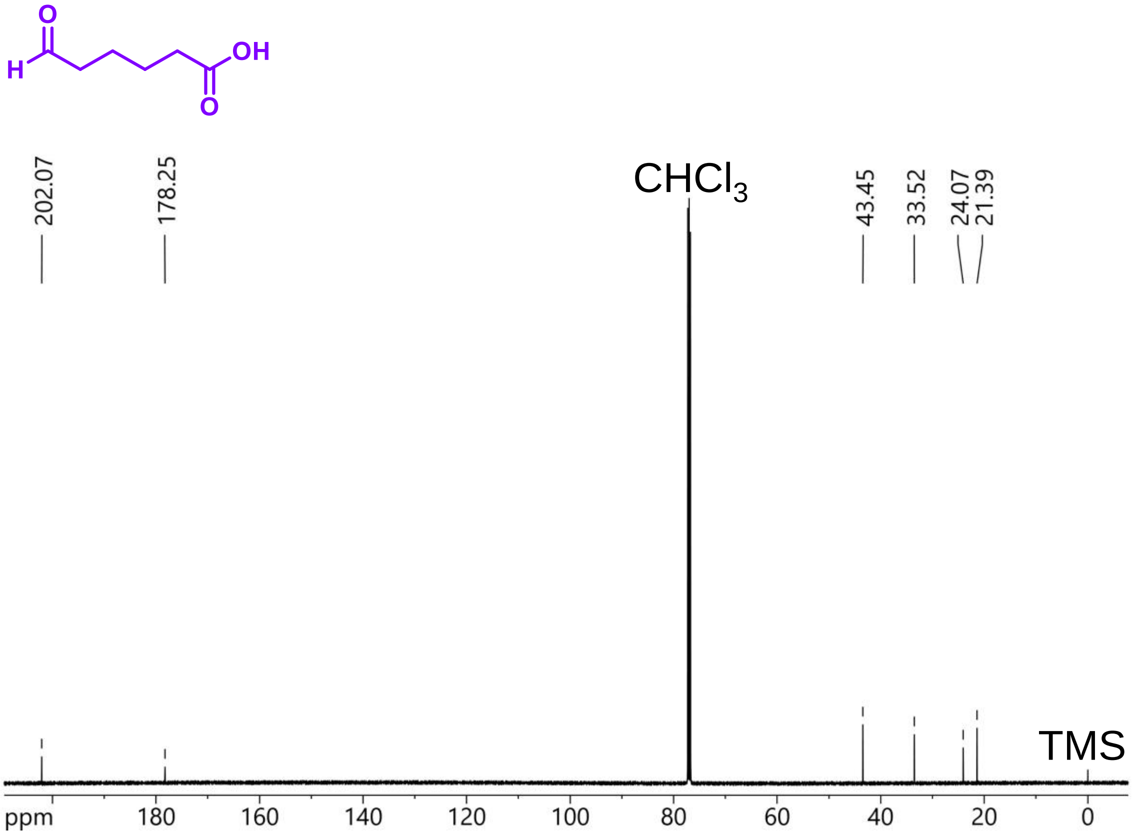


Figure S3. ^{13}C NMR spectrum ($CDCl_3$) of the MOPO hydrolysis product obtained in acetonitrile/water, extracted into $CDCl_3$. The observed signals are in good agreement with those previously reported for 6-oxohexanoic acid.[4]

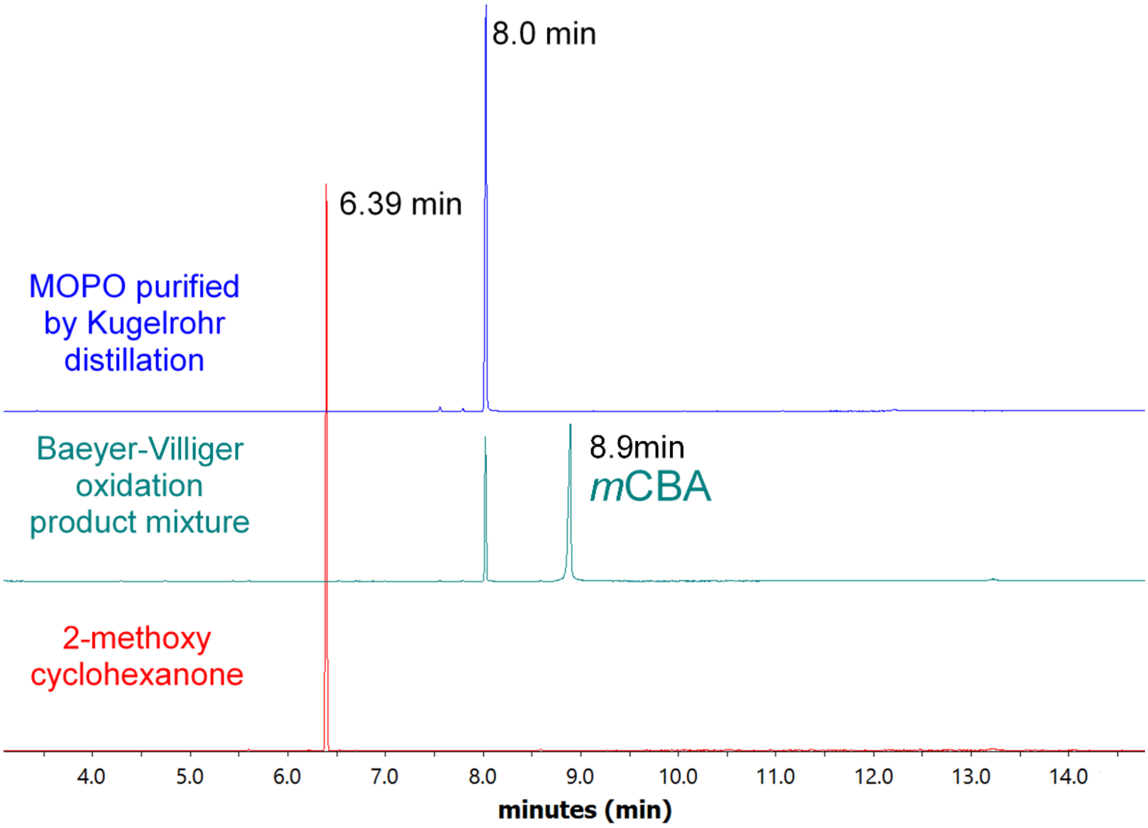


Figure S4. Gas chromatography traces of commercial 2-methoxycyclohexanone, product mixture after Baeyer-Villiger oxidation of 2-methoxycyclohexanone, and 7-methoxyoxepan-2-one (MOPO) after purification by Kugelrohr distillation. All samples were analyzed with the method 50to250SPLIT15.

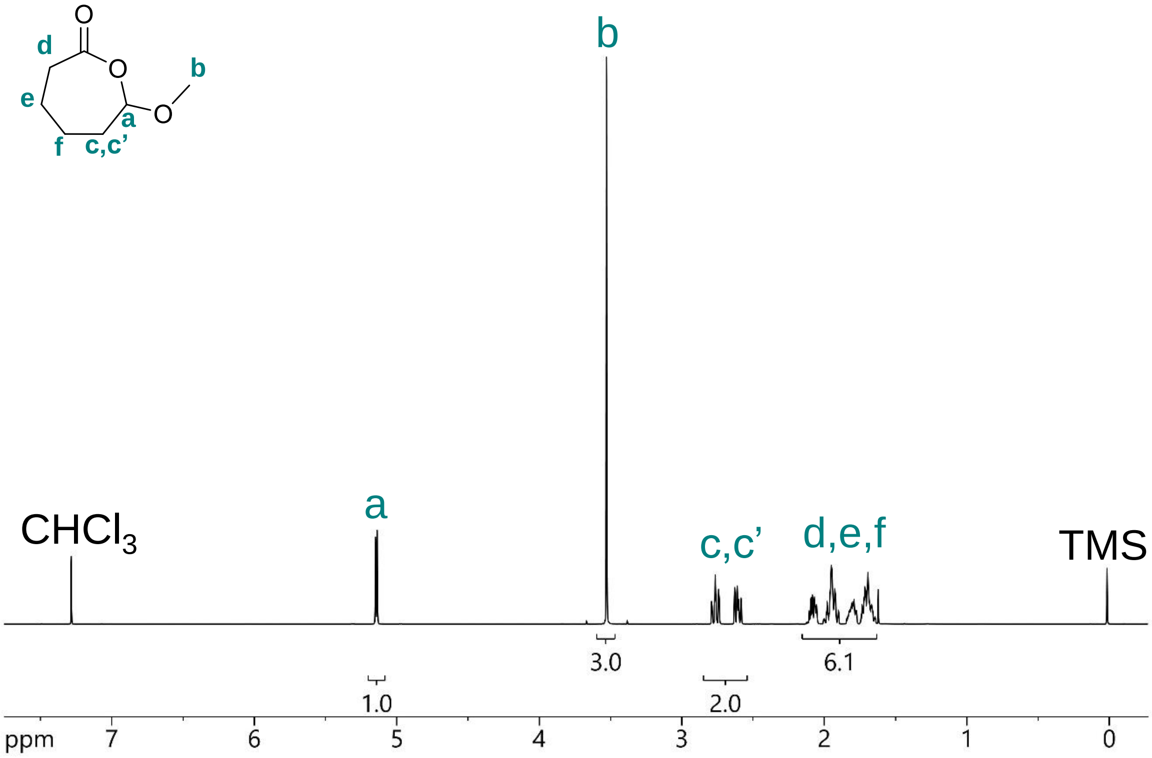


Figure S5. ^{1}H NMR spectrum ($CDCl_3$) of MOPO purified by Kugelrohr distillation.

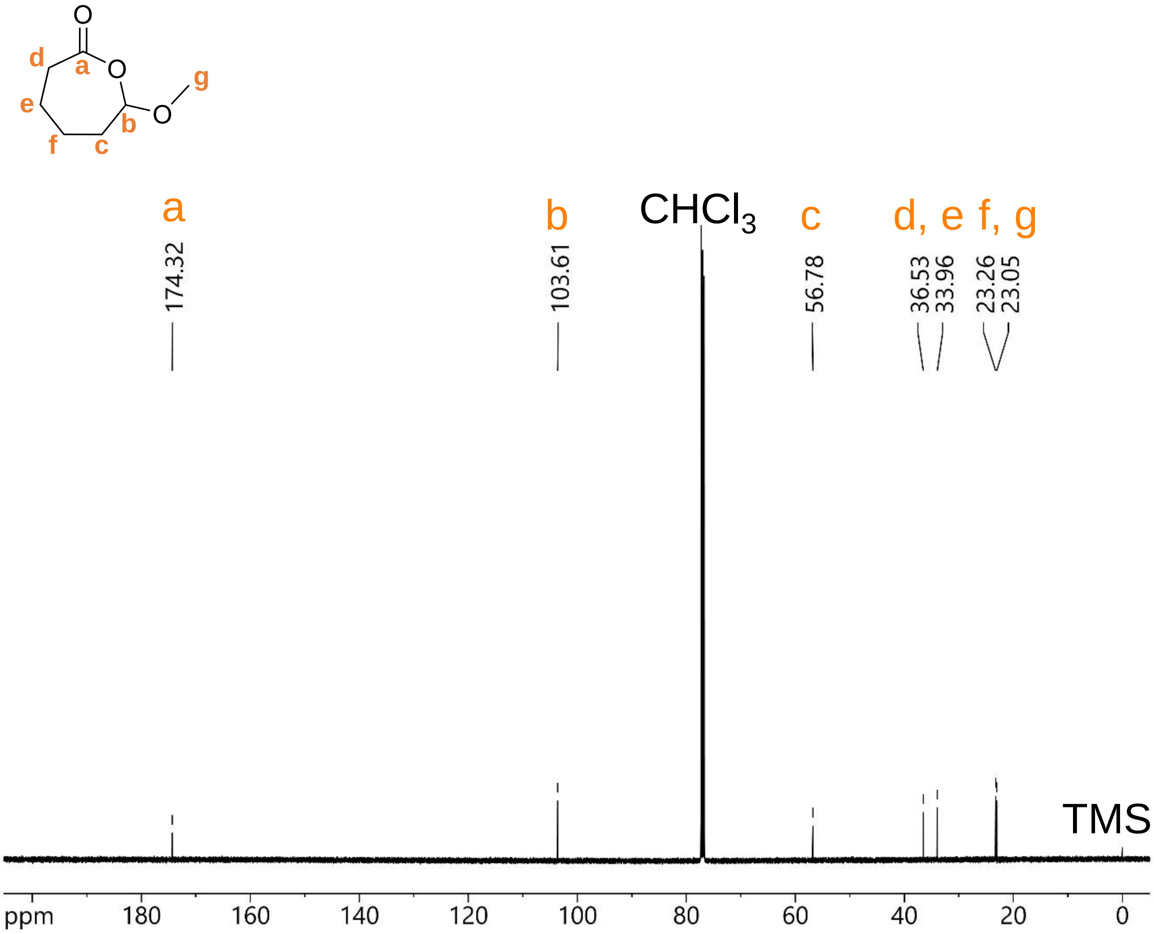


Figure S6. ^{13}C NMR spectrum (CDCl$_3$) of MOPO purified by Kugelrohr distillation.

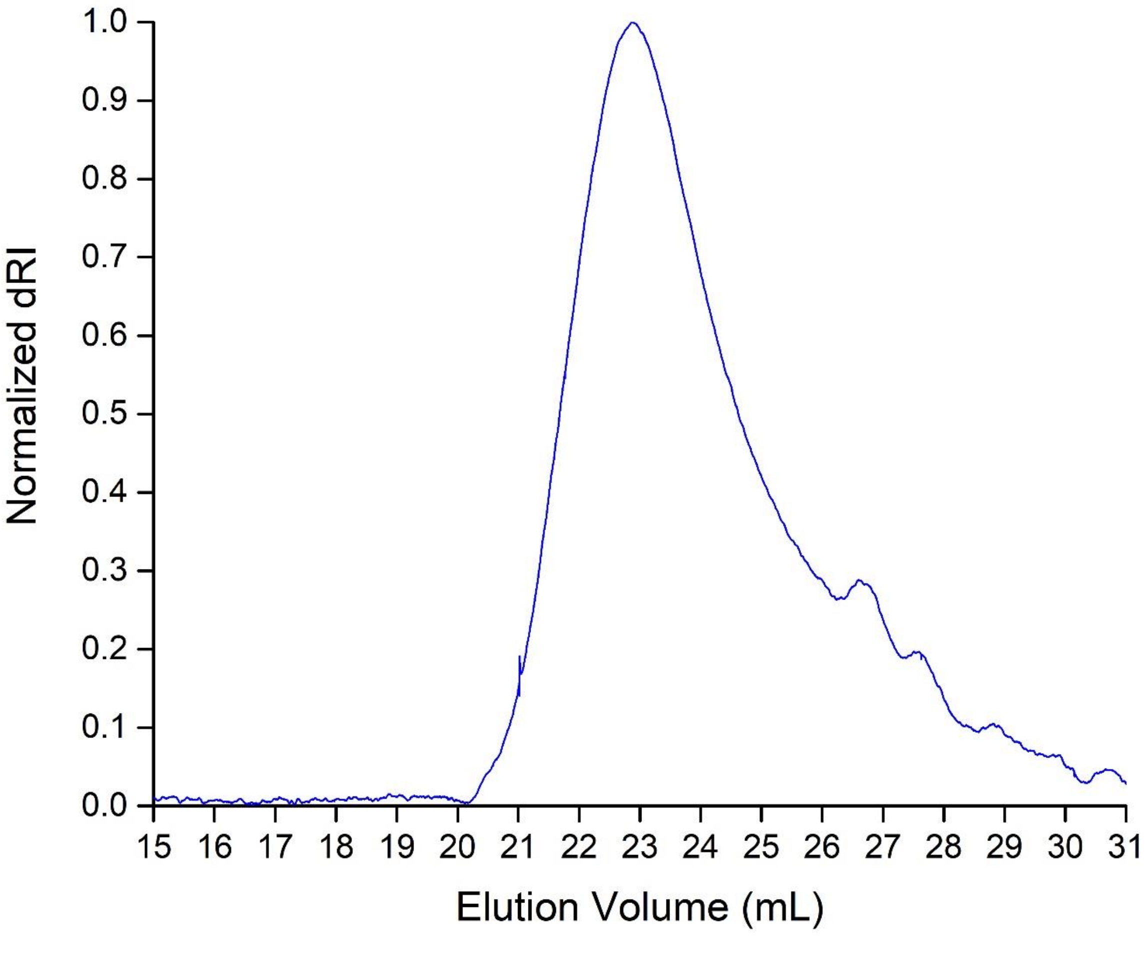


Figure S7. Chloroform SEC trace of poly(MOPO) prepared in the bulk with $[\mathrm{MOPO}]_0/[\mathrm{HCl}]_0 = 500$ and $[\mathrm{MOPO}]_0/[\mathrm{BnOH}]_0 = 50$. Molar mass analysis relative to PS standards: $M_n = 8.6$ kg/mol, $M_w = 14$ kg/mol, $Đ = 1.65$. The polymerization had ceased at 60% conversion.

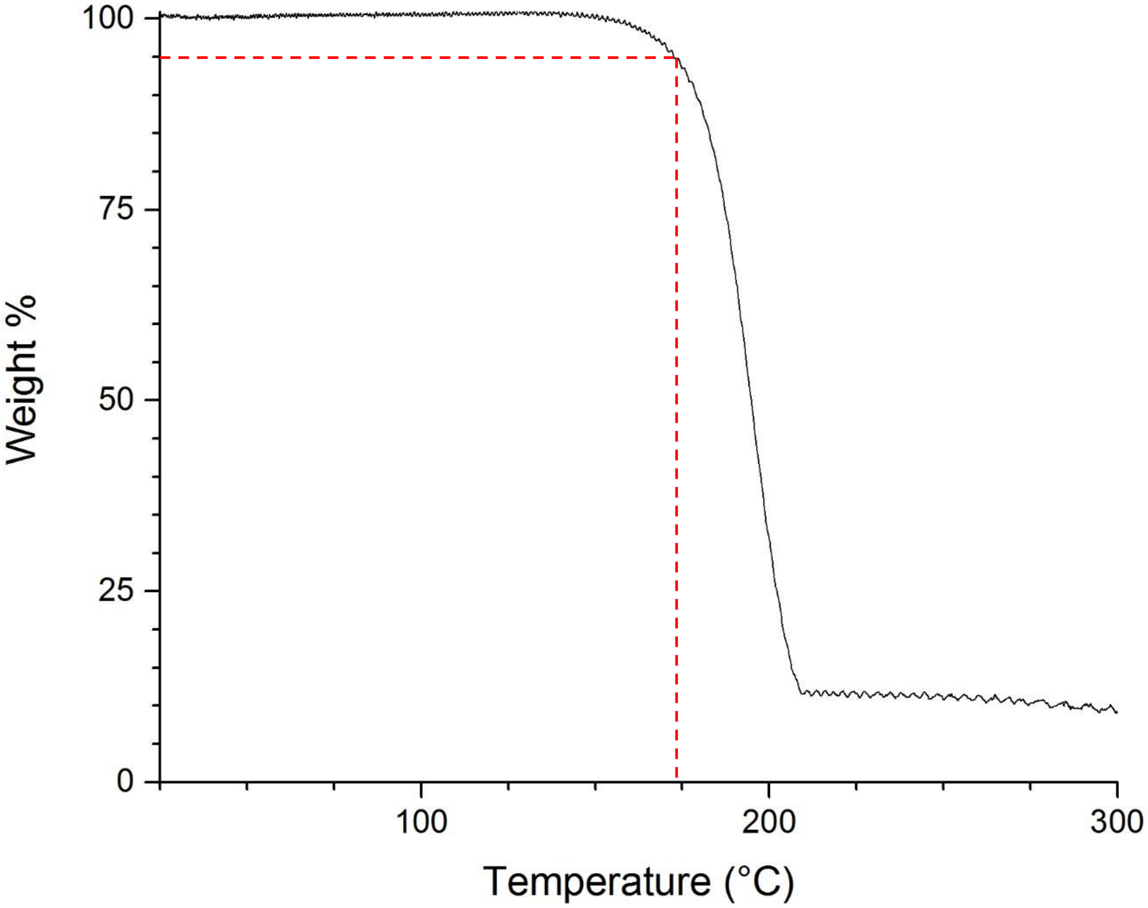


Figure S8. TGA trace obtained for poly(MOPO) of $M_{n,SEC}$ = 8.6 kg/mol (relative to PS standards). Indicated on this plot is $T_{d,95\%}$ = 175 °C.

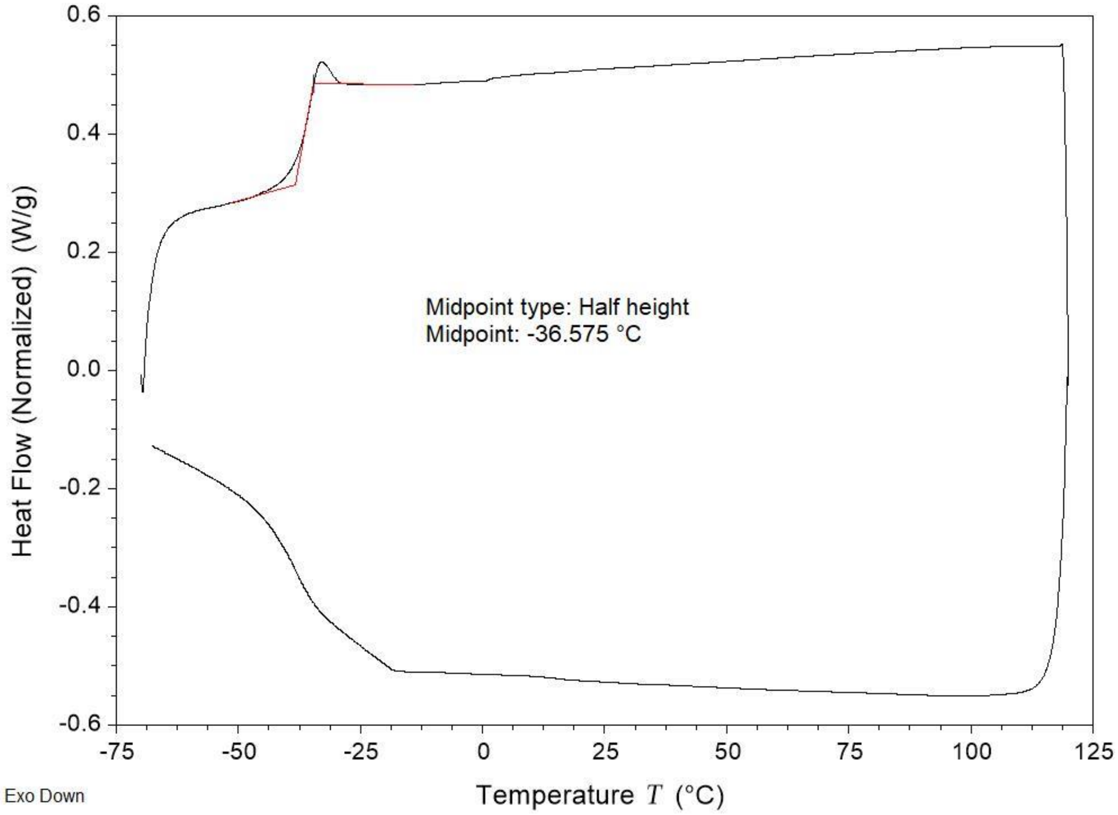


Figure S9. DSC trace for poly(MOPO) (second heat) with M_n = 8.6 kg/mol (relative to PS standards). A glass transition temperature is observed at $T_g = -37$ °C.

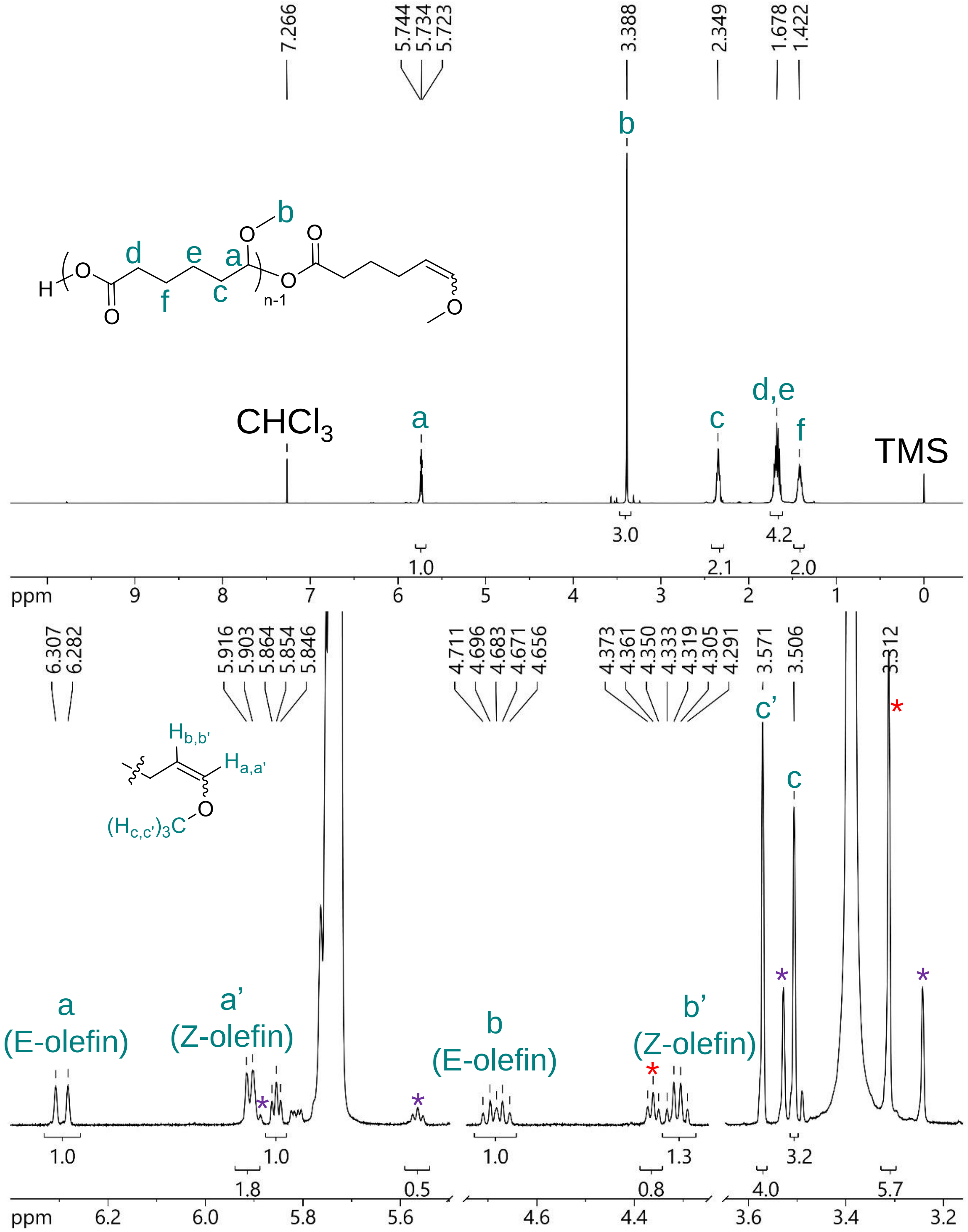


Figure S10. ^{1}H NMR spectrum (CDCl$_3$) of precipitated poly(MOPO) obtained by an ACE mechanism (in neat MOPO, [MOPO]$_0$/[HCl]$_0$ = 500). A mixture of E- and Z-enol ethers were observed as end groups, in good agreement with spectral data reported previously.[5] *Indicates satellite peaks of poly(MOPO) backbone resonances. *These signals are attributed to 6,6-dimethoxyhexanoic acid, a MOPO degradation product.

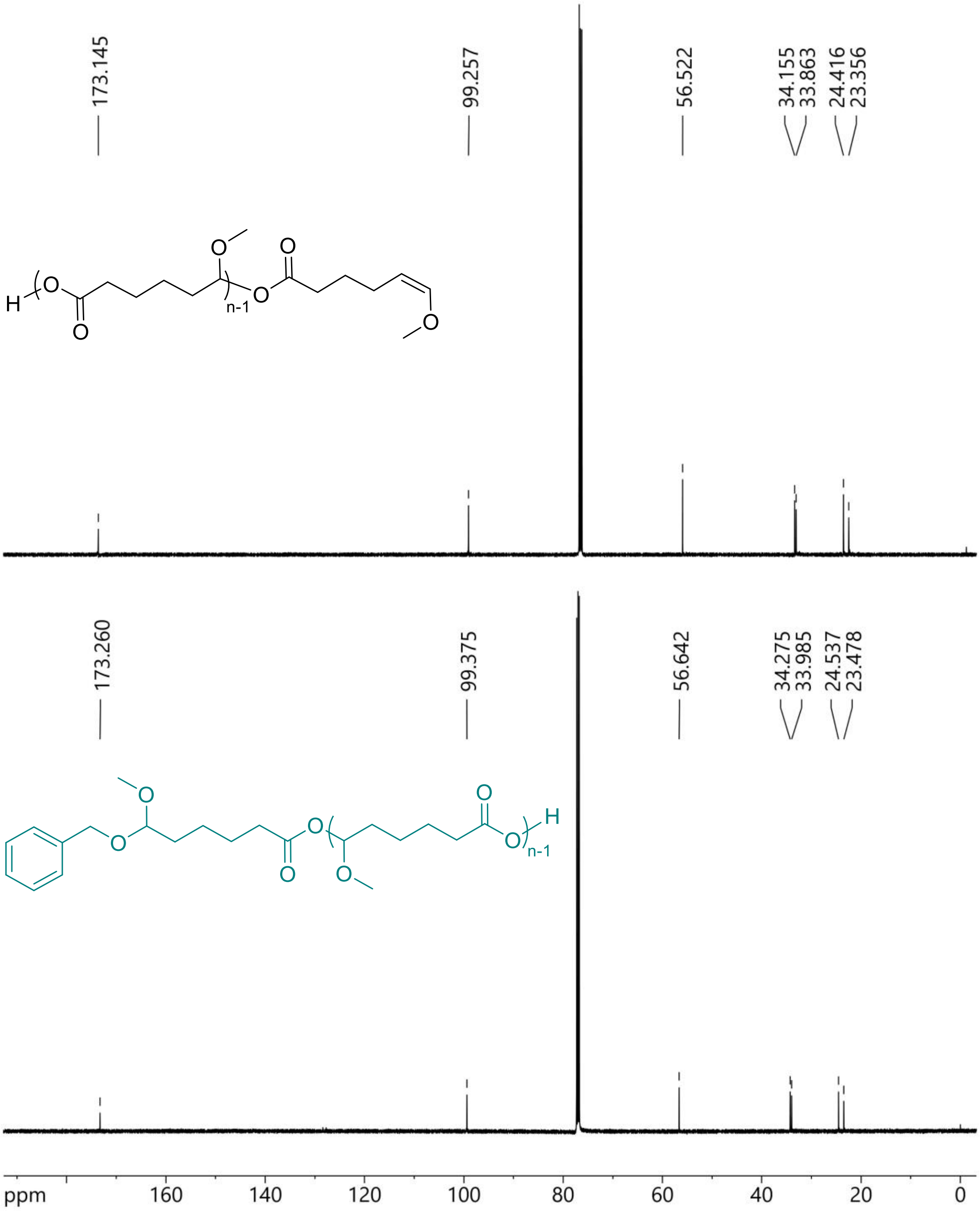


Figure S11. ^{13}C NMR spectra ($CDCl_3$) of poly(MOPO) obtained *without* BnOH (in black) and *with* BnOH (in turquoise) using HCl as the catalyst ($[MOPO]_0/[HCl]_0 = 500$, $[MOPO]_0/[BnOH]_0 = 50$).

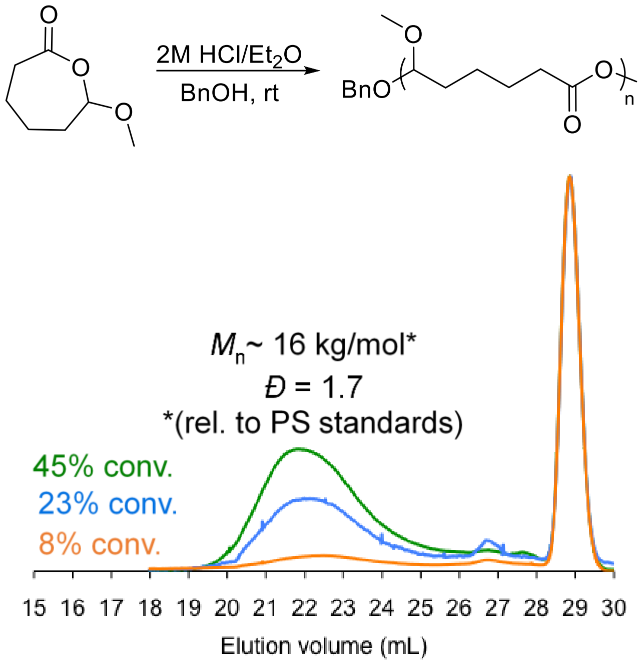


Figure S12. Evolution of molar mass in the cationic ROP of neat MOPO with HCl and BnOH ($[\mathrm{MOPO}]_0/[\mathrm{HCl}]_0$ ~ 1,000 and $[\mathrm{MOPO}]_0/[\mathrm{BnOH}]_0$ ~ 100).

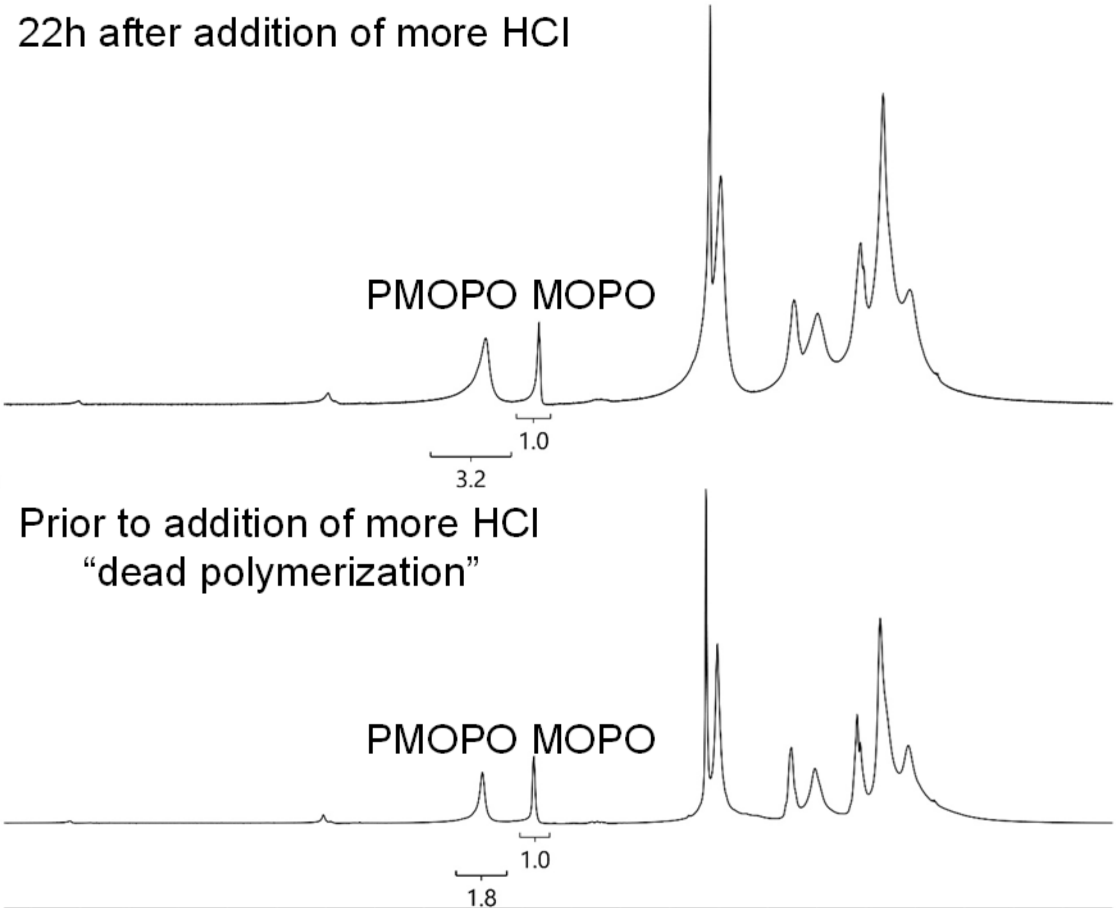


Figure S13. No deuterium ^1H NMR spectra ($CDCl_3$) of poly(MOPO) obtained with HCl and BnOH. The bottom spectrum depicts a neat MOPO polymerization where polymerization has ceased at 64% conversion. After addition of more HCl catalyst to the NMR experiment and waiting 22h conversion has increased to 76%, suggesting that the active species in the polymerization with HCl is quenched by irreversible chloride counterion collapse prior to reaching equilibrium conversion.

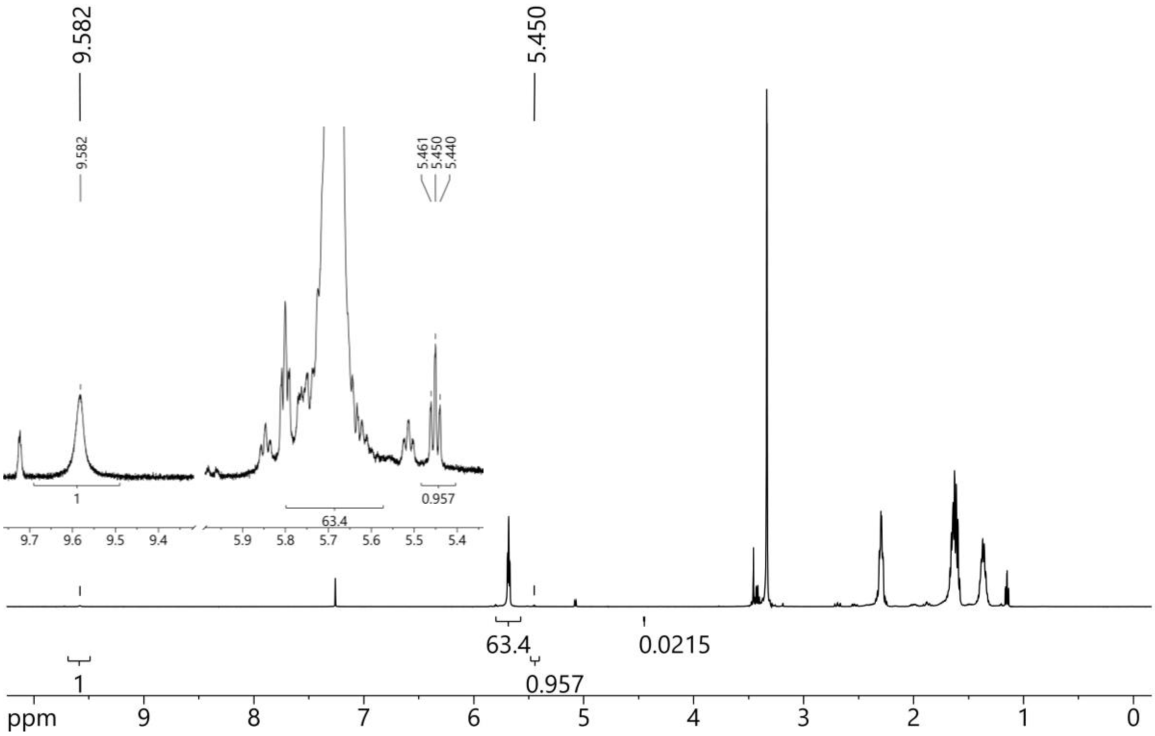


Figure S14. ^{1}H NMR spectrum ($CDCl_3$) showing 99% conversion of MOPO to poly(MOPO) when polymerized in solution ($[MOPO]_0$ = 1M, $[MOPO]_0/[HCl]_0$ = 100). A chloroalkyl methyl ether end group is observed as a triplet at δ = 5.48 ppm as well as a carboxylic acid end group at δ = 9.58 ppm, which is shifted upfield due to the high concentration of poly(MOPO) in $CDCl_3$.

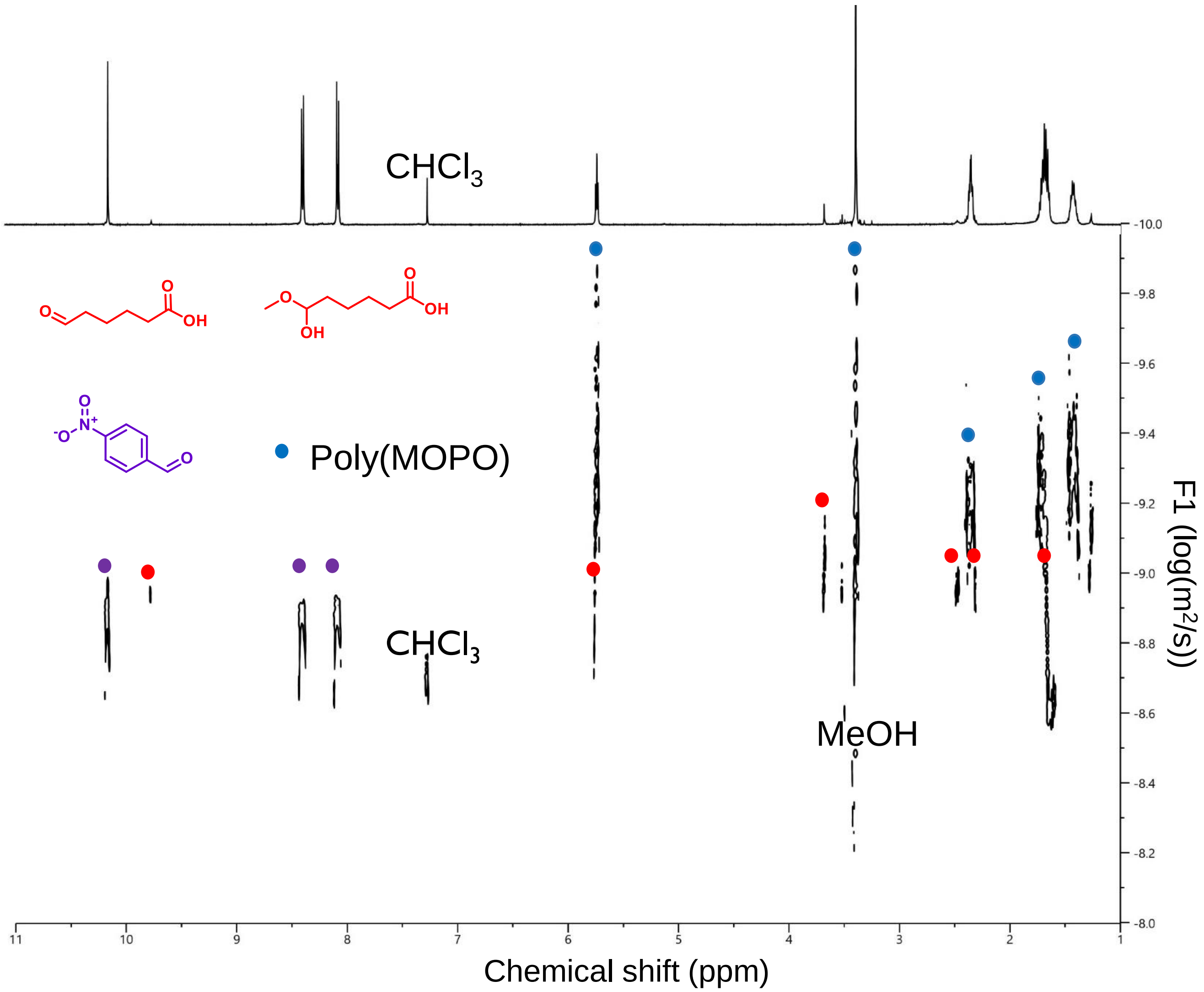


Figure S15. DOSY NMR spectrum of poly(MOPO) containing 1% 6-oxohexanoic acid contaminant. It should be noted that poly(MOPO) in this instance was synthesized using diethylzinc as the catalyst rather than HCl. However, the NMR shifts observed for 6-oxohexaoic acid in this instance are in good agreement with those observed in HCl-catalyzed MOPO cationic ROP.

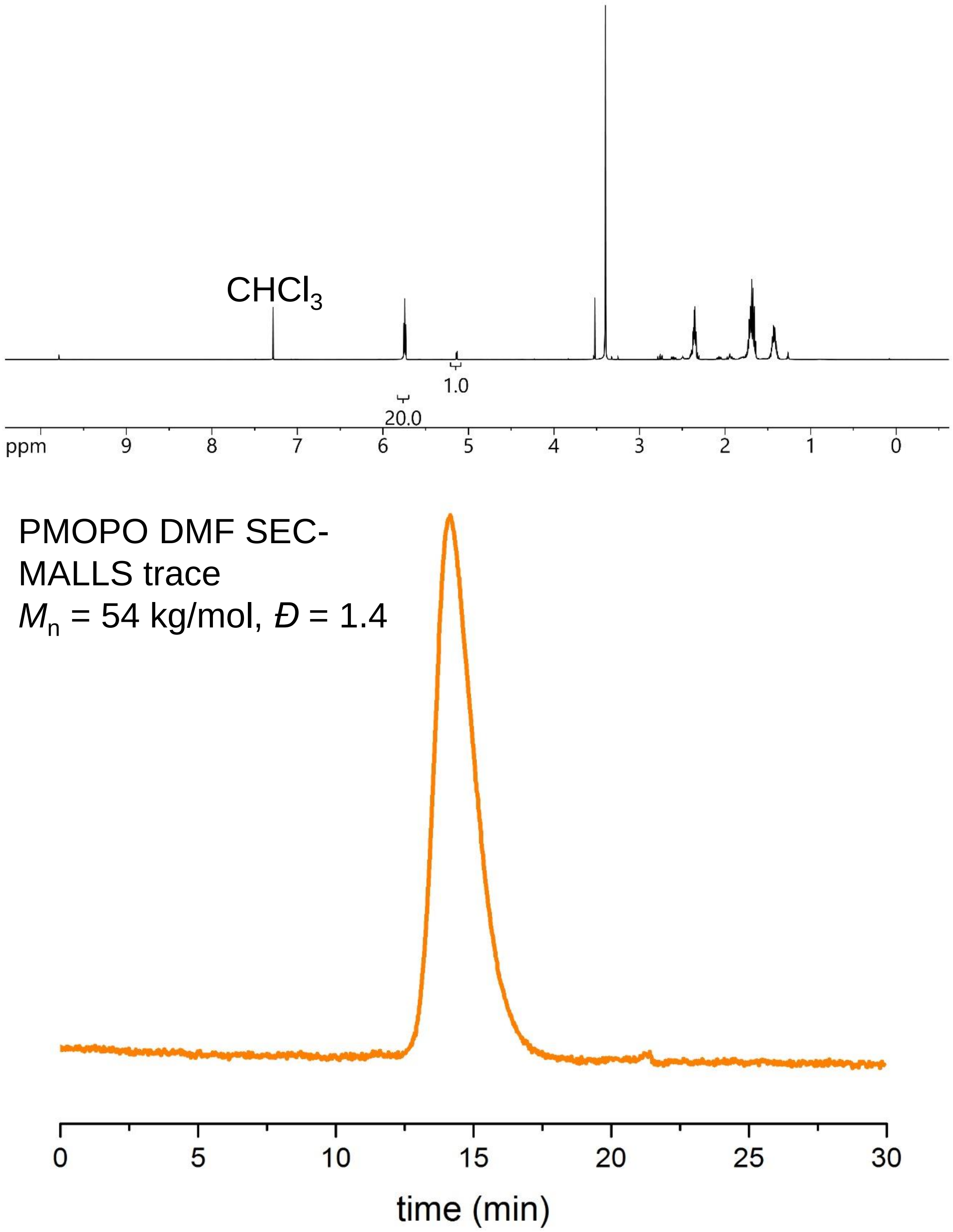


Figure S16. Top: ^{1}H NMR spectrum showing > 95% conversion of MOPO to poly(MOPO) when polymerized in $CDCl_3$ solution with MeOTf ($[MOPO]_0 = 2.25M$, $[MOPO]_0/[MeOTf]_0 = 550$). Bottom: DMF SEC-MALLS trace of purified poly(MOPO) obtained via solution polymerization with MeOTf.

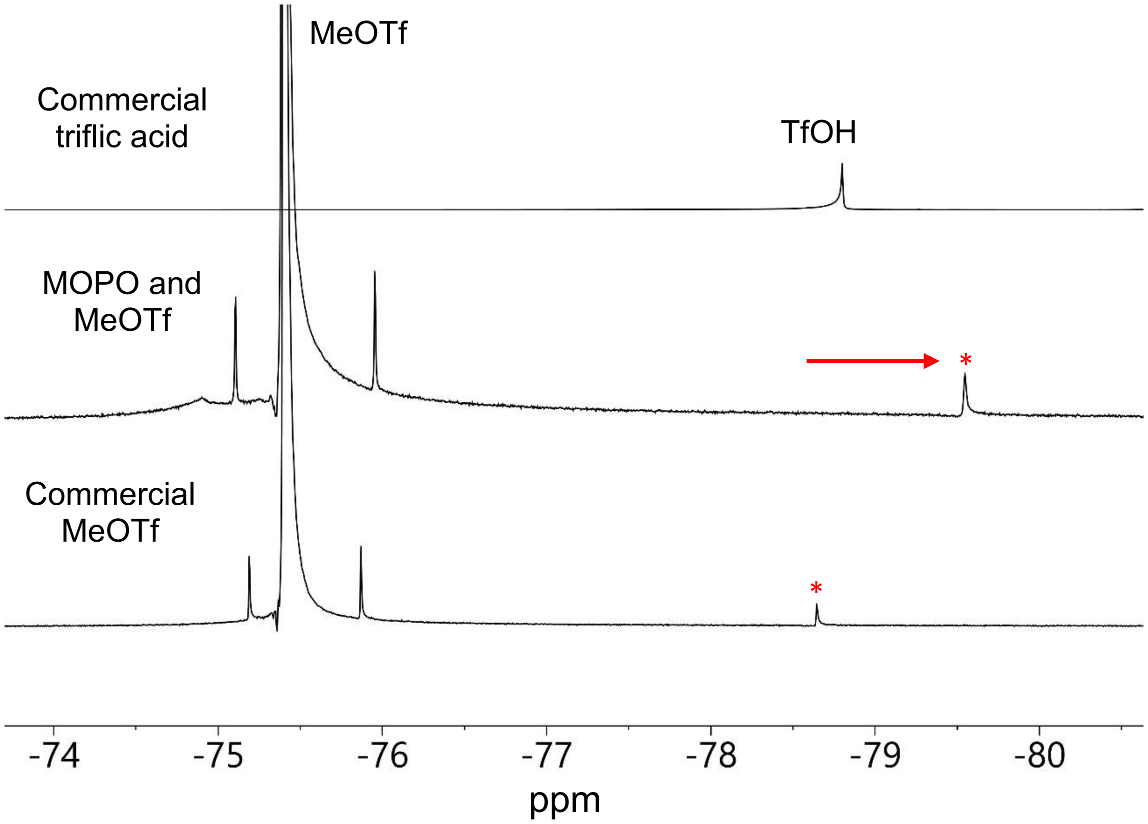


Figure S17. ^{19}F NMR spectra ($CDCl_3$) of: methyl triflate (bottom), a 1/1 mixture of methyl triflate and MOPO (middle), and triflic acid (top).

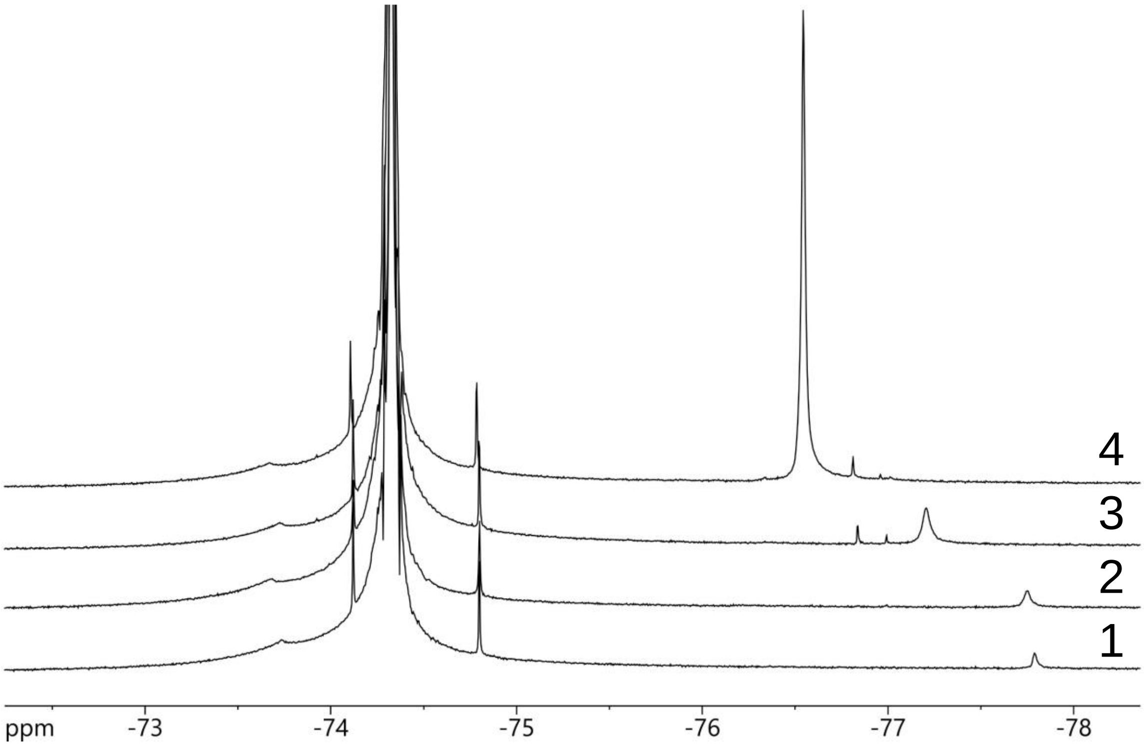


Figure S18. Dependence of triflic acid ^{19}F NMR shift on concentration. **1:** 10 μL commercial MeOTf in 0.4 mL $CDCl_3$. **2:** After addition of 1 μL 0.94 M TfOH to **1**. **3:** After addition of another 8 μL of 0.94M TfOH to **2**. **4:** after addition of 1 μL concentrated TfOH to **3**.

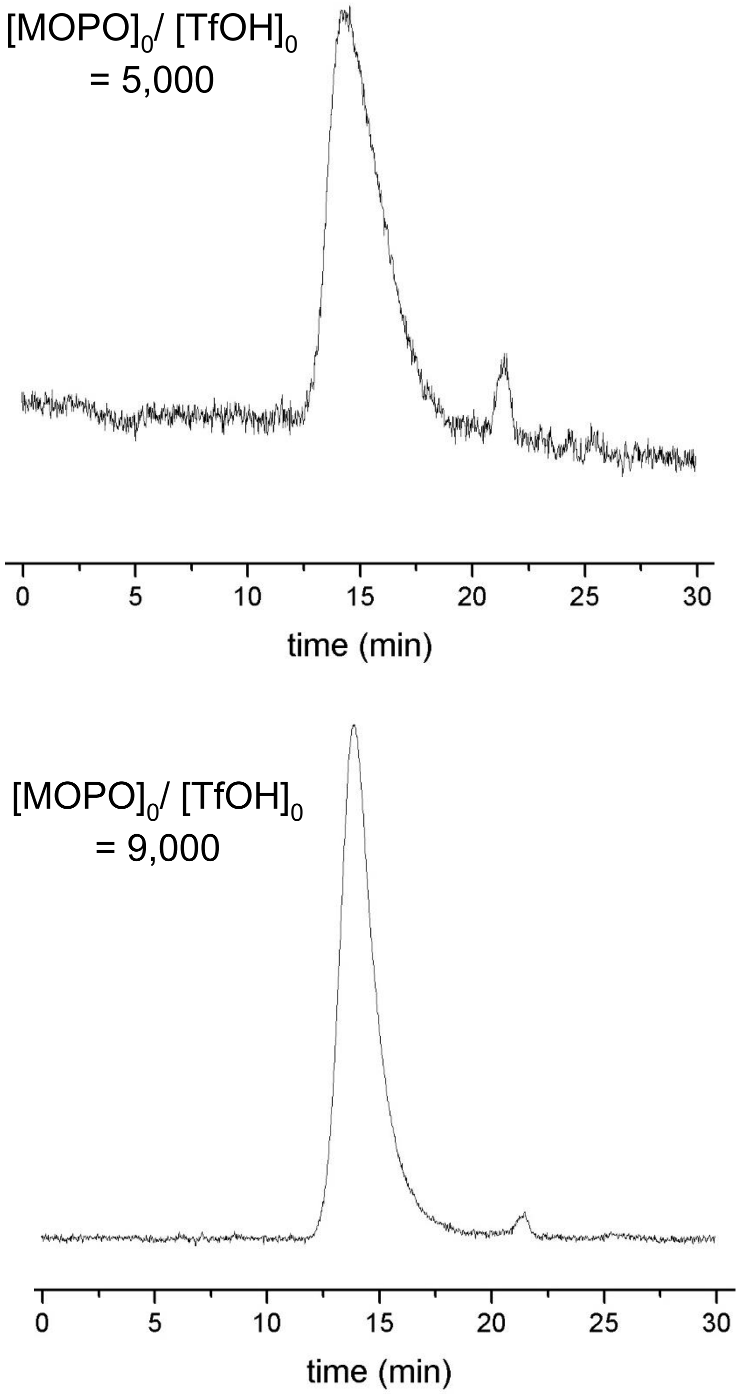


Figure S19. DMF SEC-MALLS traces for poly(MOPO) synthesized with TfOH. Top: M_n = 23 kg/mol, $Đ$ = 2.1. Bottom: M_n = 64 kg/mol, $Đ$ = 1.7.

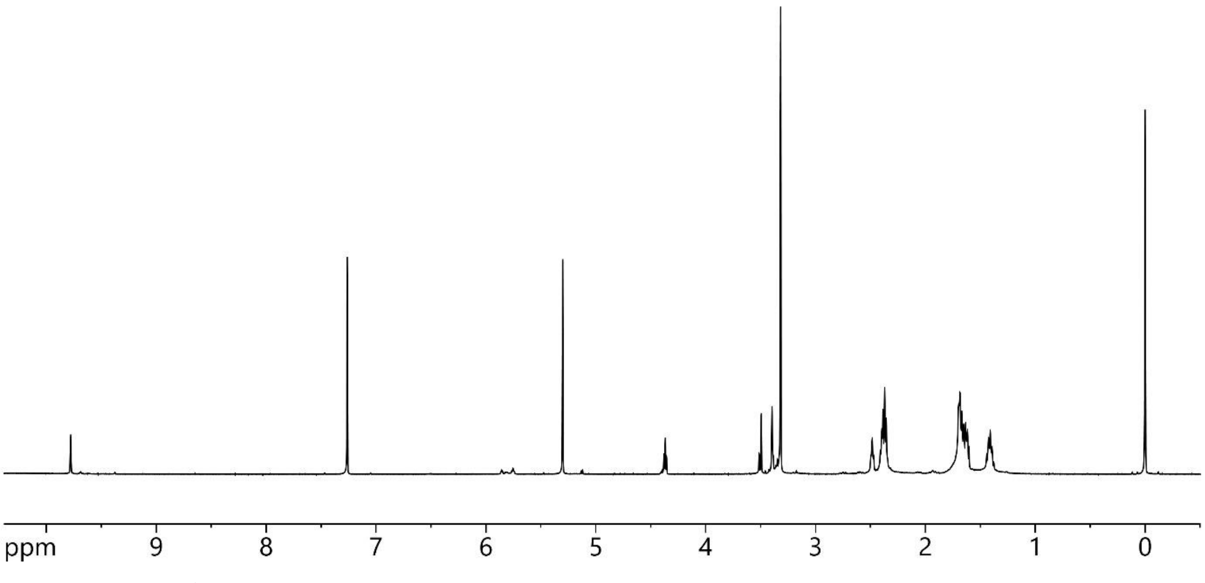


Figure S20. ^{1}H NMR ($CDCl_3$) spectrum of $[MOPO]_0$ = 4M in $CDCl_3$ treated with $[MOPO]_0/[TfOH]_0$ = 600 at −20 °C and quenched after 1 minute with Amberlyst A21 beads. Discoloration of the reaction medium was observed immediately, indicating decomposition. The spectrum shows a mixture of 6-oxohexanoic acid and related hemiacetals (c.f. Figure S2).

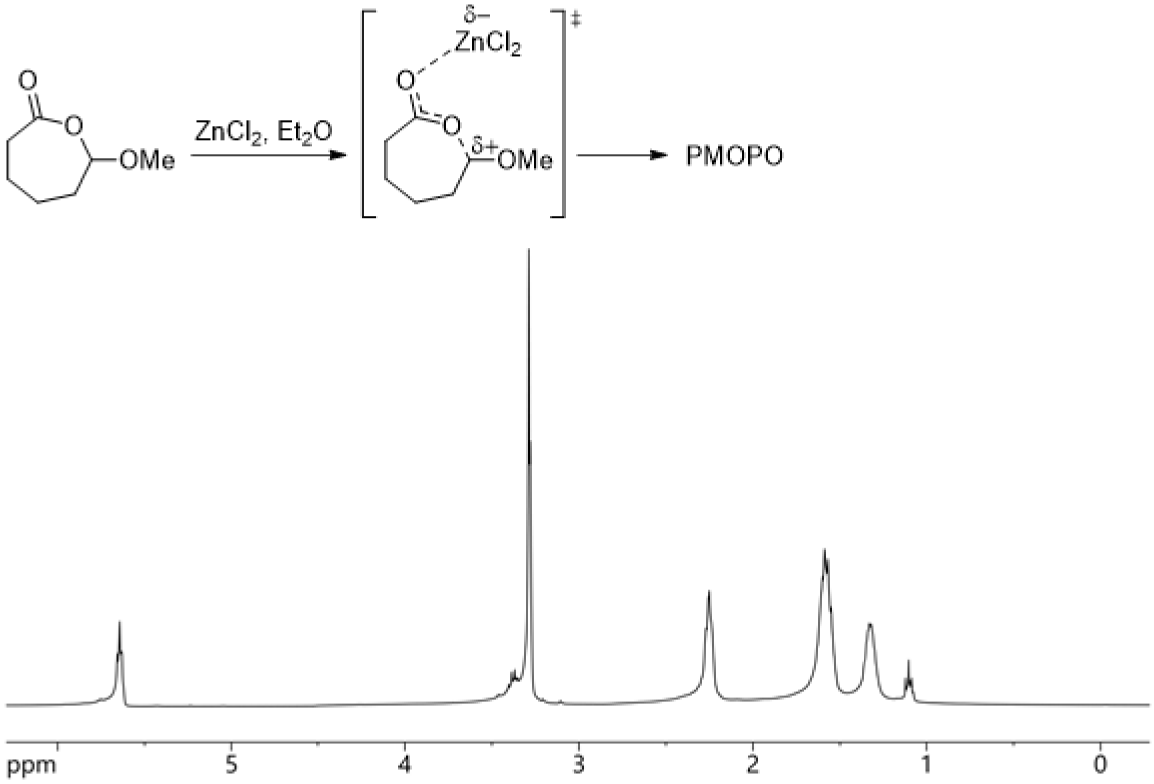


Figure S21. ^{1}H NMR spectrum of 2.24 M MOPO in $CDCl_3$ treated with 3 μL of 0.215 M $ZnCl_2$ in Et_2O at room temperature, resulting in the immediate and quantitative formation of poly(MOPO) as seen here.

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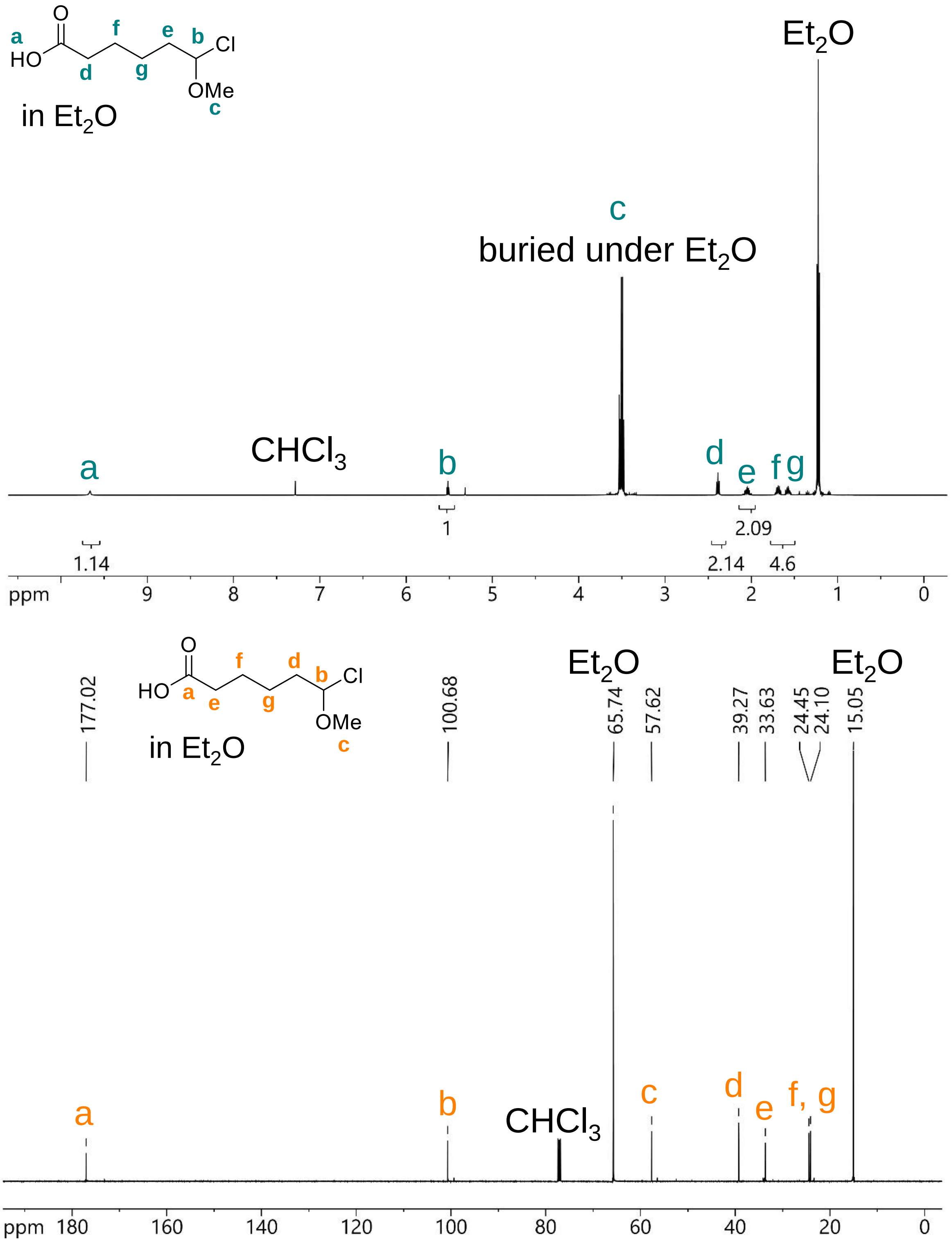
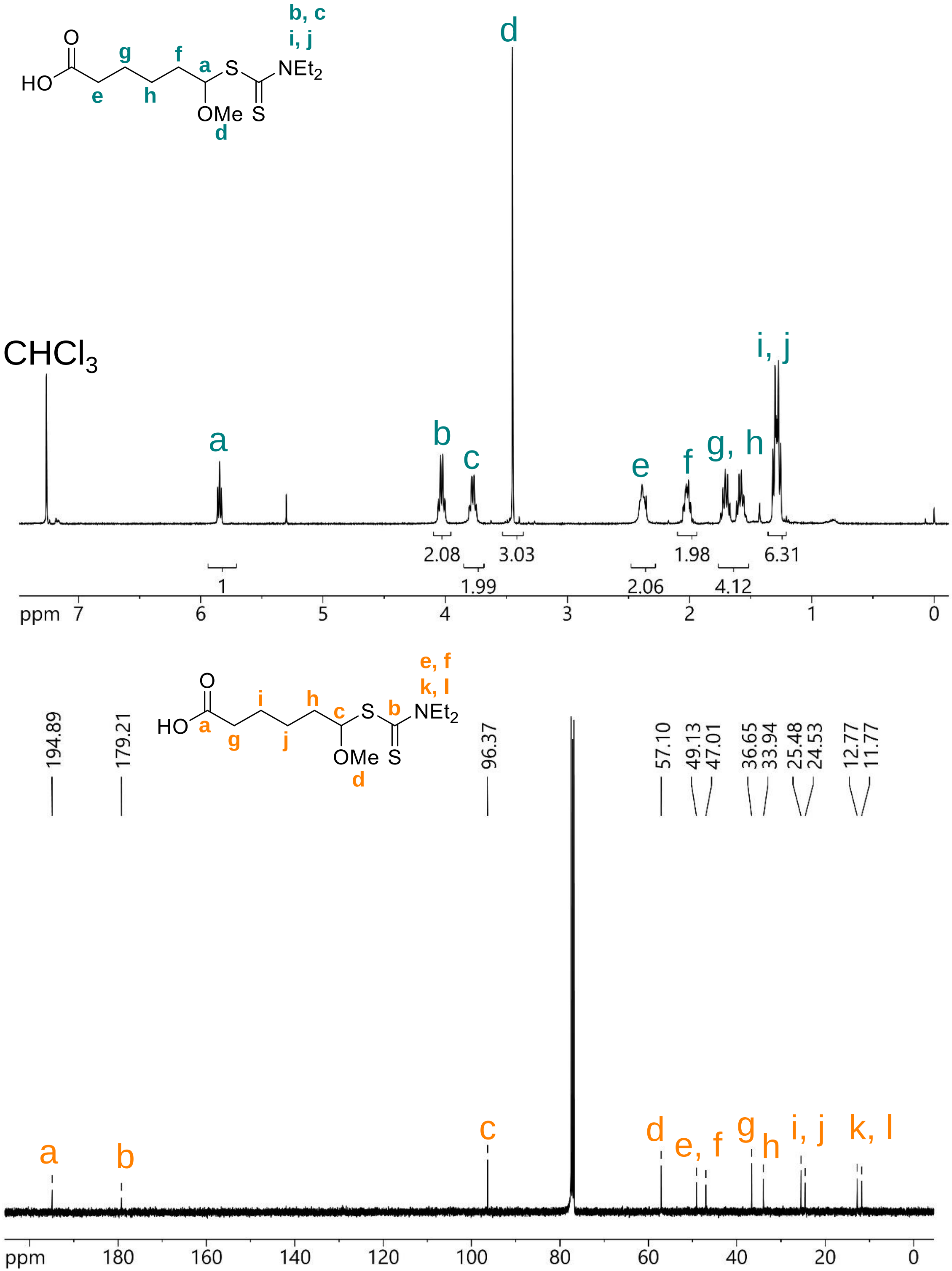


Figure S22. Top: ^{1}H NMR spectrum of chloromethylether in $CDCl_3$ and Et_2O. Bottom: ^{13}C NMR spectrum of chloromethylether in $CDCl_3$ and Et_2O.



FigureS23. Top: ^{1}H NMR spectrum of dithiocarbamate in $CDCl_3$. Bottom: ^{13}C NMR spectrum of dithiocarbamate in $CDCl_3$.

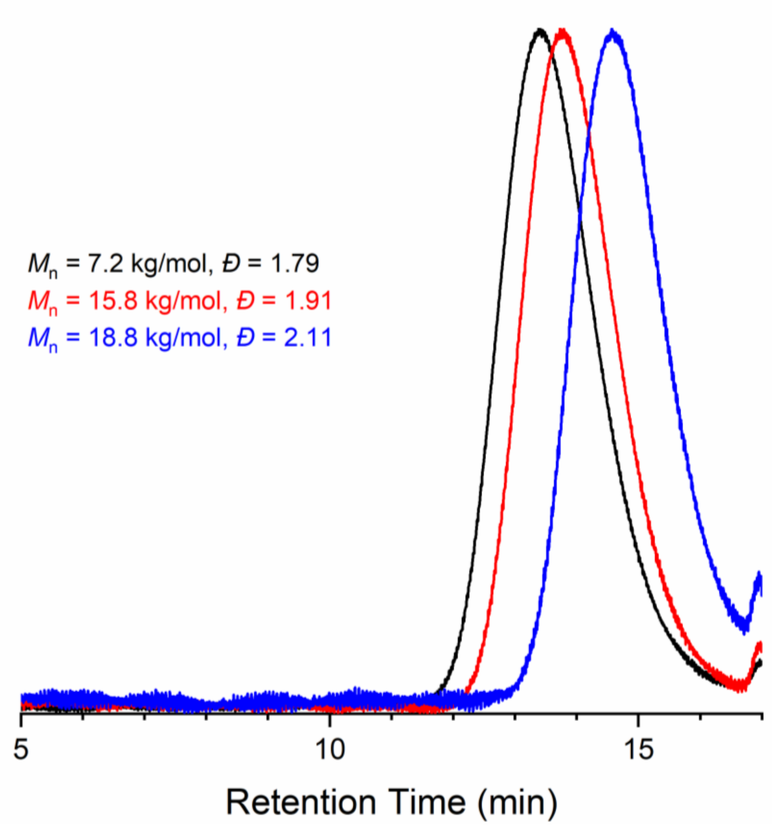


Figure S24. SEC traces for photomediated polymerizations of MOPO using various CTAs (black: **7**; red: **8**; blue: **9**).

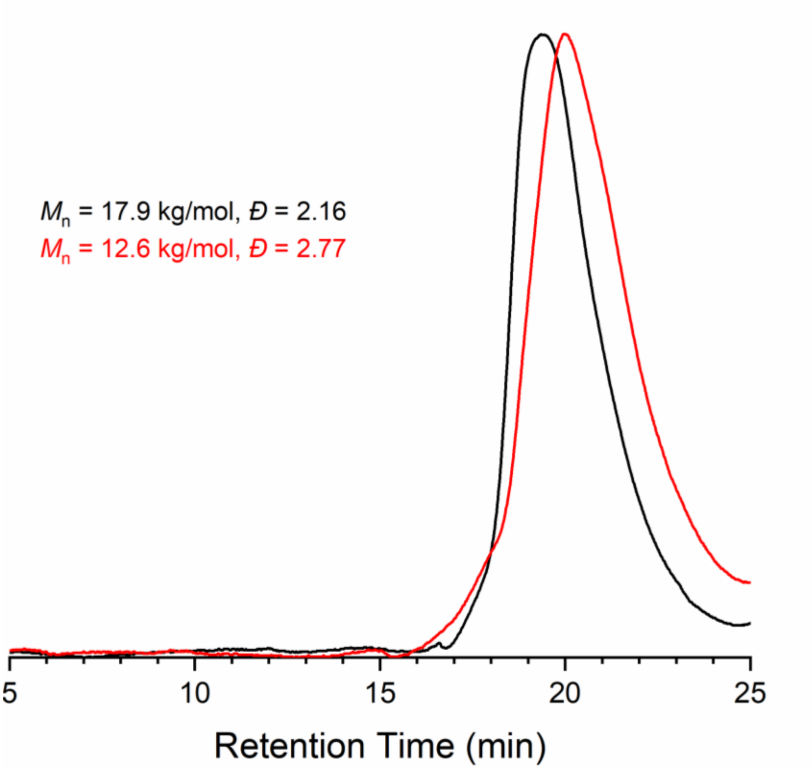


Figure S25. THF SEC traces for photomediated polymerizations of MOPO in $CDCl_3$ with CTA **7** at –15 °C (**black:** 30/1 MOPO/CTA, 15% conversion; **red:** 15/1 MOPO/CTA, 12% conversion).

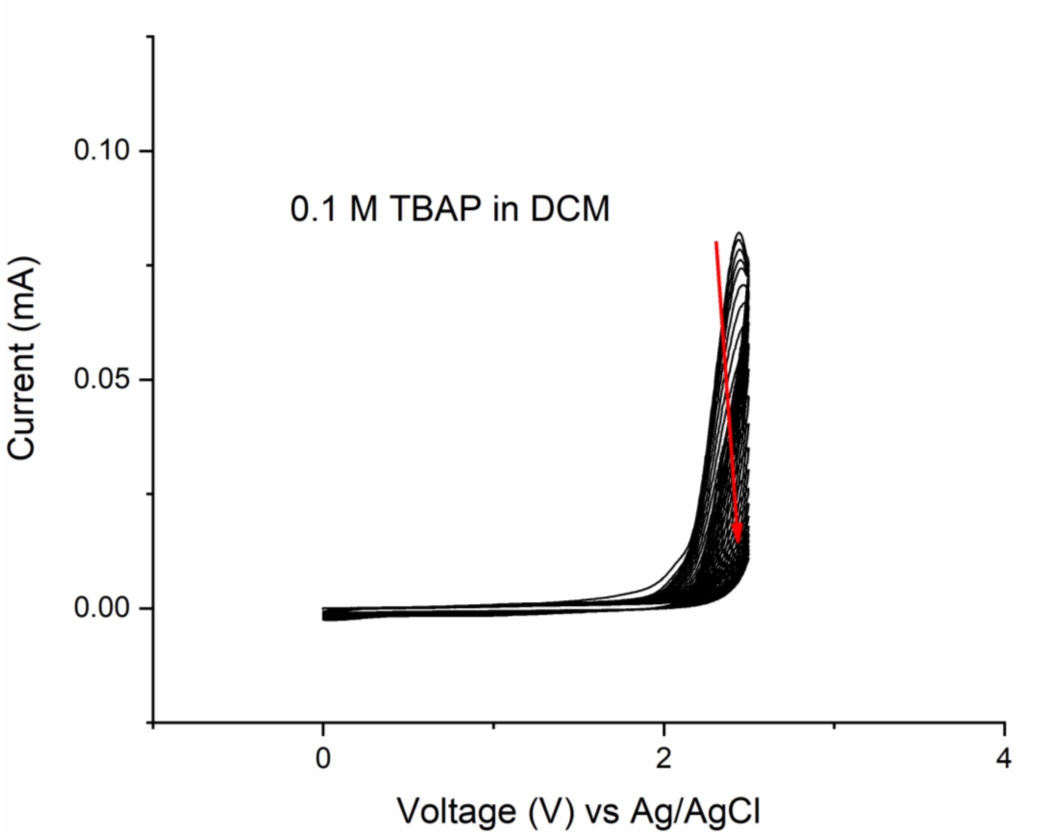


Figure S26. CVs of the 0.1 M TBAP electrolyte solution in DCM. CV measurements were taken to constant trace (24 scans total). The red arrow indicates the decrease in current measured for each successive scan.

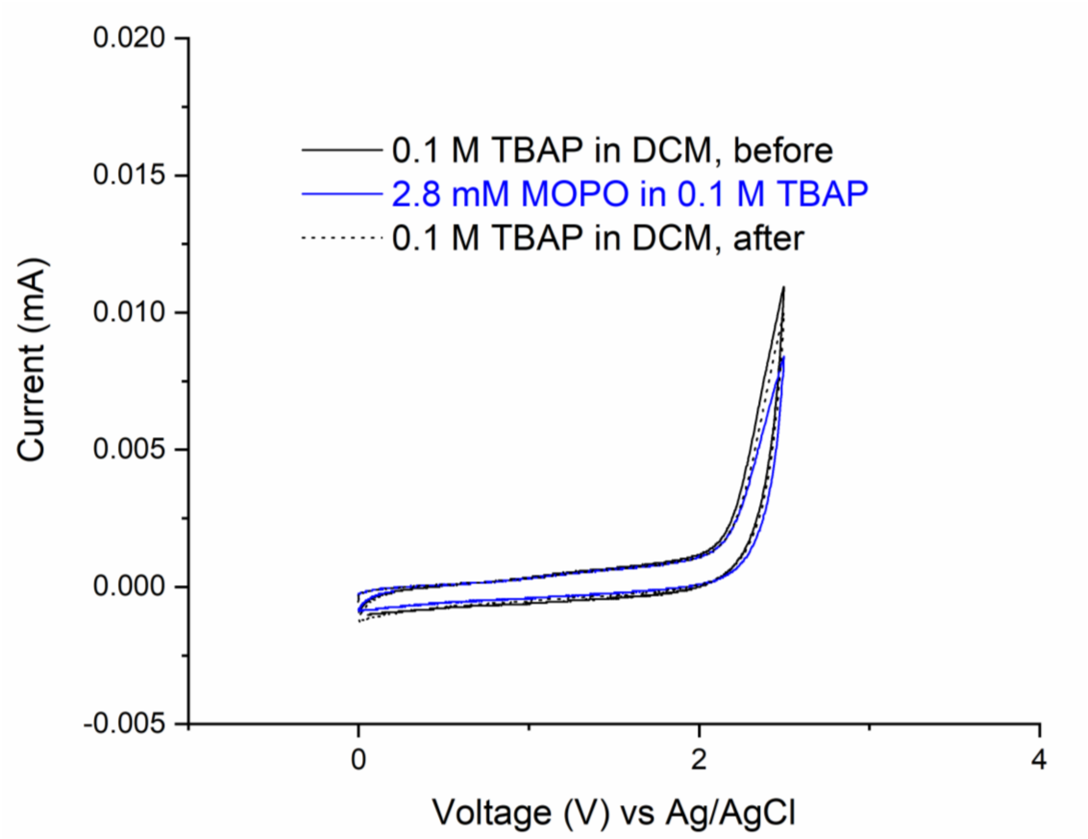


Figure S27. CV of 0.1 M TBAP electrolyte solution in DCM before (black, solid line) and after (black, dashed line) and 2.8 mM MOPO CV (blue, solid line).

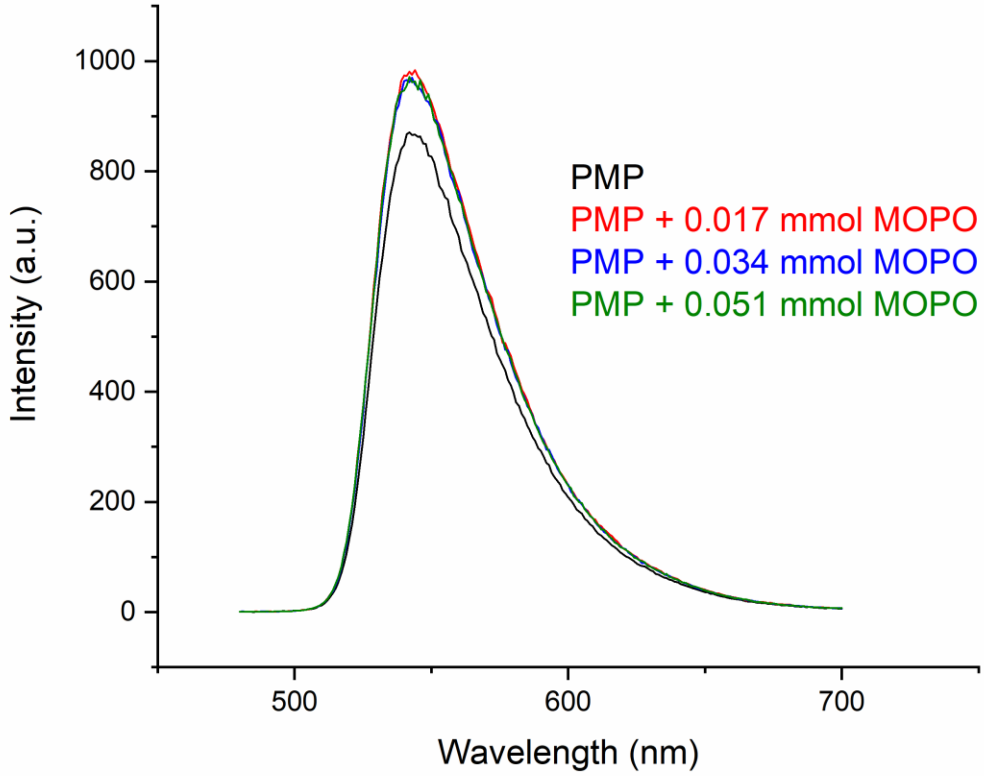


Figure S28. Fluorescence quenching was not observed for aliquots of MOPO added to a solution of PMP (**10**) in DCM.

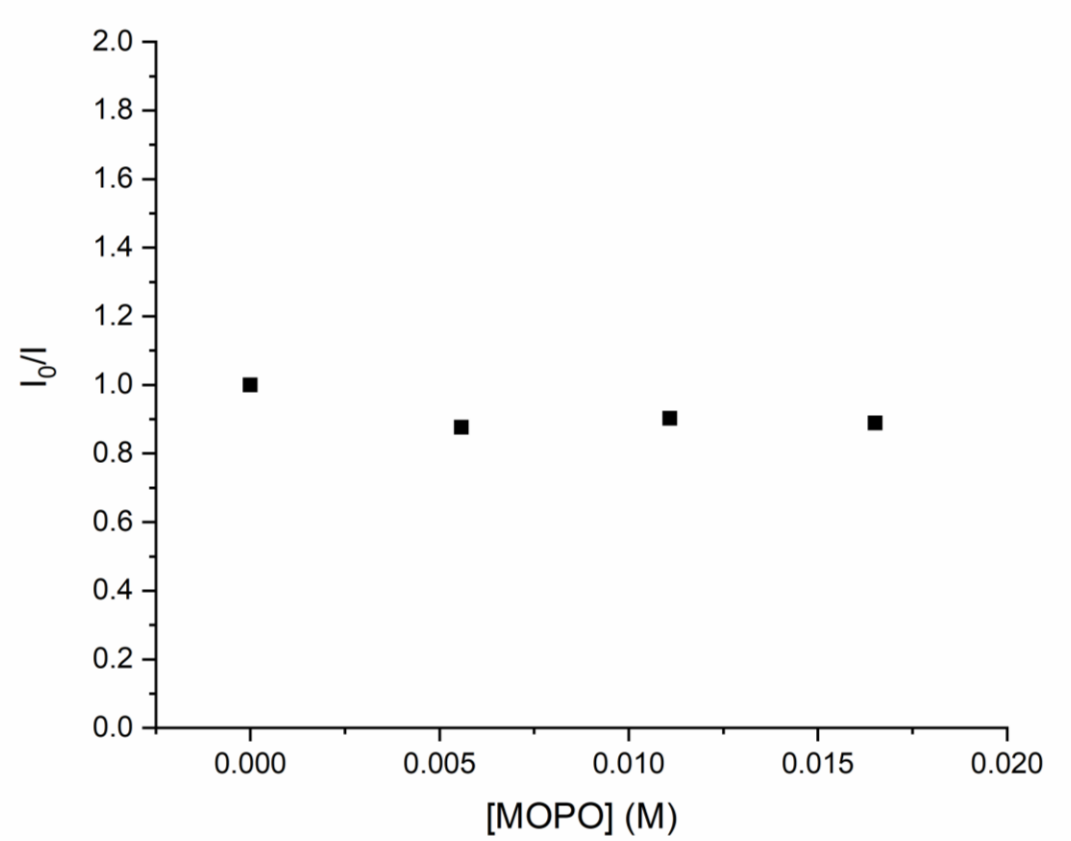


Figure S29. A Stern-Volmer plot reveals no observed fluorescence quenching when aliquots of MOPO are added to a solution of 2,4,6-tri-(*p*-methoxyphenyl)pyrylium tetrafluoroborate (**10**) in DCM.

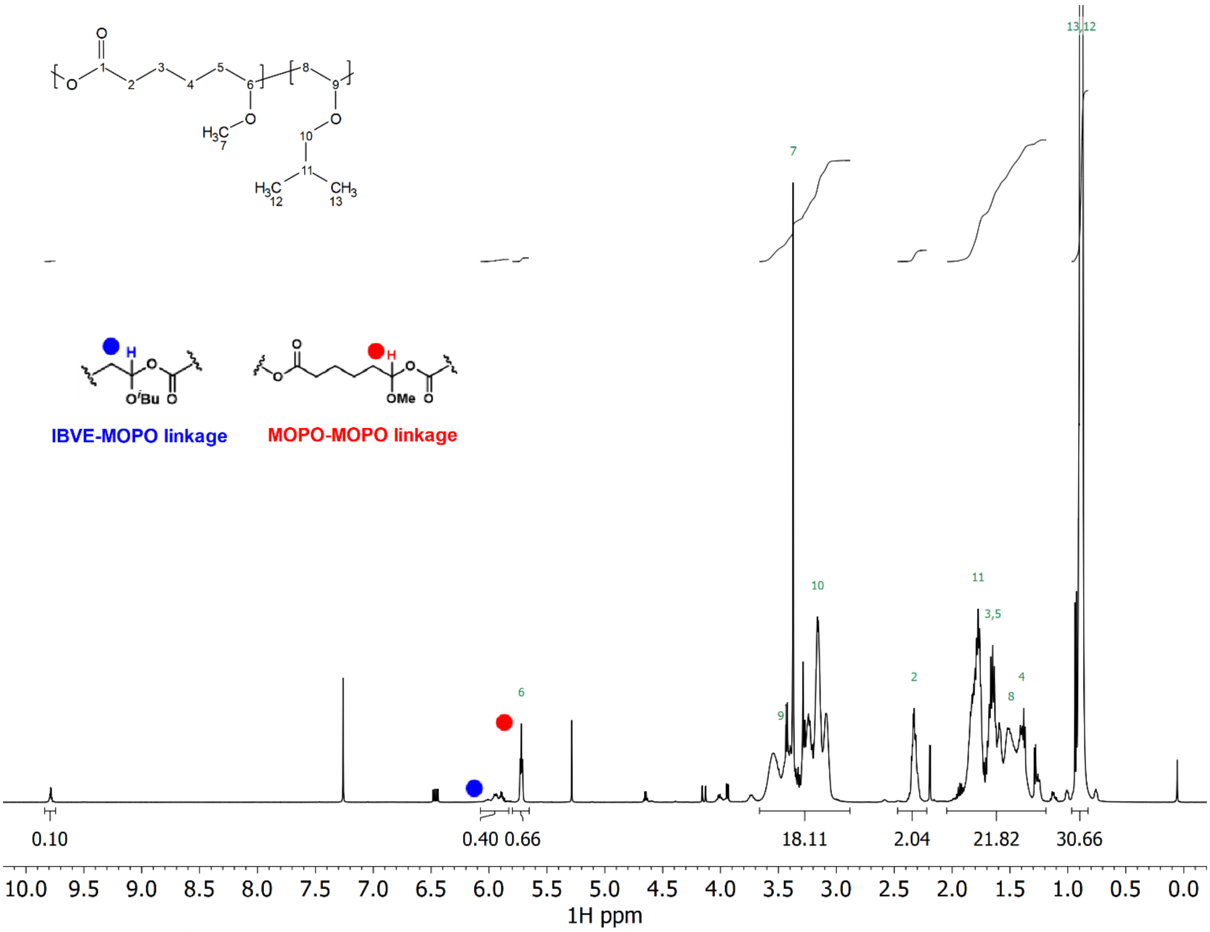


Figure S30. ^{1}H NMR spectrum of crude poly(MOPO-*co*-IBVE) in $CDCl_3$ with structural assignments indicated. The aldehyde peak at 9.8 ppm corresponds to residual hydrolyzed MOPO in the crude copolymer.

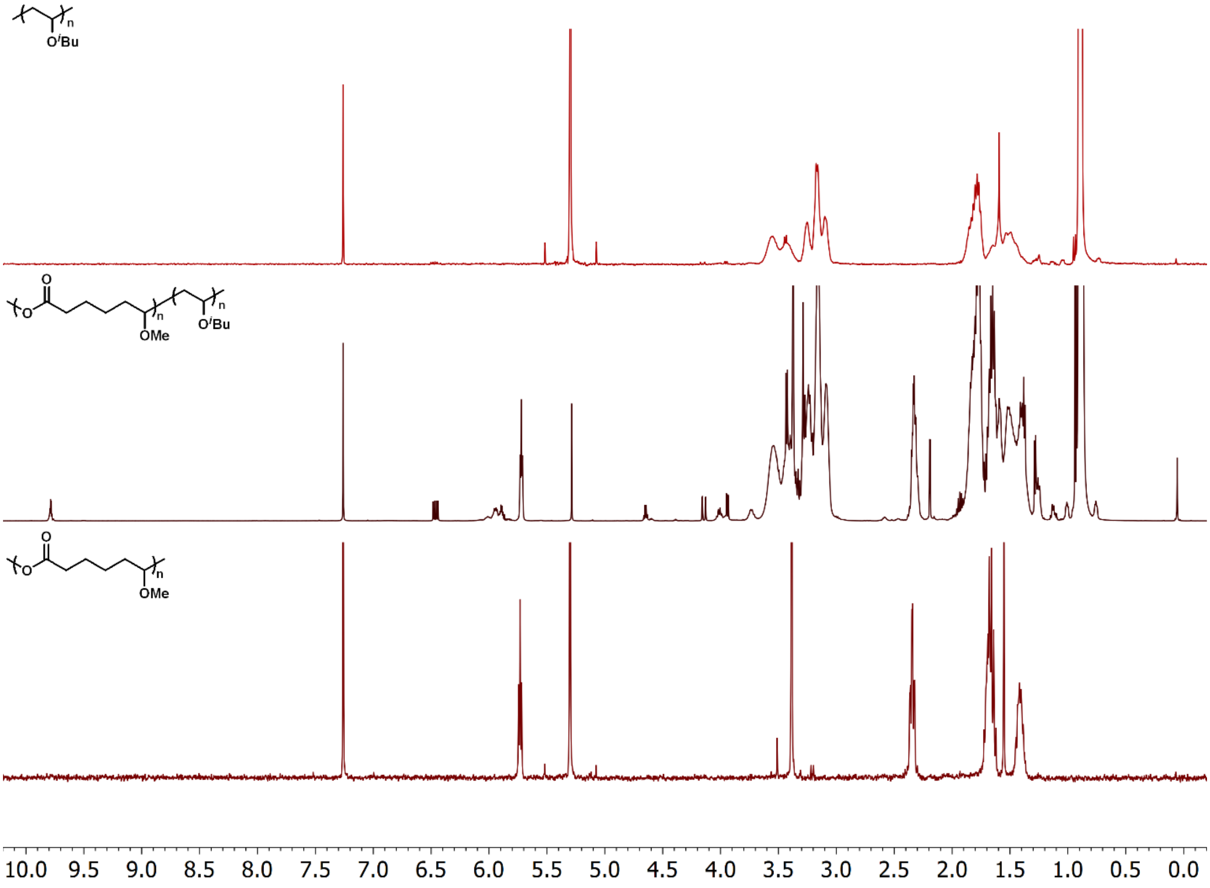


Figure S31. Stacked overlay of the ^{1}H NMR spectra of poly(IBVE) (top), crude poly(MOPO-*co*-IBVE) (middle), and poly(MOPO) (bottom) in $CDCl_3$.

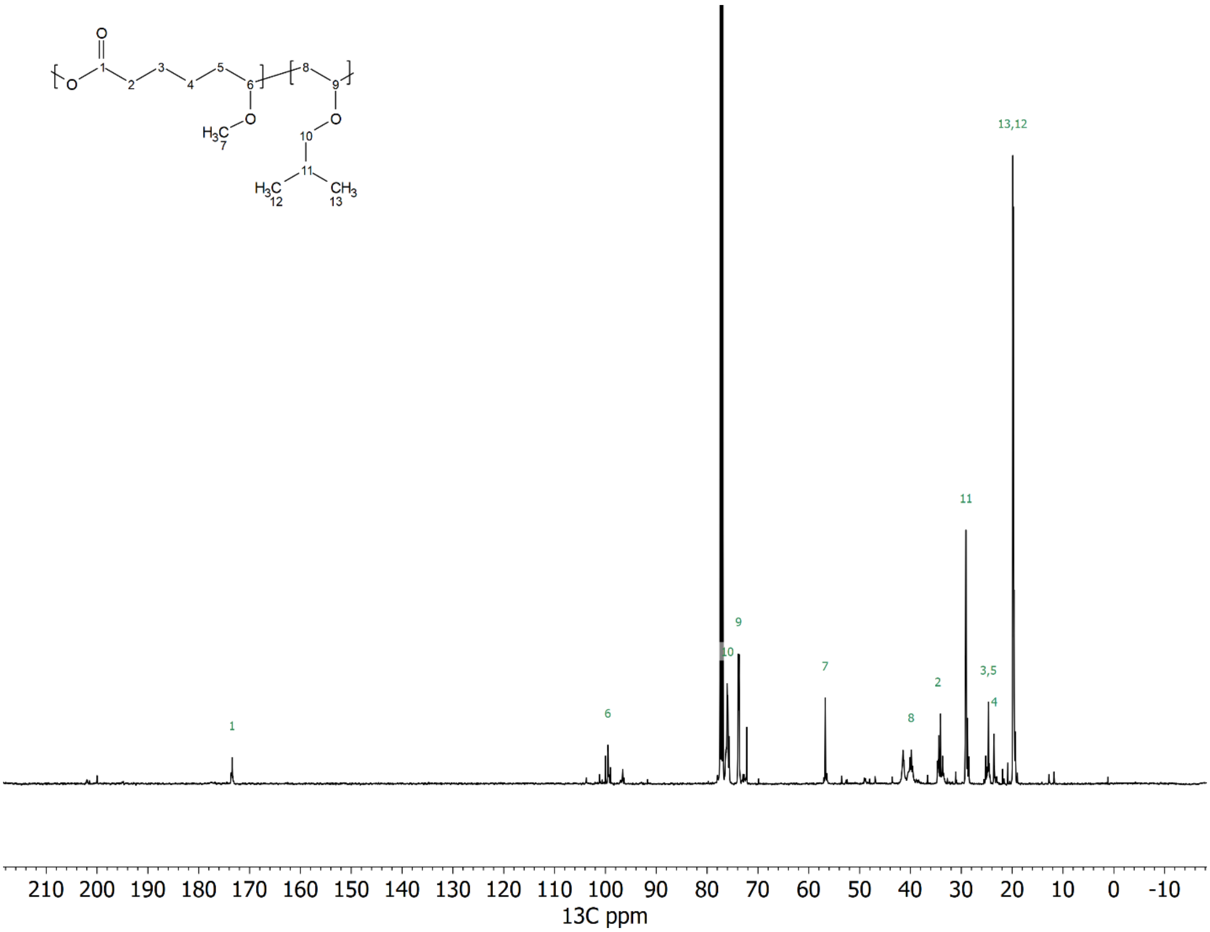


Figure S32. ^{13}C NMR spectrum of crude poly(MOPO-*co*-IBVE) in $CDCl_3$.

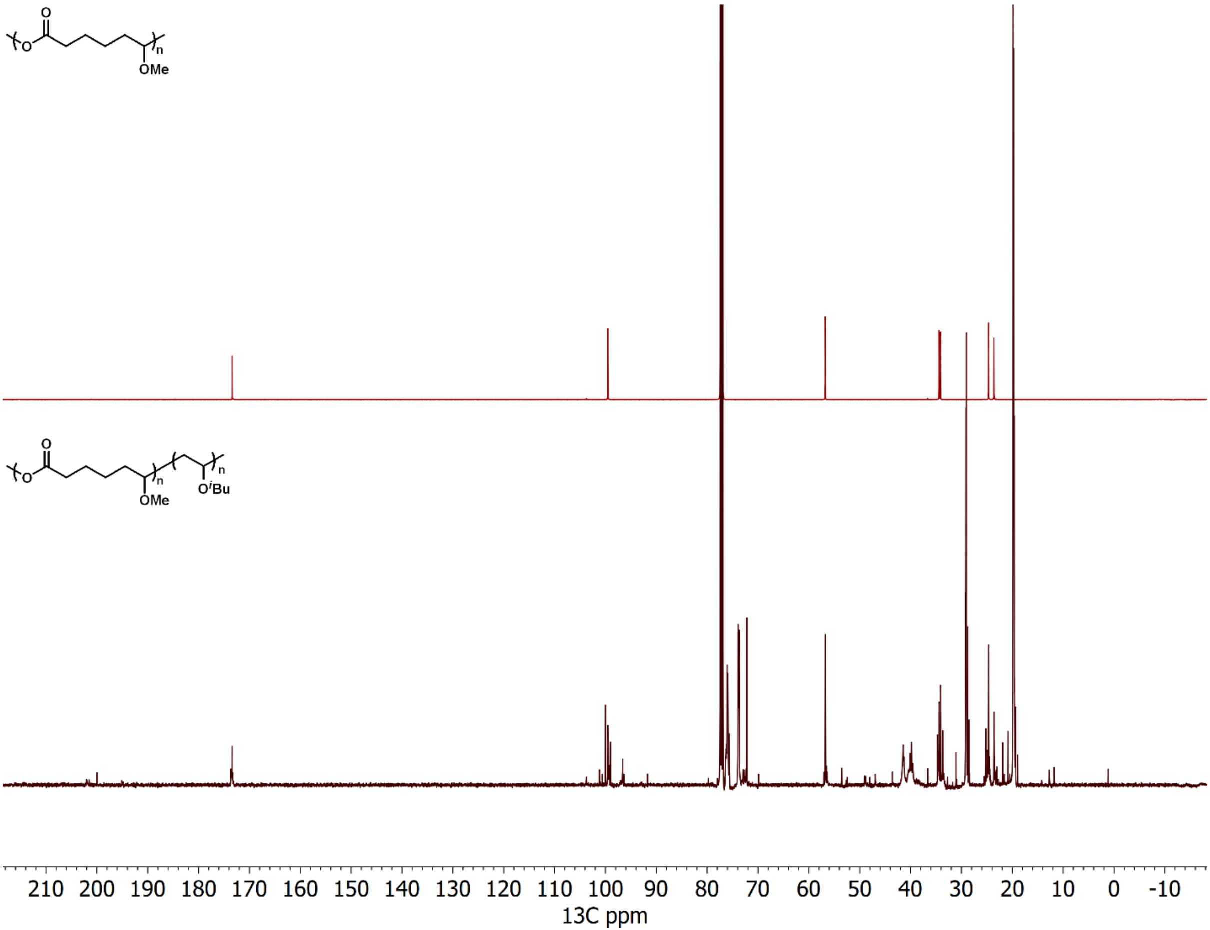


Figure S33. Stacked overlay of the ^{13}C NMR spectra of poly(MOPO) (top) and crude poly(MOPO-*co*-IBVE) (bottom) in $CDCl_3$.

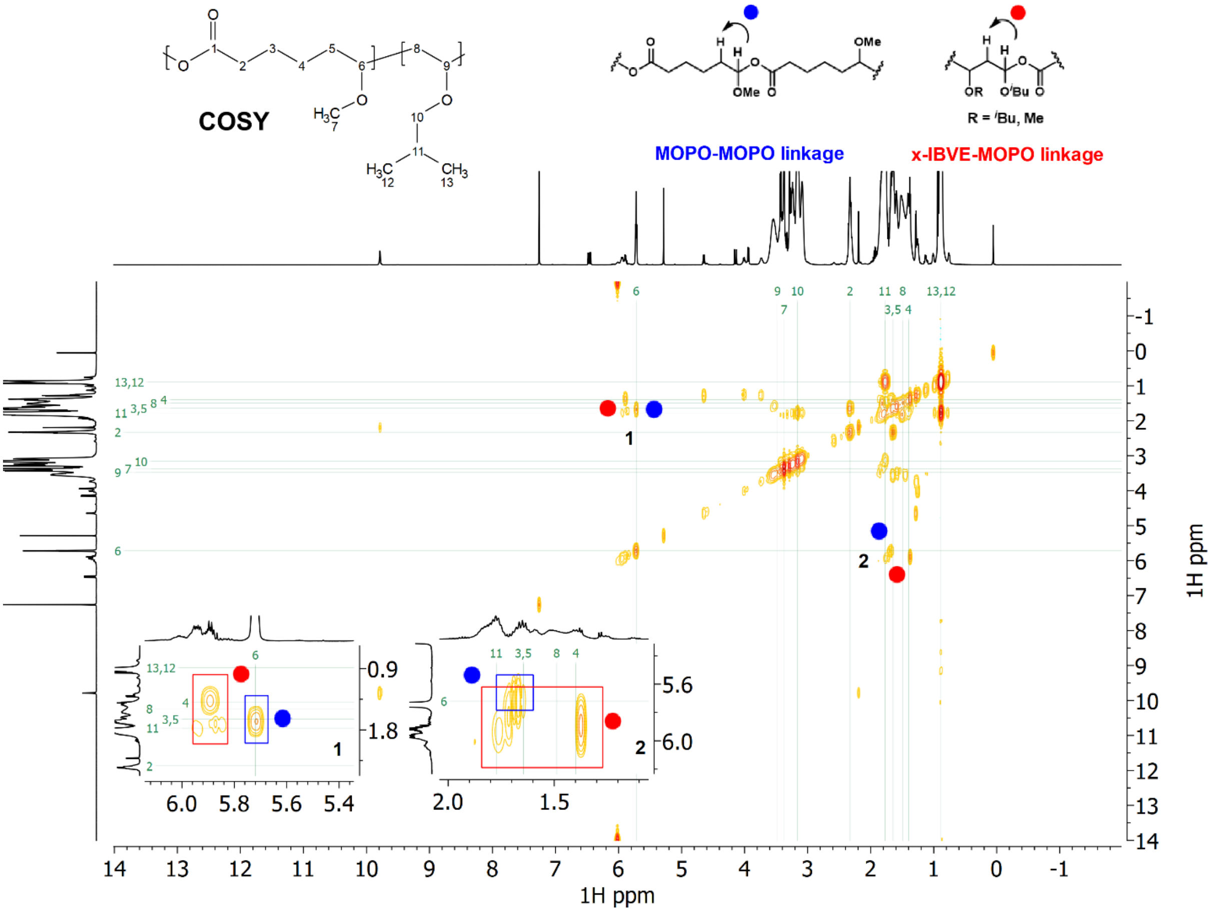


Figure S34. COSY spectrum of crude poly(MOPO-*co*-IBVE) in $CDCl_3$.

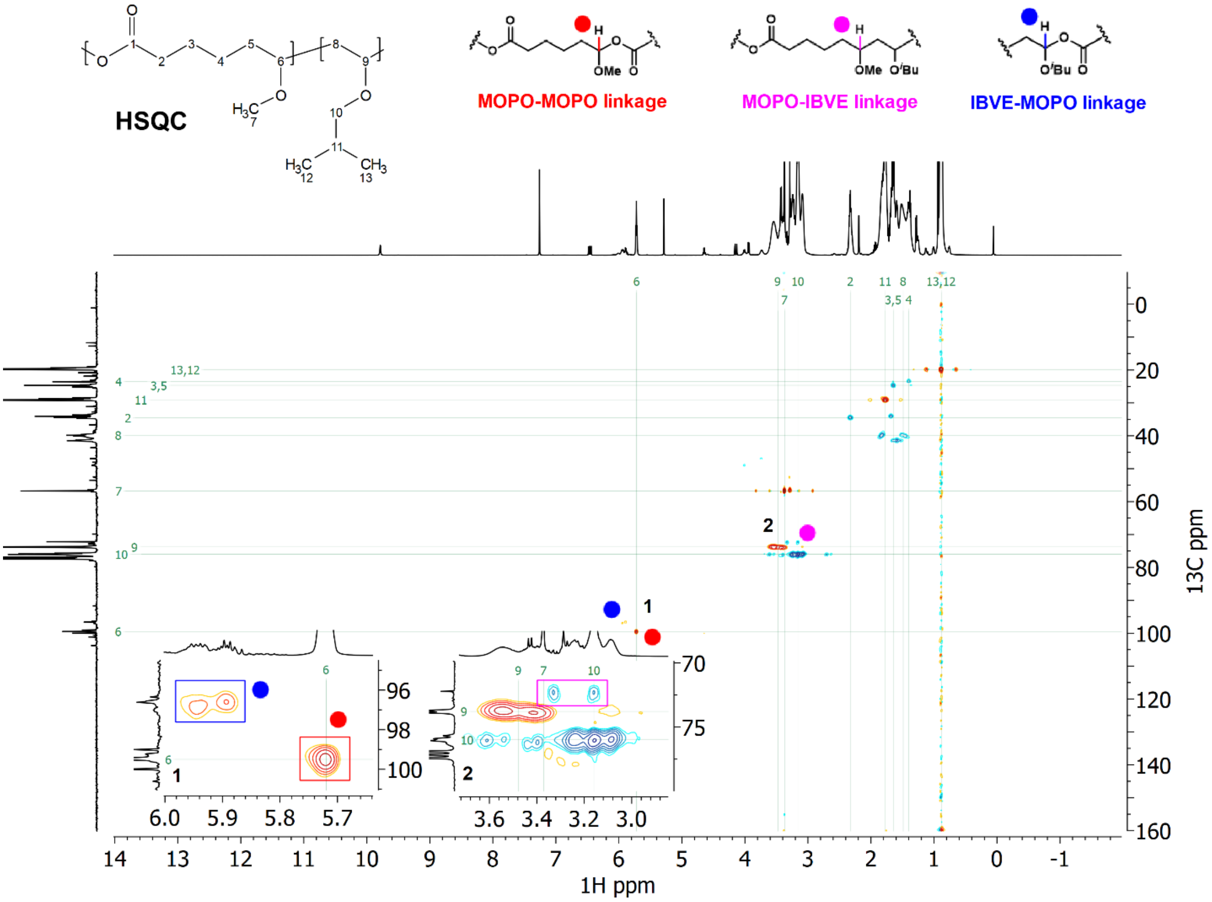


Figure S35. HSQC spectrum of crude poly(MOPO-*co*-IBVE) in $CDCl_3$.

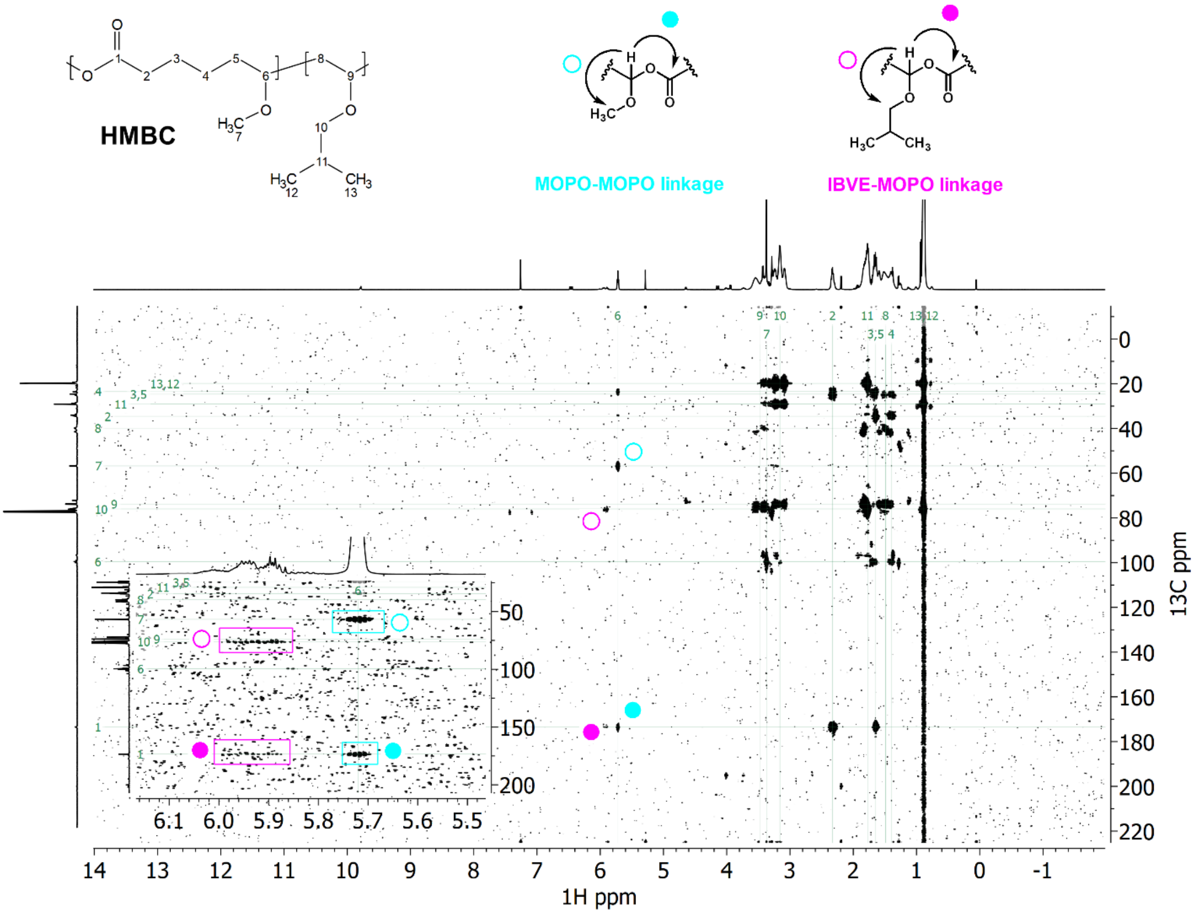


Figure S36. HMBC spectrum of crude poly(MOPO-*co*-IBVE) in $CDCl_3$.

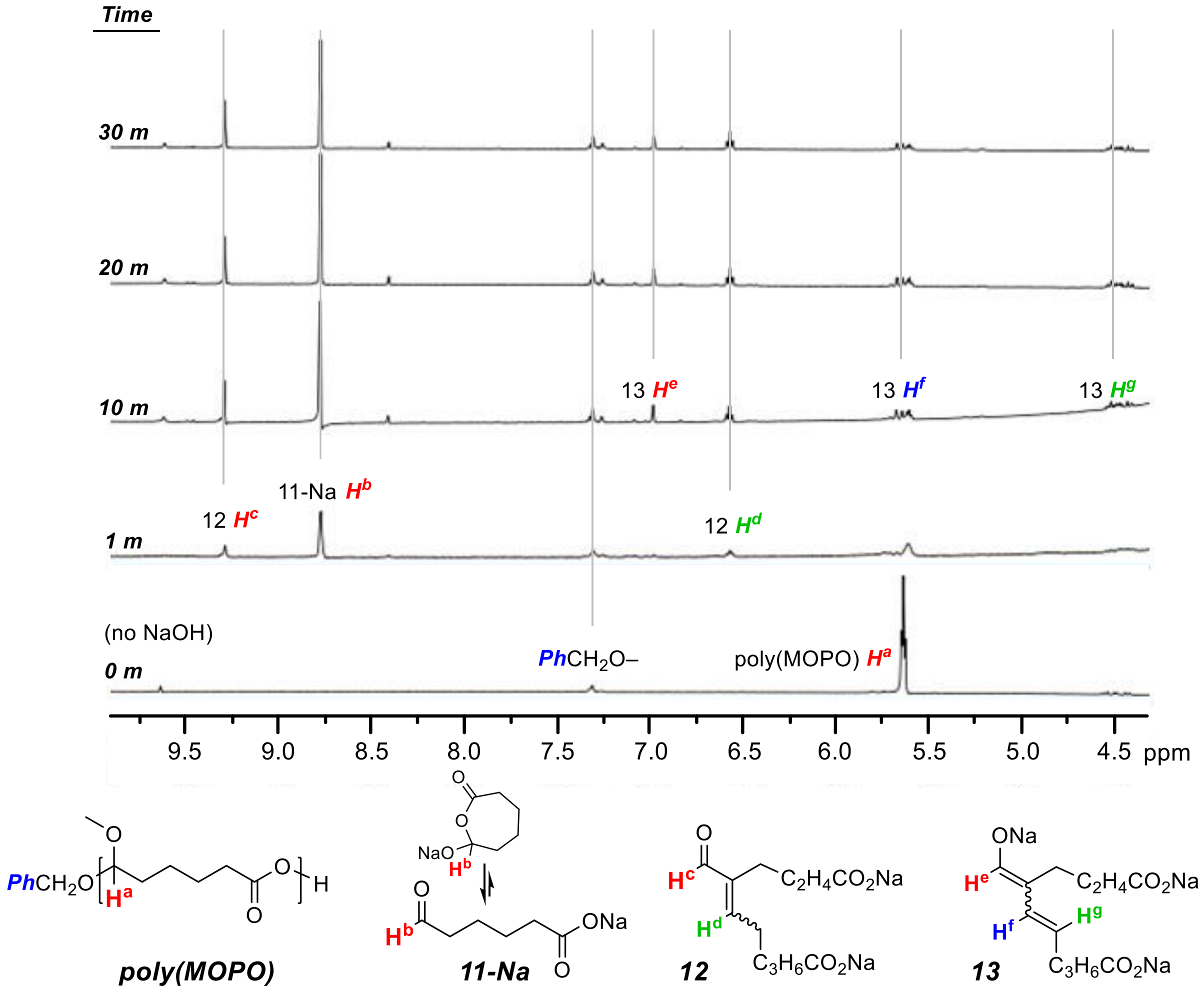
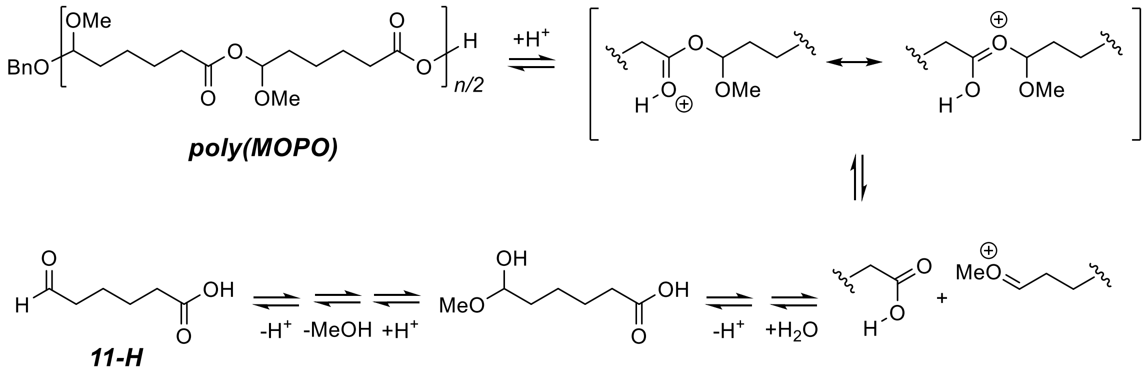


Figure S37. Overlay of ^{1}H NMR spectra of the NaOH-induced degradation of **poly(MOPO)**. Notice the atypical upfield shift of proton $\mathbf{H_b}$ in **11-Na**, attributable to rapid equilibration between the (major) open aldehyde and (minor) closed pseudo-acid anion.

Acid degradation



Base degradation

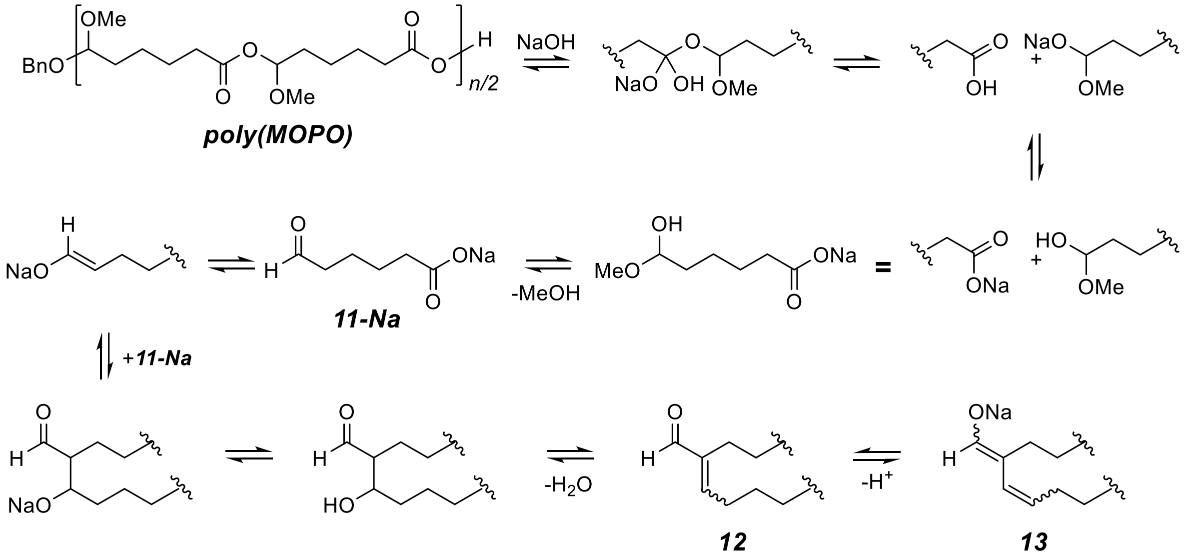


Figure S38. Plausible mechanisms for the degradation of poly(MOPO) in acidic or basic conditions.

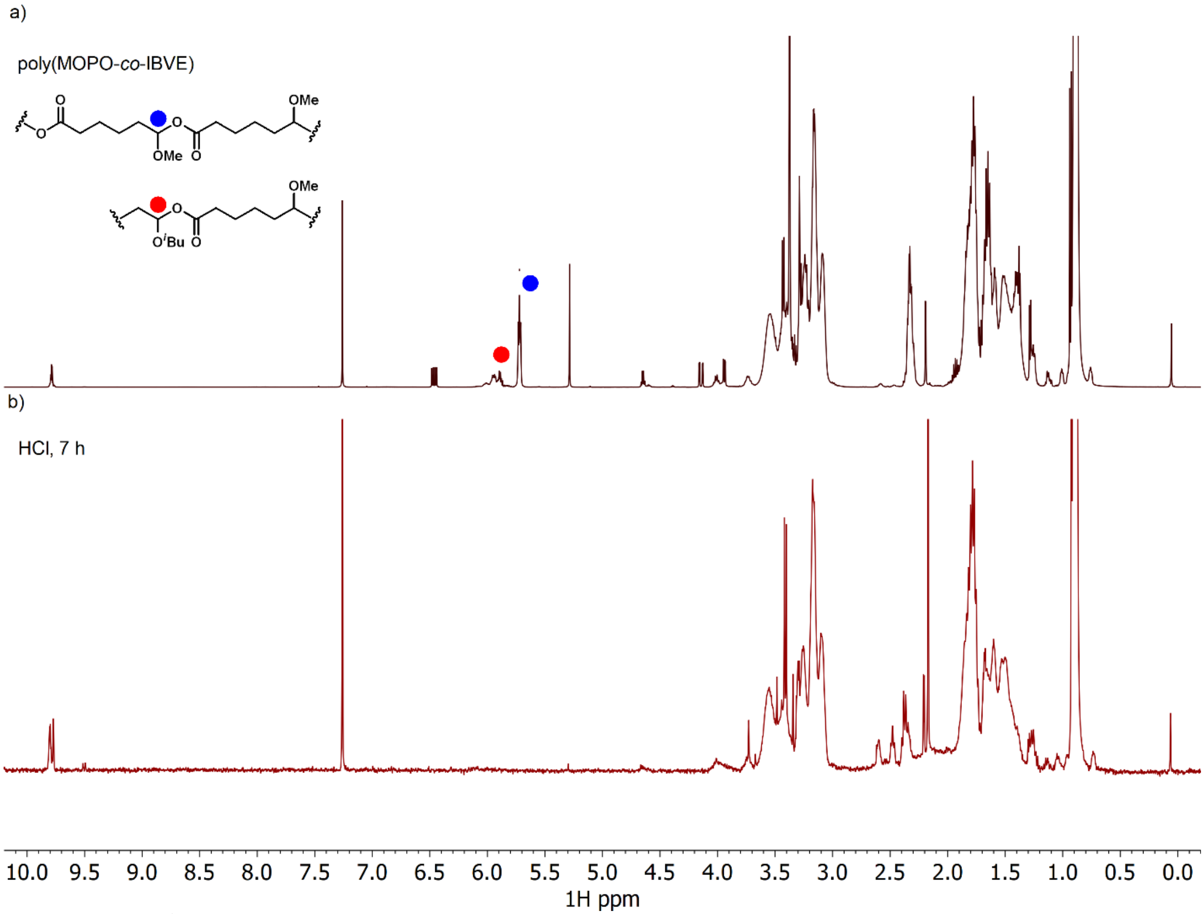


Figure S39. ^{1}H NMR spectrum of crude poly(MOPO-*co*-IBVE) in $CDCl_3$: a) before and b) after HCl treatment. The blue circle indicates the MOPO-MOPO acylacetal proton resonance, while the red circle indicates the IBVE-MOPO acylacetal proton resonance.

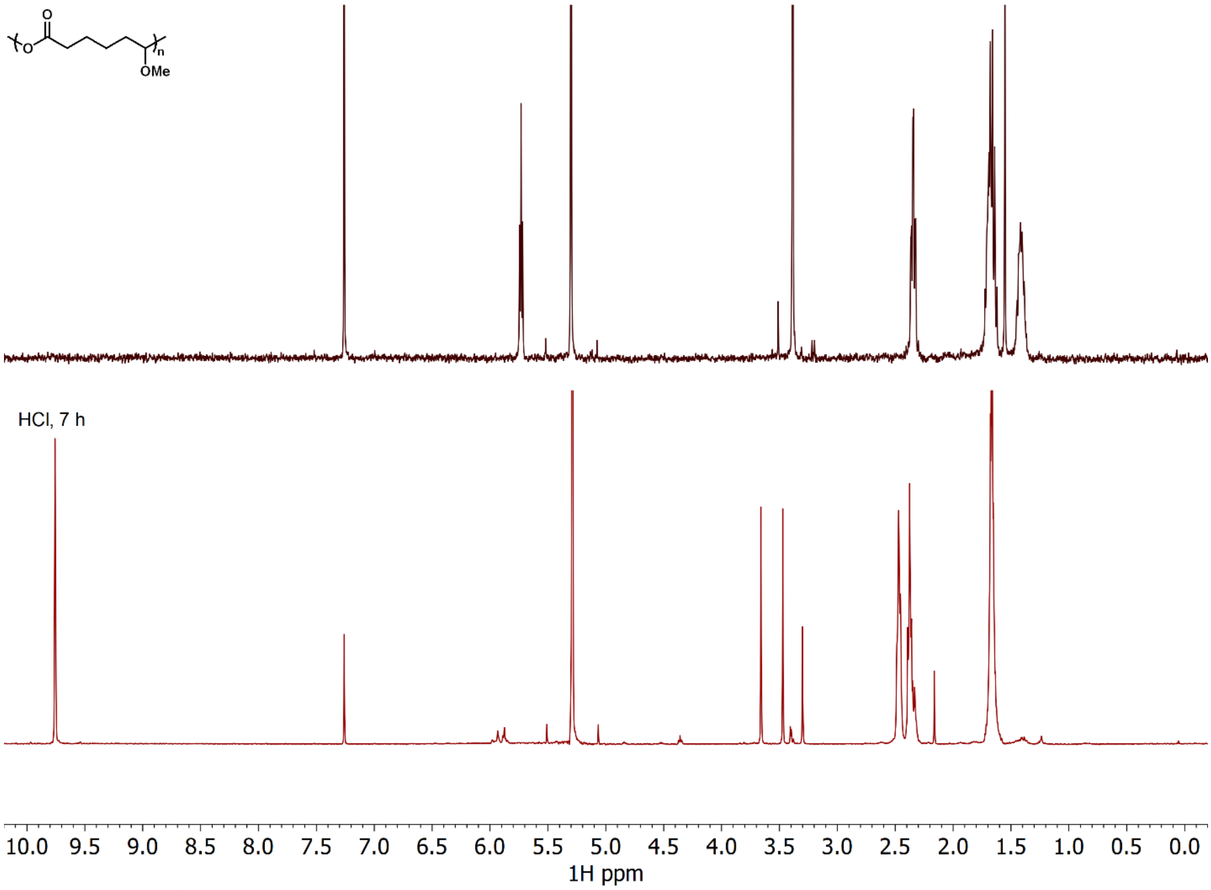


Figure S40. ^{1}H NMR spectrum of poly(MOPO) in $CDCl_3$ top) before and bottom) after HCl treatment.

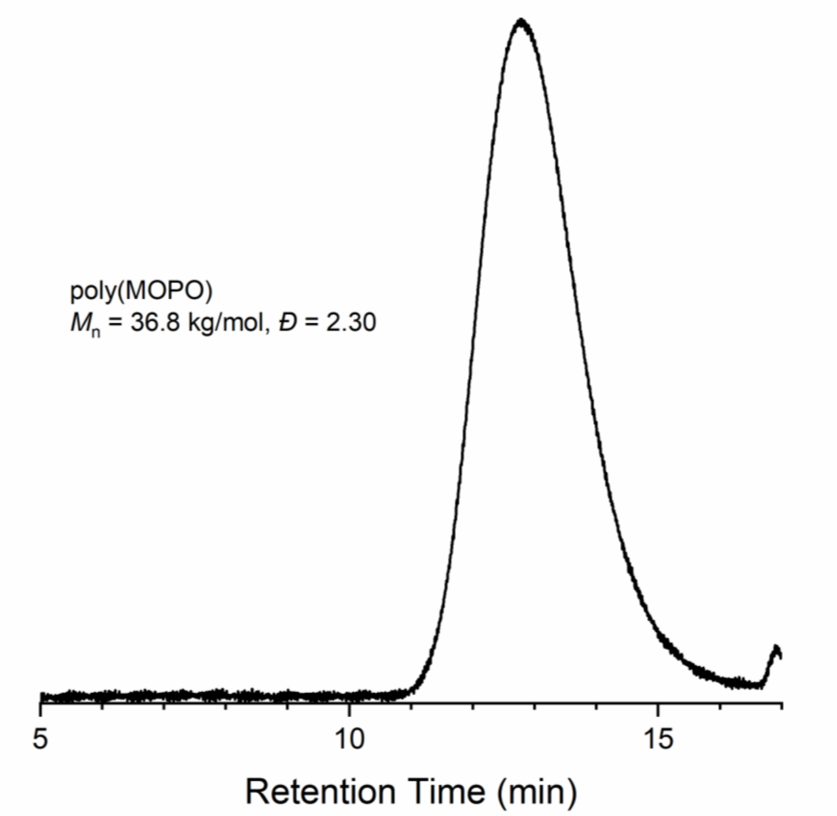


Figure S41. SEC trace of poly(MOPO) before (black) stirring in HCl. Complete degradation was observed after 7 h stirring in HCl and no polymer was detected by SEC after this.

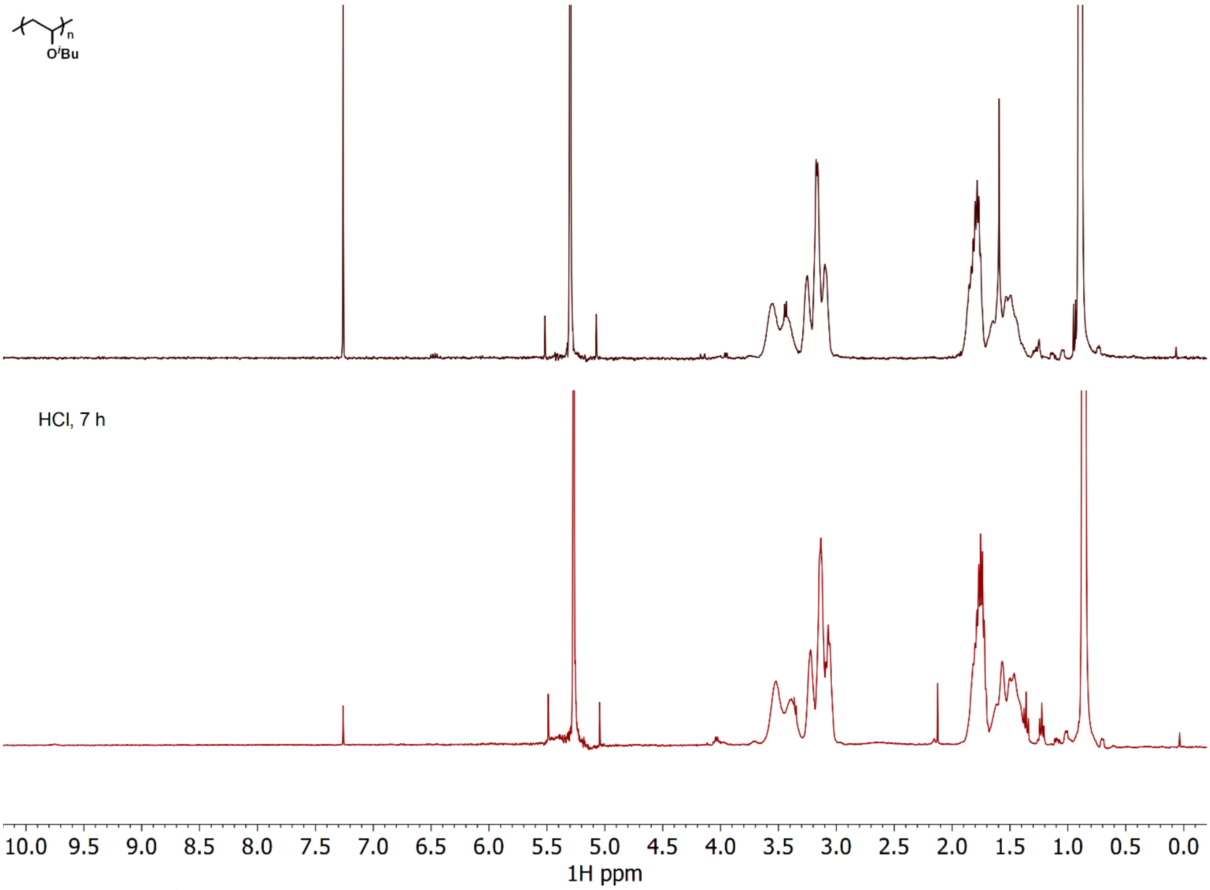


Figure S42. ^{1}H NMR spectrum of poly(IBVE) in CDCl$_3$: top) before and bottom) after HCl treatment.

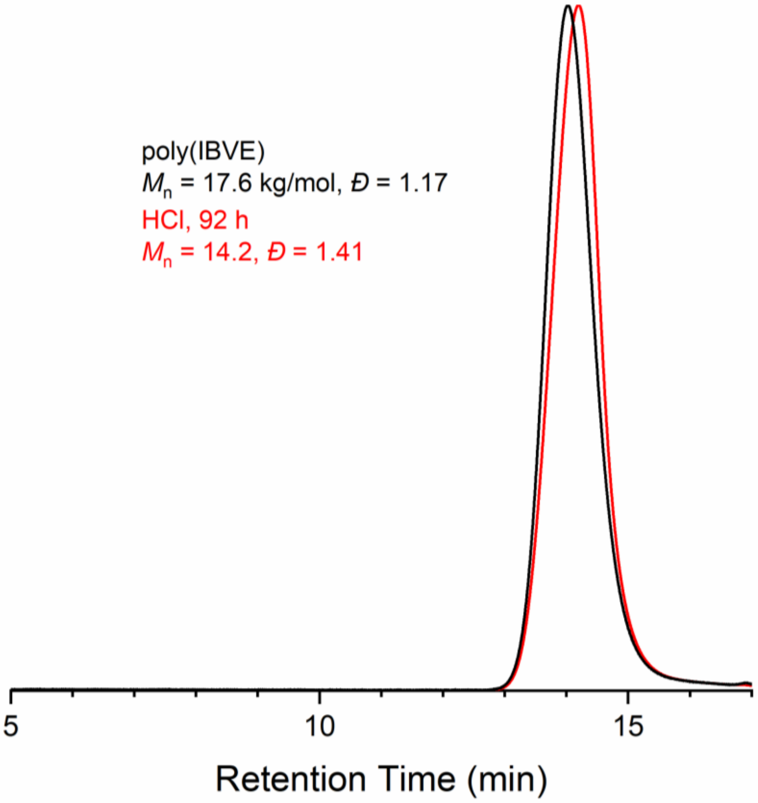


Figure S43. SEC trace of poly(IBVE) before (black) and after (red) stirring in HCl.

References

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2) Kottisch, V.; Michaudel, Q.; Fors, B. P. Cationic polymerization of vinyl ethers controlled by visible light. *J. Am. Chem. Soc.* **2016**, *138*, 15535 – 15538.

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4) Rajabi, M.; Lanfranchi, M.; Campo, F.; Panza, L. Synthesis of a series of hydroxycarboxylic acids as standards for oxidation of nonanoic Acid. *Synth. Commun.* **2014**, *44*, 1149−1154.

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