# Synthesis and Ring-Opening Polymerization of Lactones Derived from the Cotelomerization of Isoprene, Butadiene, and $CO_2$

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## Table of Contents



## Materials and Methods

Solvents and reagents were purchased from MilliporeSigma, STREM, Oakwood Chemicals, Matheson, and Airgas and were used without further purification unless otherwise noted. SiliaMetS Thiol (SH) Metal Scavenger was purchased from SiliCycle and used as purchased. Deuterated chloroform ($CDCl_3$) was purchased from Cambridge Isotope Laboratories and used without further purification. All polymerizations were carried out in a nitrogen-filled glovebox (MBraun) unless otherwise specified. Size exclusion chromatography (SEC) was performed in tetrahydrofuran (THF) using a Thermo Separation Products AS1000 system equipped with a Waters 515 Pump connected in series with two Agilent PLgel MIXED-C columns and fitted with a Waters 2410 refractive index detector at 25 °C and a flow rate of 1 mL/min. Determination of molar masses and dispersities was made by calibration against polystyrene standards. Thermogravimetric analyses (TGA) were performed on a TA Instruments Q500 under a nitrogen atmosphere at a heating rate of 10 °C/min. Differential scanning calorimetry (DSC) analysis was performed on a TA Instruments DSC Q1000 using hermetically sealed aluminum T-zero pans. Scans were conducted under a nitrogen atmosphere at a heating/cooling rate of 10 °C/min unless otherwise noted. Results are from the second scan cycle. $^{1}$H NMR, $^{13}$C NMR, $^{31}$P NMR and $^{19}$F spectra were recorded on Bruker Avance III HD 400 MHz spectrometer. $^{1}$H NMR spectra of all polymers were run with a relaxation delay of 10 seconds unless otherwise noted. Chemical shifts are reported with respect to tetramethylsilane (TMS). GC-FID chromatographs were collected on an Agilent 7890B GC system equipped with an HP-5 column (30 m, 0.32 mm, 0.25 μm, 7 in cage), an oxidation-methanation reactor (Polyarc® System, Activated Research Company) and an FID detector for quantitative carbon detection. A Sciex X500R quadrupole time-of-flight (qtof) mass spectrometer was used for accurate mass measurement of EPeP and EVMeP.

Electrospray ionization mass spectra in positive ionization mode were collected over the range m/z 50-1200 during the analysis. MS parameters were as follows: Ion source gas 1: 38 psi; Ion source gas 2: 38 psi; Curtain gas: 30 psi; CAD gas: 7; Temp: 500 °C; Spay voltage: 5500V; Declustering potential: 50V; DP spread: 0V; CE: 10V; CE spread: 0V. Matrix-assisted laser desorption/ionization spectra were obtained using a Bruker Autoflex Max MALDI/TOF-MS system in Reflectron Positive Mode with dithranol as the matrix.

## Initial Screening of Isoprene Cotelomerization

**General procedure for small scale optimization**

All reactions were run in a custom made 6-well high-pressure reactor (Figure S1).[1] The wells themselves can be individually pressurized and reactions were placed in 8-mL vials equipped with stir bars. Vials were flame dried before the catalyst system was added to each followed by acetonitrile. To ensure consistency, stock solutions of Pd catalyst and phosphine ligand were made and added to each vial individually. Hydroquinone and diisopropylethylamine (DIPEA) were added directly by mass and syringe respectively. Once all the catalyst system components were added, vials were placed in the 6-well and allowed to stir for 3-5 minutes. The reactor was then placed in a dry ice/acetone bath. Isoprene was filtered through silica to remove the inhibitor before being added to each vial *via* syringe. Freshly condensed butadiene was then added by using a pre-marked Pasteur pipet. Acetonitrile was added to the outside of each vial to prevent solvent evaporation. The reactor was then sealed and purged 3x with 200 psig $CO_2$ while still in the dry ice bath. During each purge cycle, vials were stirred for 3-5 minutes before being vented to ensure proper $CO_2$ incorporation into the solution. The reactor was then heated to room temperature before being pressurized with the desired amount of $CO_2$. Once pressurized, the reactor was heated to the desired temperature in an aluminum bead bath for 20-72 h. Upon completion, the reactor was placed in an ice bath and vented once cooled below 34 °C. Vials were removed and dimethyl terephthalate (DMT) was added as an NMR standard. Dichloromethane was also added, and vials were stirred until all the DMT had dissolved. An aliquot was taken, pumped down and analyzed via $^1$H NMR. For a few reactions, an aliquot was taken, filtered through thiol-functionalized silica to remove any residual Pd and subjected to GC-FID analysis.

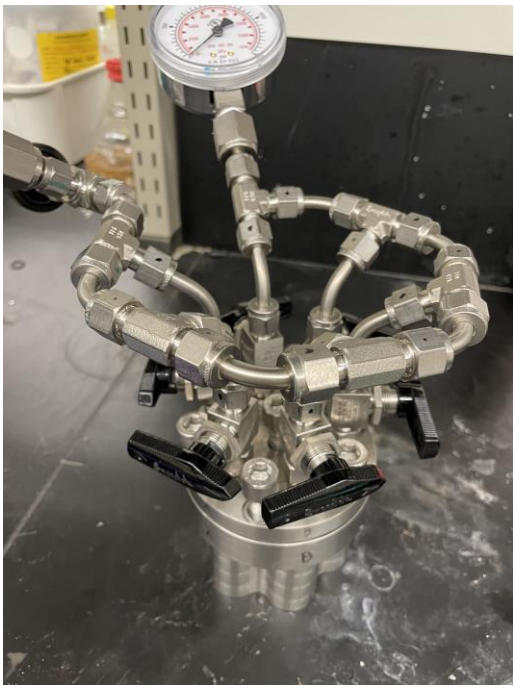
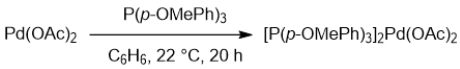


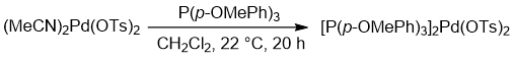
**Figure S1:** 6-well high-pressure apparatus.

**Synthesis of Pre-formed Pd catalysts**




**Scheme 1.** Synthesis of **[P(*p*-OMePh)$_3$]$_2$Pd(OAc)$_2$**

**[P(*p*-OMePh)$_3$]$_2$Pd(OAc)$_2$.** In a nitrogen-filled glovebox, Pd(OAc)$_2$ (50.0 mg, 0.22 mmol, 1.0 eq) and P(*p*-OMePh)$_3$ (235 mg, 0.67 mmol, 3.0 eq.) were weighed into a 20 mL vial equipped with a stir bar. 4 mL of benzene was added, and the reaction mixture was allowed to stir overnight. Yellow precipitate was filtered off and washed with toluene before residual solvent was removed *on vacuo*. $^1$H NMR (400 MHz, $CDCl_3$ δ, ppm) 7.67-7.61 (m, 12H), 6.92-6.86 (d, 12H), 3.81 (s, 18H), 0.94 (s, 6H)**;** $^{31}$P{$^1$H} NMR (162 MHz, $CDCl_3$, δ, ppm) 11.6.




**Scheme 2.** Synthesis of **[P(*p*-OMePh)$_3$]$_2$Pd(OTs)$_2$**

**[P(p-OMePh)$_3$]$_2$Pd(OTs)$_2$.** (MeCN)$_2$Pd(OTs)$_2$ was prepared as according to the literature procedure.[2] In a Nitrogen-filled glovebox, (MeCN)$_2$Pd(OTs)$_2$ (40 mg, 0.076 mmol, 1.0 eq) and P(*p*-OMePh)$_3$ (53.5 mg, 0.15mmol, 2.0 eq.) were weighed into a 20 mL vial equipped with a stir bar. 2 mL DCM was added, and the reaction mixture was allowed to stir overnight. Excess pentane was added, and the resulting precipitate was filtered and washed with pentane. The precipitate was then dried *on vacuo* to give the desired product. $^1$H NMR (400 MHz, $CDCl_3$, δ, ppm) 7.58-7.47 (m, 12H), 7.48-7.44 (d, 4H), 6.91-6.86 (d, 4H), 6.80-6.47 (d, 12H), 3.79 (s, 18H), 2.25 (s, 6H); $^{31}$P{$^1$H} NMR (162 MHz, $CDCl_3$, δ, ppm) 33.6.

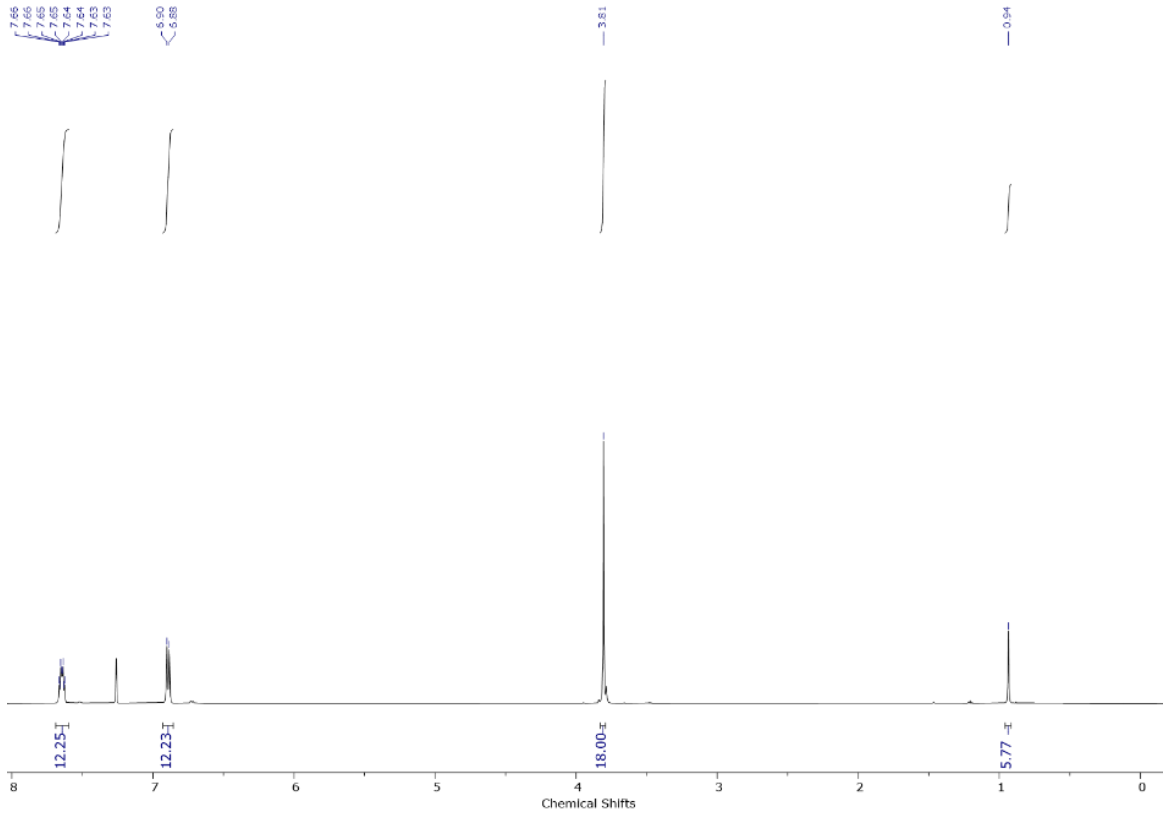



**Figure S2.** $^{1}H$ NMR spectrum of $[P(p\text{-}OMePh)_3]_2Pd(OAc)_2$ in $CDCl_3$.

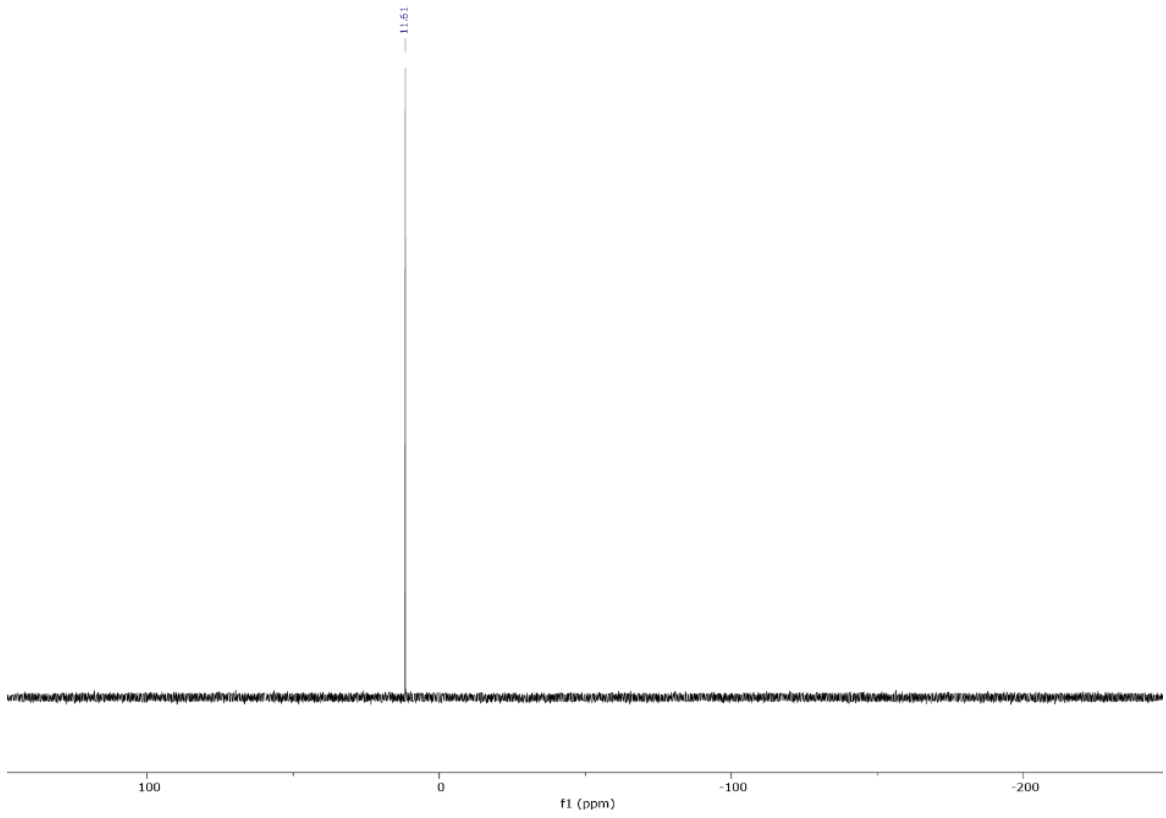


**Figure S3.** $^{31}P\{^{1}H\}$ NMR spectrum of $[P(p\text{-}OMePh)_3]_2Pd(OAc)_2$ in $CDCl_3$.

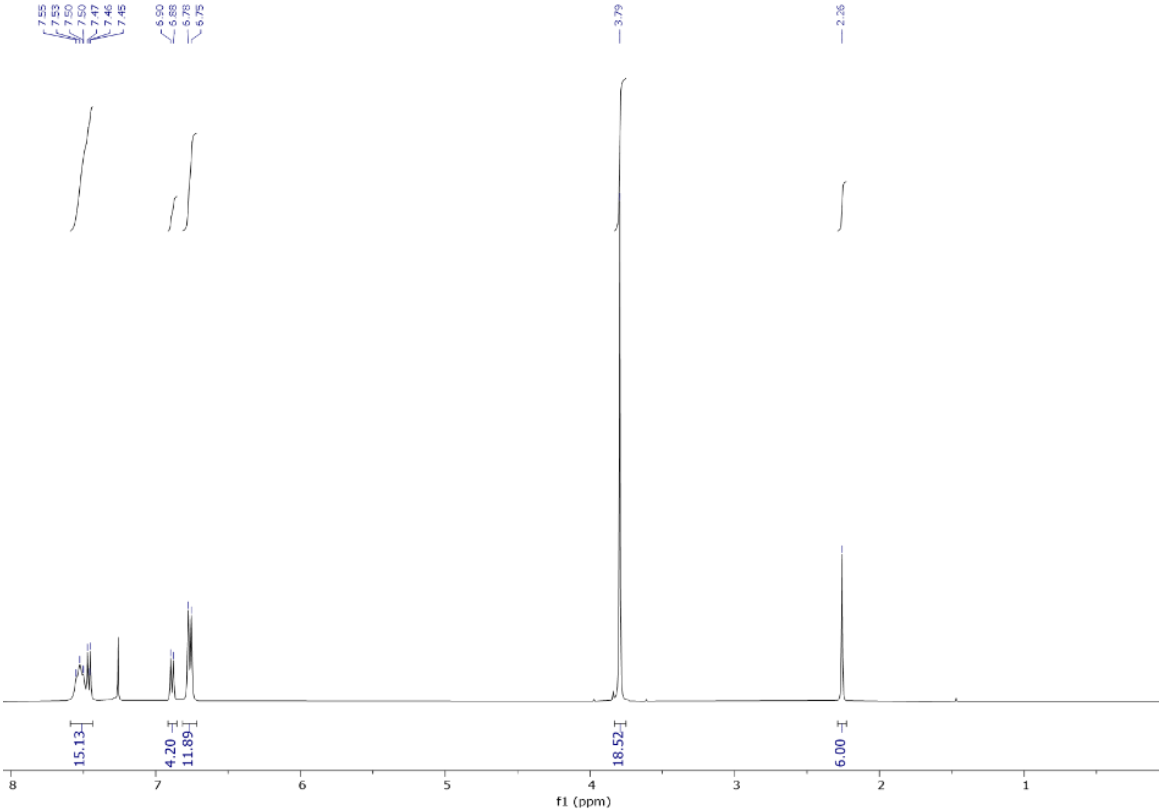



**Figure S4.** $^{1}H$ NMR spectrum of $[P(p\text{-}OMePh)_3]_2Pd(OTs)_2$ in $CDCl_3$

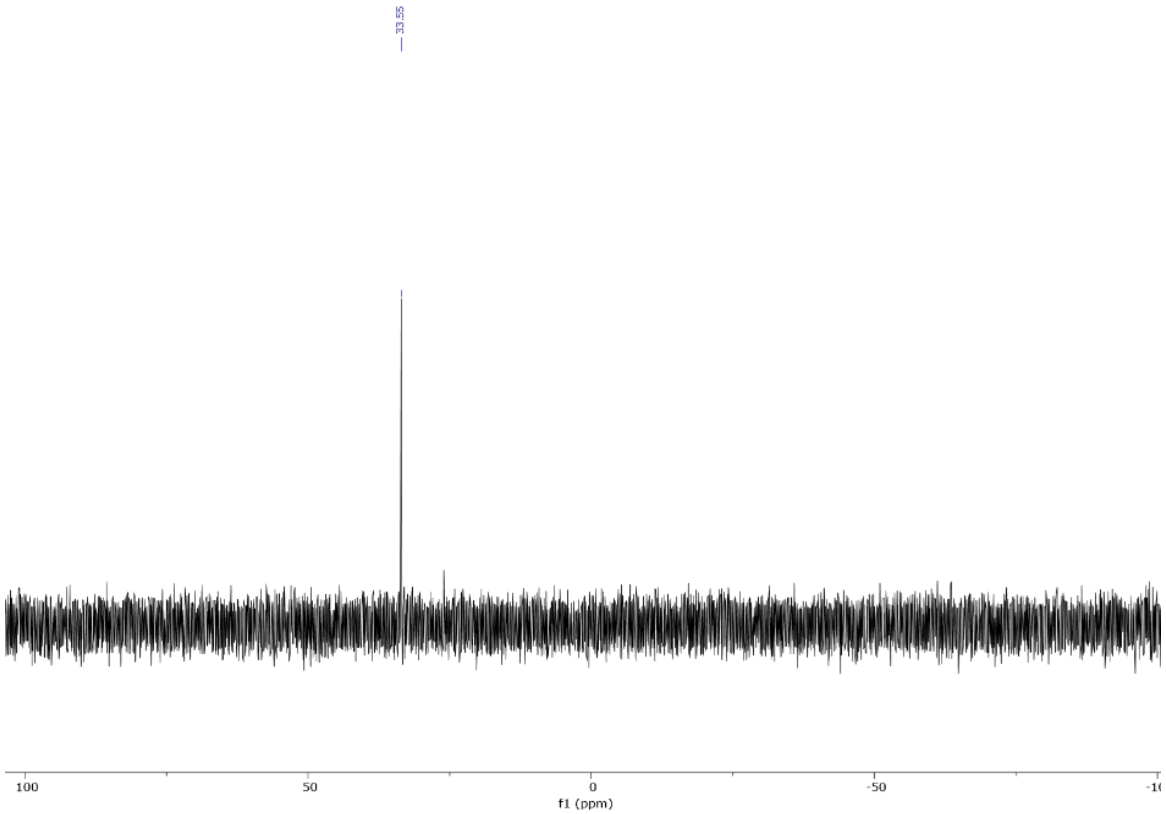
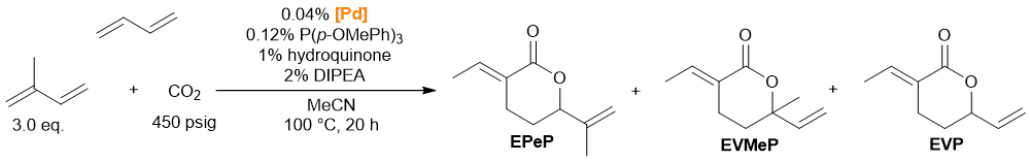



**Figure S5.** $^{31}P\{^{1}H\}$ NMR spectrum of $[P(p\text{-}OMePh)_3]_2Pd(OTs)_2$ in $CDCl_3$

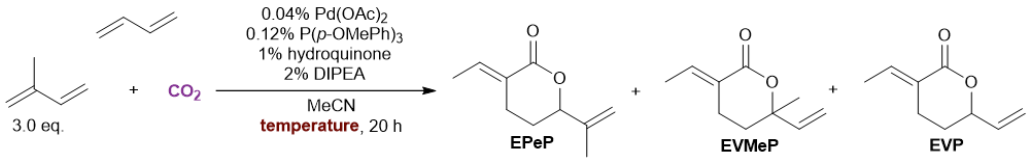
**Table S1.** Pd precatalyst screen




| Entry | Precatalyst | EPeP/EVMeP (%)[b] | EPeP/EVMeP:EVP[b] |
|---|---|---|---|
| 1 | $Pd(OAc)_2$ | 4.4 | 31:69 |
| 2 | $PdCl_2$ | 0.4 | 19:81 |
| 3 | $Pd(dba)_2$ | 2.2 | 23:77 |
| 4 | $[P(p\text{-}OMePh)_3]_2Pd(OAc)_2$ | 0.7 | 35:65 |
| 5 | $[P(p\text{-}OMePh)_3]_2Pd(OTs)_2$ | 0.7 | 28:72 |

[a]Reaction conditions: 5.04 mmol butadiene, 15.1 mmol isoprene in 2.2 mL acetonitrile; 0.04% [Pd], 0.12% $P(p\text{-}OMePh)_3$, 1% hydroquinone, 2% DIPEA, given temperature and pressure for 20 h.
[b]calculated *via* $^{1}H$ NMR spectroscopy using DMT standard.

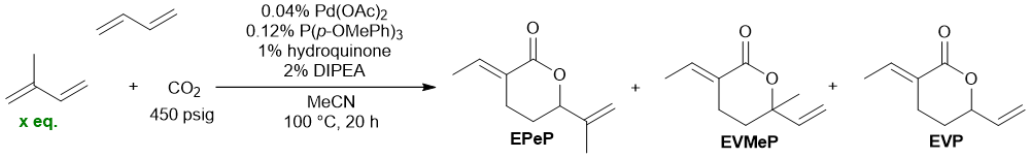
**Table S2.** Temperature and pressure screen




| Entry | Temperature (°C) | Pressure (psig) | EPeP/EVMeP Yield (%)[b] | EPeP/EVMeP:EVP[b] |
|---|---|---|---|---|
| 1 | 80 | 450 | 2.4 | 20:80 |
| 2 | 100 | 450 | 4.4 | 31:69 |
| 3 | 120 | 450 | 2.2 | 26:74 |
| 4 | 100 | 350 | 4.3 | 24:76 |
| 5 | 100 | 600 | 1.2 | 31:69 |

[a]Reaction conditions: 5.04 mmol butadiene, 15.1 mmol isoprene in 2.2 mL acetonitrile; 0.04% [Pd], 0.12% P(*p*-OMePh)$_3$, 1% hydroquinone, 2% DIPEA, given temperature and pressure for 20 h. [b]calculated *via* $^1$H NMR spectroscopy using DMT standard.

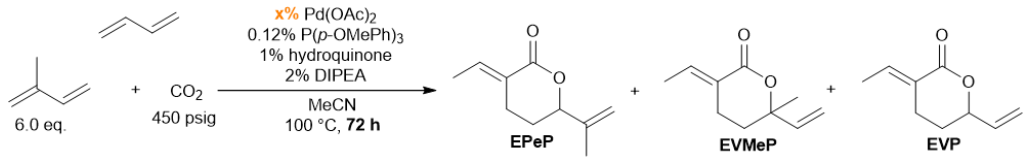
**Table S3.** Isoprene equivalents




| Entry | Isoprene Eq. | EPeP/EVMeP Yield (%) | EPeP/EVMeP:EVP |
|---|---|---|---|
| 1 | 1 | 1.0 | 11:89 |
| 2 | 3 | 4.4 | 31:69 |
| 3 | 6 | 5.1 | 42:58 |
| 4[c] | 10 | 1.1 | 61:39 |

[a]Reaction conditions: 5.04 mmol butadiene, given isoprene eq. in acetonitrile to make 5 mL of total solution; 0.04% [Pd], 0.12% P(*p*-OMePh)$_3$, 1% hydroquinone, 2% DIPEA, given temperature for 20 h. [b]calculated *via* $^1$H NMR spectroscopy using DMT standard. [c]scaled-up in a 25 mL Parr reactor.

**Table S4.** Increased reaction times with various catalyst loadings

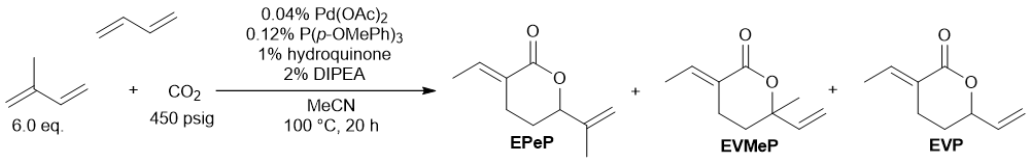



| Entry | Catalyst Loading (mol %) | EPeP/EVMeP Yield (%)[b] | EPeP/EVMeP:EVP[b] |
|---|---|---|---|
| 1 | 0.02 | 0.6 | 11:89 |
| 2 | 0.07 | 10.0 | 31:69 |
| 3 | 0.20 | 11.2 | 42:58 |

| | | | |
|---|---|---|---|
| 4 | 0.50 | < 4.9 | n.d.[c] |

[a]Reaction conditions: 5.04 mmol butadiene, 15.1 mmol isoprene in 2.2 mL acetonitrile; given [Pd], 3.0 eq (relative to [Pd]) P(*p*-OMePh)$_3$, 1% hydroquinone, 2% DIPEA, given temperature for 72 h. [b]calculated *via* $^1$H NMR spectroscopy using DMT standard. [c]product ratios could not be determined due to peak overlap.

**Table S5.** Screening of reactor headspace and when $CO_2$ is added




| Entry | Temperature Pressurized | Total Solution Volume (mL)[b] | EPeP/EVMeP Yield (%)[c] | EPeP/EVMeP:EVP[c] |
|---|---|---|---|---|
| 1 | < -4 °C | 5.0 | 3.9 | 48:52 |
| 2 | > -4 °C, < 34 °C | 5.0 | 3.6 | 52:48 |
| 3 | > 34 °C | 5.0 | 5.0 | 48:52 |
| 4 | > 34 °C | 6.0 | 3.8 | 46:54 |

[a]Reaction conditions: 5.04 mmol butadiene, 30.3 mmol isoprene in 1.5 or 2.5 mL acetonitrile; 0.04% [Pd], 0.12% P(*p*-OMePh)$_3$, 1% hydroquinone, 2% DIPEA, given temperature and pressure for 20 h. [b] total volume after MeCN, isoprene, and butadiene were added. [c]calculated *via* $^1$H NMR spectroscopy using DMT standard.

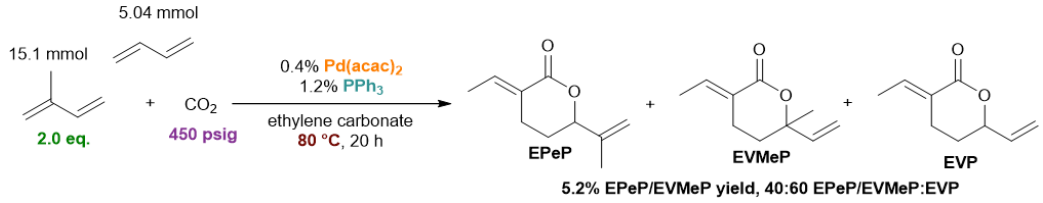



**Figure S6.** Nozaki cotelomerization catalyst system[3] reproduced in 6-well reactor

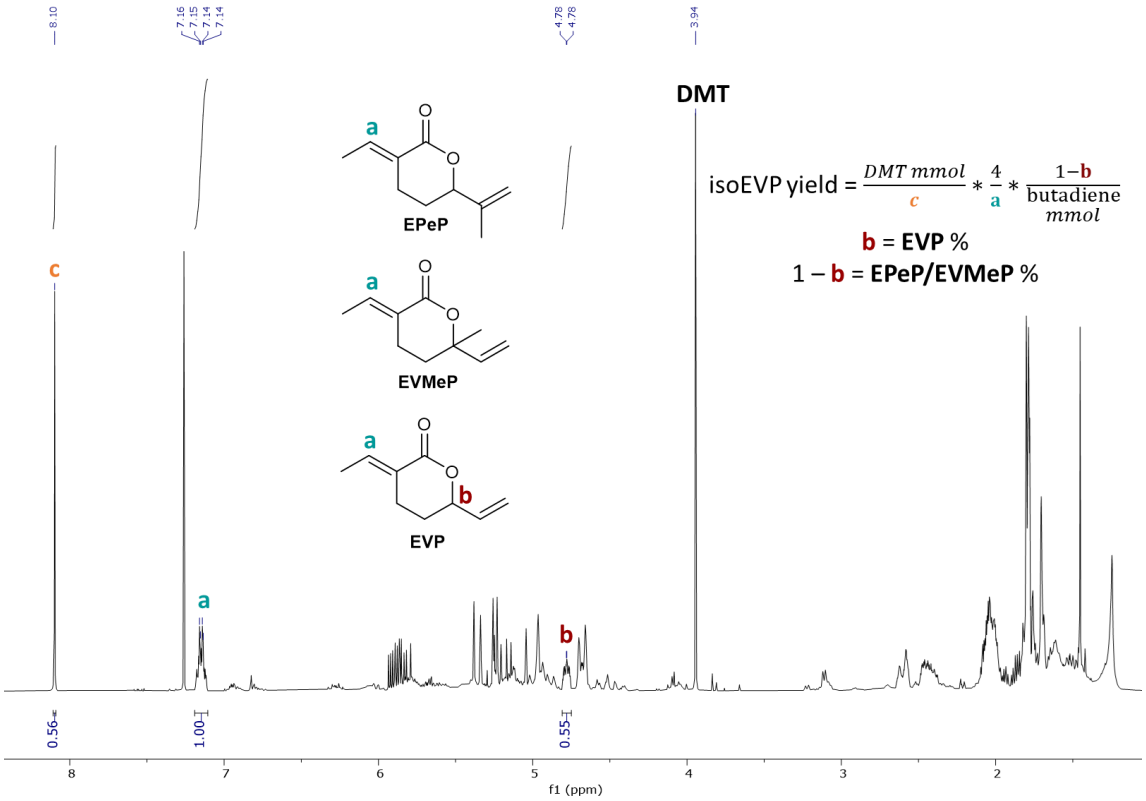



**Figure S7.** Typical $^{1}$H NMR spectrum of crude cotelomerization screening used for EPeP/EVMeP yield and EPeP/EVMeP:EVP (Table S4, entry 2) in $CDCl_3$. Monomer ratios are determined as rough estimates by setting the α-β-ester-H(a) to 1.0.

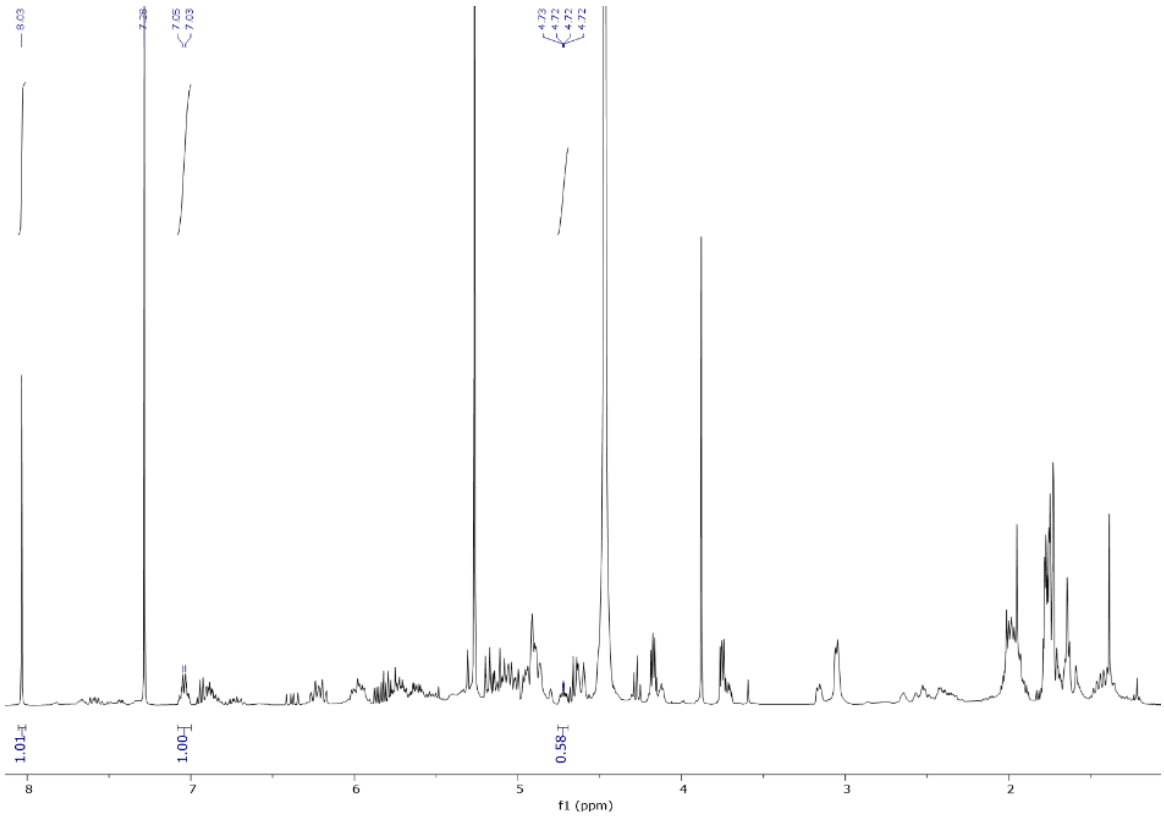



**Figure S8.** $^{1}H$ NMR spectrum of Nozaki catalyst system from Figure S6 in $CDCl_3$.

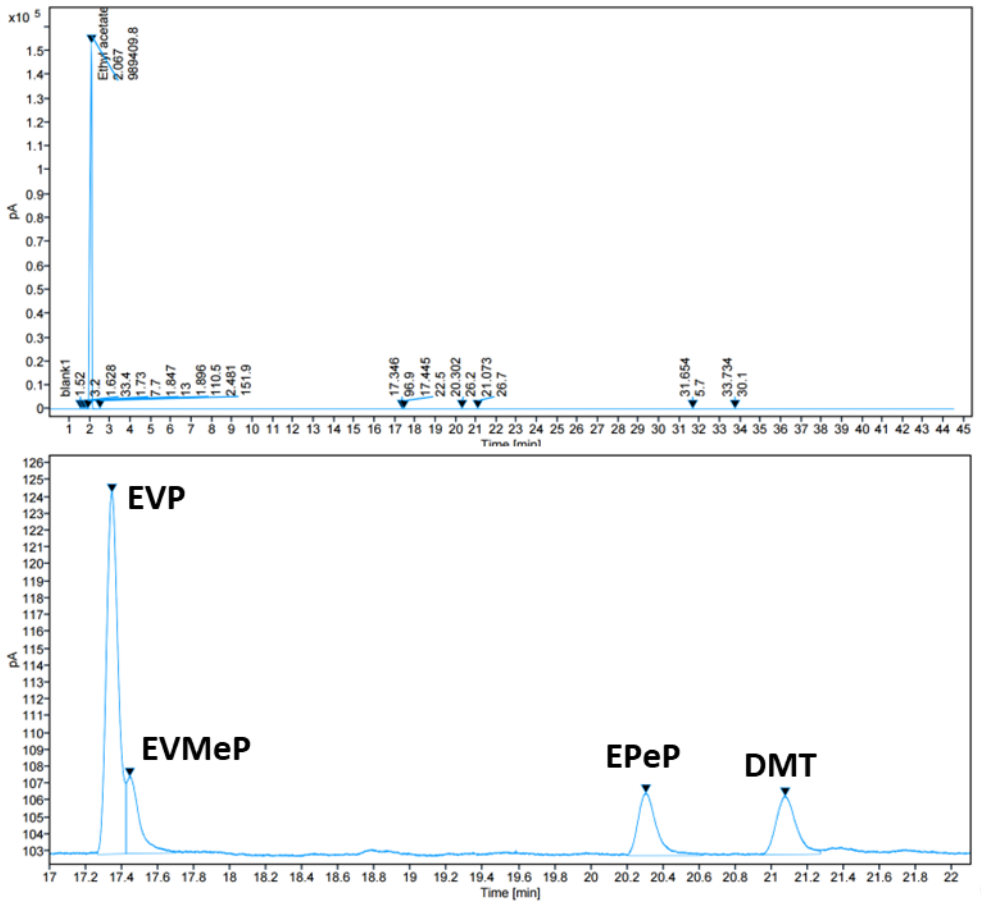



**Figure S9.** GC-FID analysis of standard cotelomerization catalyst system (Table S1, entry 1).

## Cotelomerization Scale-Up with Isoprene Recycling

$Pd(OAc)_2$ (54 mg, 0.24 mmol, 0.0007 eq.) and P(*p*-OMePh)$_3$ (254 mg, 0.72 mmol, 0.0021 eq.) were weighed out and added to a 1 L parr reactor. 150 mL of MeCN was added, and the reaction mixture was stirred with a spatula until all of the solids had dissolved. Hydroquinone (379 mg, 3.4 mmol, 0.01 eq.) and DIPEA (1.2 mL, 6.9 mmol, 0.02 eq.) were added to the reactor which was then placed in a dry ice/acetone bath. Freshly filtered isoprene (206 mL, 2.1 mol, 6.0 eq.) was added and stirred followed by freshly condensed butadiene (30 mL, 0.34 mol, 1.0 eq.). The reactor was sealed and purged 3x with 150 psig $CO_2$ while still in the ice bath. After the last purging cycle, the reactor was heated to room temperature using a heat gun. The Reactor was then pressurized to 450 psig $CO_2$ and heated to 80 °C while stirring. After 72 h, the reactor was cooled in an ice bath before being vented out. Excess isoprene was collected *via* rotary evaporator (typically about 50% of the original amount) and used in further telomerizations. $^1$H NMR (400 MHz, $CDCl_3$, δ, ppm ) 7.20-7.20 (m, 3H, EVP, EPeP and EVMeP), 5.95-5.78 (m, 2H, EVP and EVMeP, 5.41-5.13 (m, 4H, EVP and EVMeP), 5.05 (s, 1H, EPeP), 4.95 (S, 1H, EPeP), 4.81-4.75 (m, 1H, EVP), 4.69-4.64 (m, 1H, EPeP), 2.66-2.37 (m, 6H, EVP, EPeP and EVMeP), 2.11-1.72 (m, 18H, EVP, EPeP and EVMeP), 1.45 (s, 3H, EVMeP); $^{13}$C NMR (101 MHz, $CDCl_3$, δ, ppm) 166.4, 166.4, 166.2, 142.4, 141.1, 140.9, 140.4, 135.8, 126.1, 126.0, 125.4, 116.8, 114.5, 113.0, 81.7, 81.6, 78.9, 31.9, 27.8, 27.6, 26.3, 22.2, 21.9, 20.2, 18.1, 14.1.

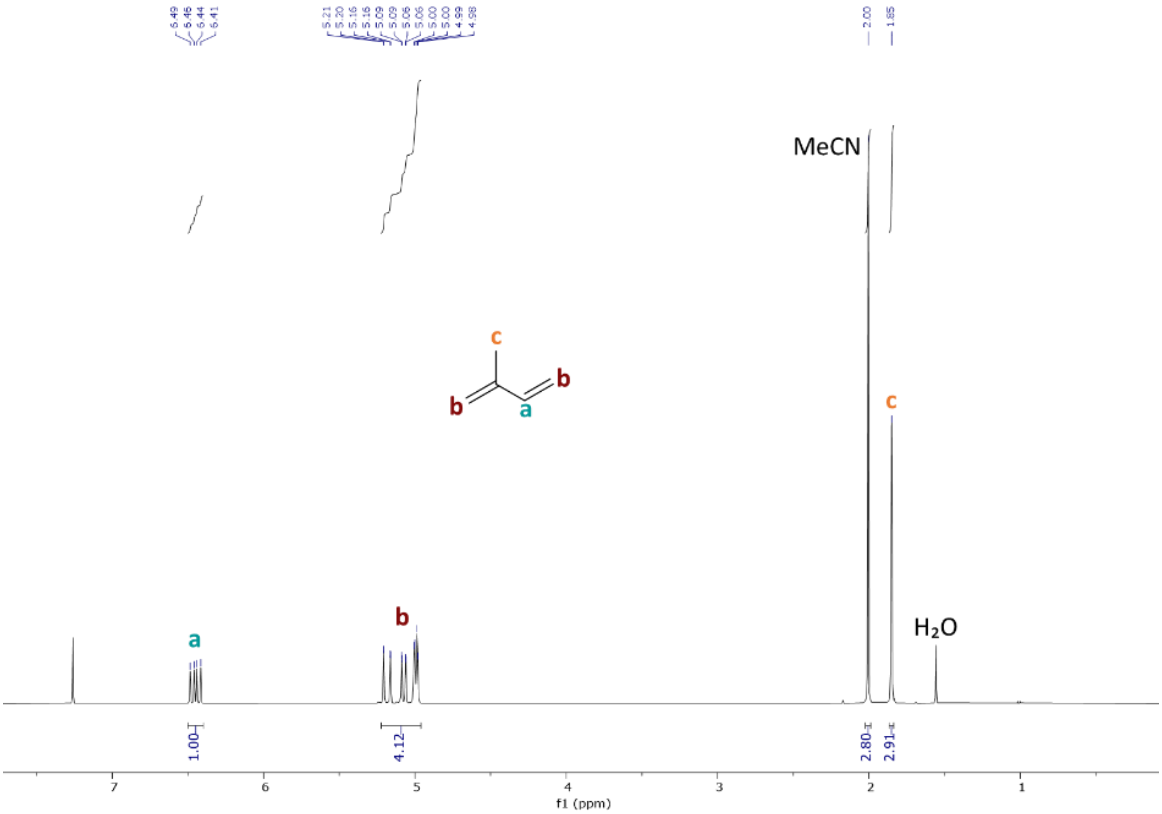



**Figure S10.** $^{1}$H NMR spectrum of recycled isoprene in $CDCl_3$.

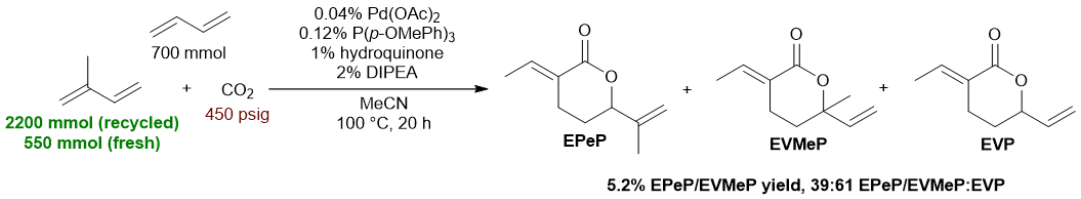



**Figure S11.** Large-scale telomerization with recycled isoprene in $CDCl_3$.

After multiple runs (2-3), products were combined and vacuum distilled. Everything collected between 115-160 °C was combined and columned on silica gel using 4:1 hexanes:ethyl acetate. Fractions containing various ratios of pure EPeP:EVMeP:EVP were obtained. These mixtures were then selectively hydrogenated following a reported protocol using trichlorosilane ($Cl_3SiH$) and hexamethylphosphoramide (HMPA).[4] After work-up, lactone mixtures were purified with 1-2 columns again using 4:1 hexanes:ethyl acetate. $^{1}$H NMR (400 MHz, $CDCl_3$, δ, ppm) 5.93-5.73 (m, 2H, EtVP and EtVMeP), 5.37-5.09 (m, 4H, EtVP and EtVMeP), 5.03 (s, 1H, EtPeP), 4.97-4.92 (d, 2H, EtPeP), 4.86-4.66 (m, 2H, EtVP and EtPeP), 2.45-2.25 (m, 3H, EtVP, EtPeP and EtVMeP), 2.12-1.45 (m, 18H, EtVP, EtPeP and EtVMeP), 1.78 (s, 3H, EtPeP), 1.45.3 (two s, 3H, EtVMeP), 1.03-0.90 (m, 3H, EtVP, EtPeP and EtVMeP); $^{13}$C NMR (101 MHz, CDCl3, δ, ppm) 174.8, 174.6, 173.4, 143.0, 142.5, 141.7, 136.4, 136.0, 116.9, 116.6, 113.0, 112.8, 83.8, 83.0, 81.0, 80.6, 78.2, 77.2, 42.0, 41.9, 40.3, 40.0, 31.5, 28.8, 28.1, 27.7, 27.0, 25.5, 24.9, 24.8, 24.7, 24.5, 24.0, 22.5, 22.4, 21.6, 18.3, 17.8, 11.5, 11.4, 11.4, 11.1.

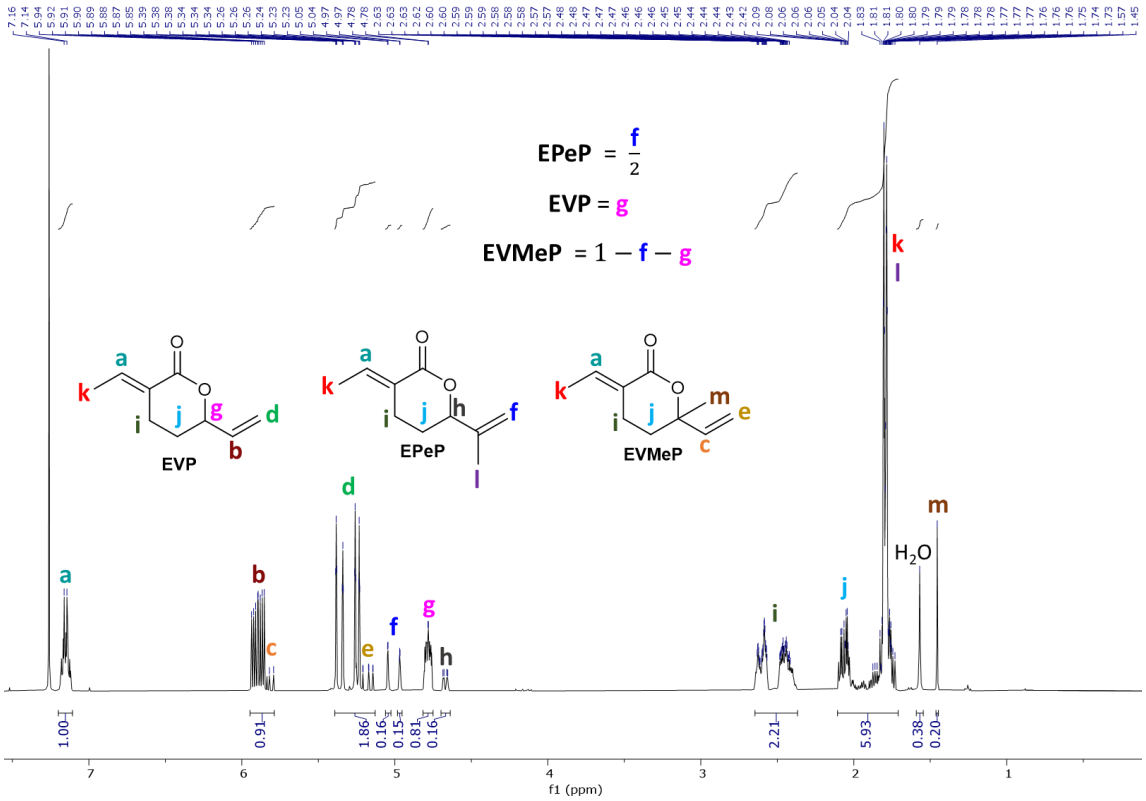



**Figure S12.** Typical $^{1}$H NMR spectrum of purified EPeP:EVMeP:EVP in $CDCl_3$. Mixtures vary depending on catalyst system and reaction conditions. Monomer ratios are determined as rough estimates by setting the $\alpha$-$\beta$-ester-H(a) to 1.0.

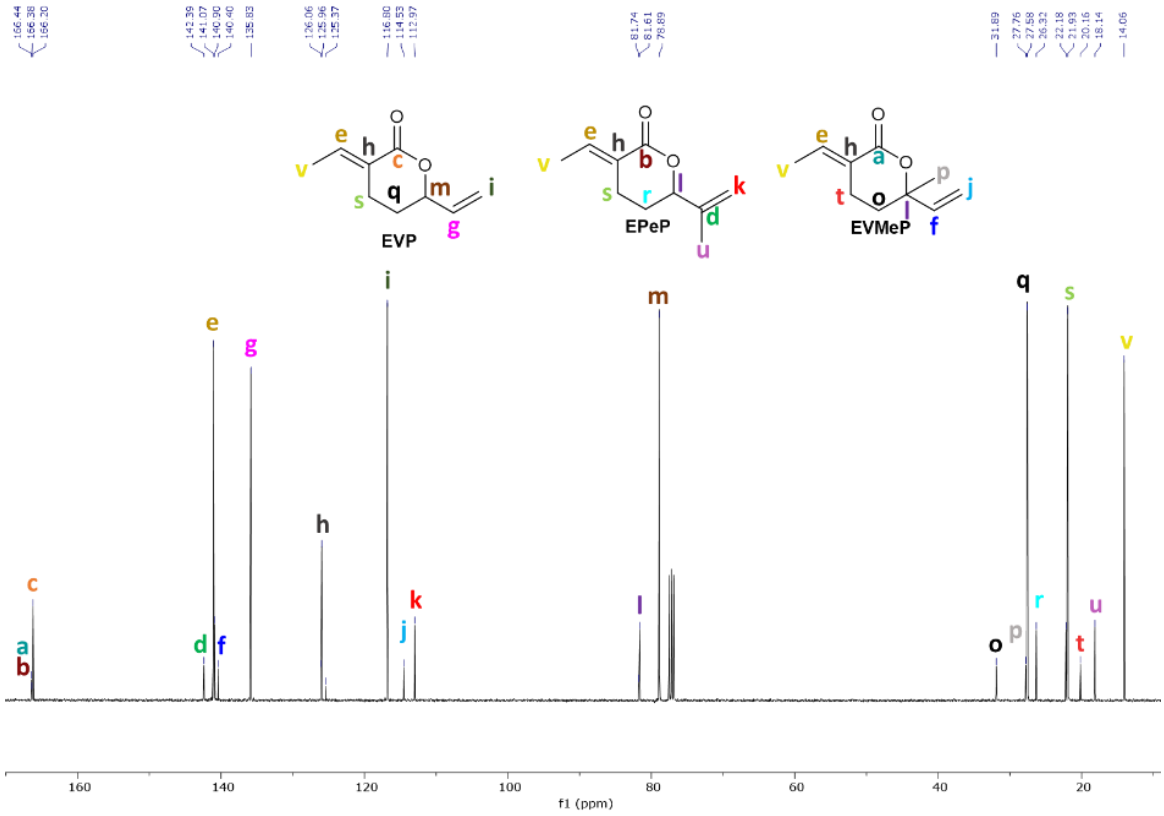



**Figure S13.** Typical $^{13}C$ NMR spectrum of purified EPeP:EVMeP:EVP in $CDCl_3$. Mixtures vary depending on catalyst system and reaction conditions.

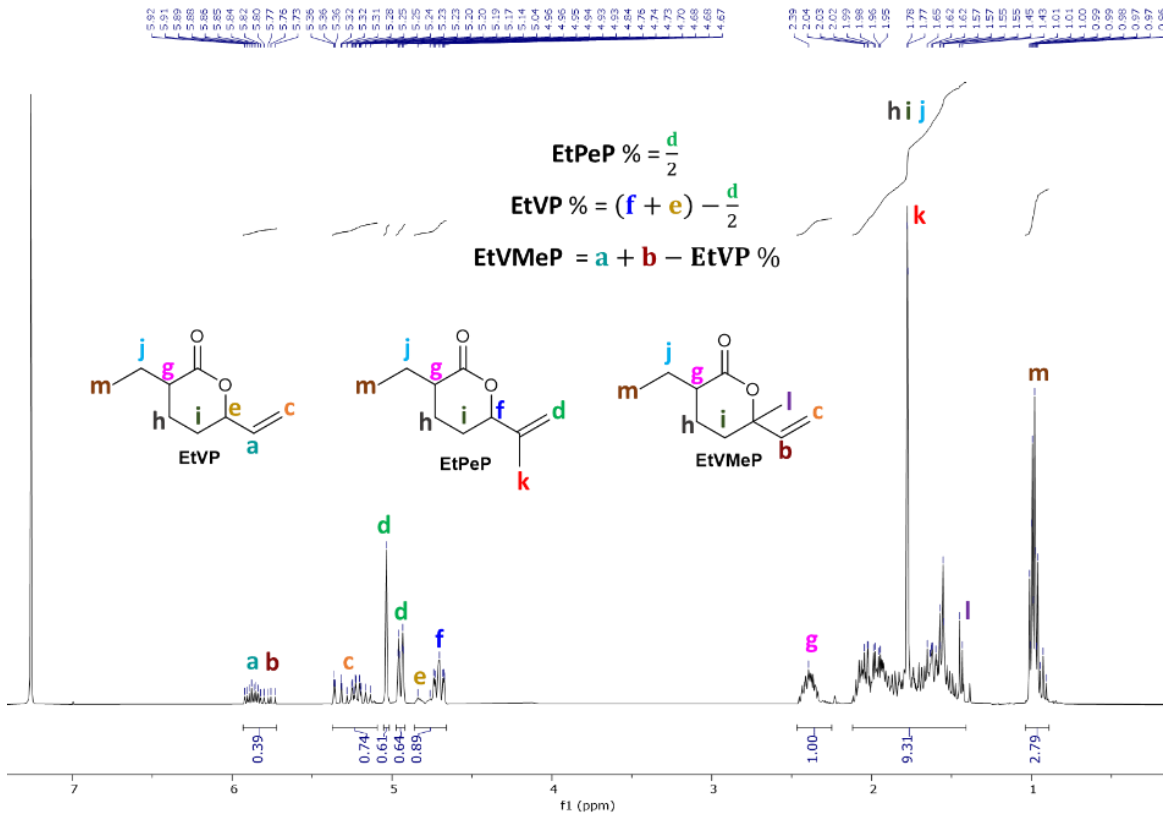



**Figure S14.** Typical $^{1}$H NMR spectrum of purified EtPeP: EtVMeP:EtVP in $CDCl_3$. Mixtures vary depending on catalyst system and reaction conditions. Monomer ratios are determined as rough estimates by setting the $\alpha$-H (g) to 1.0.

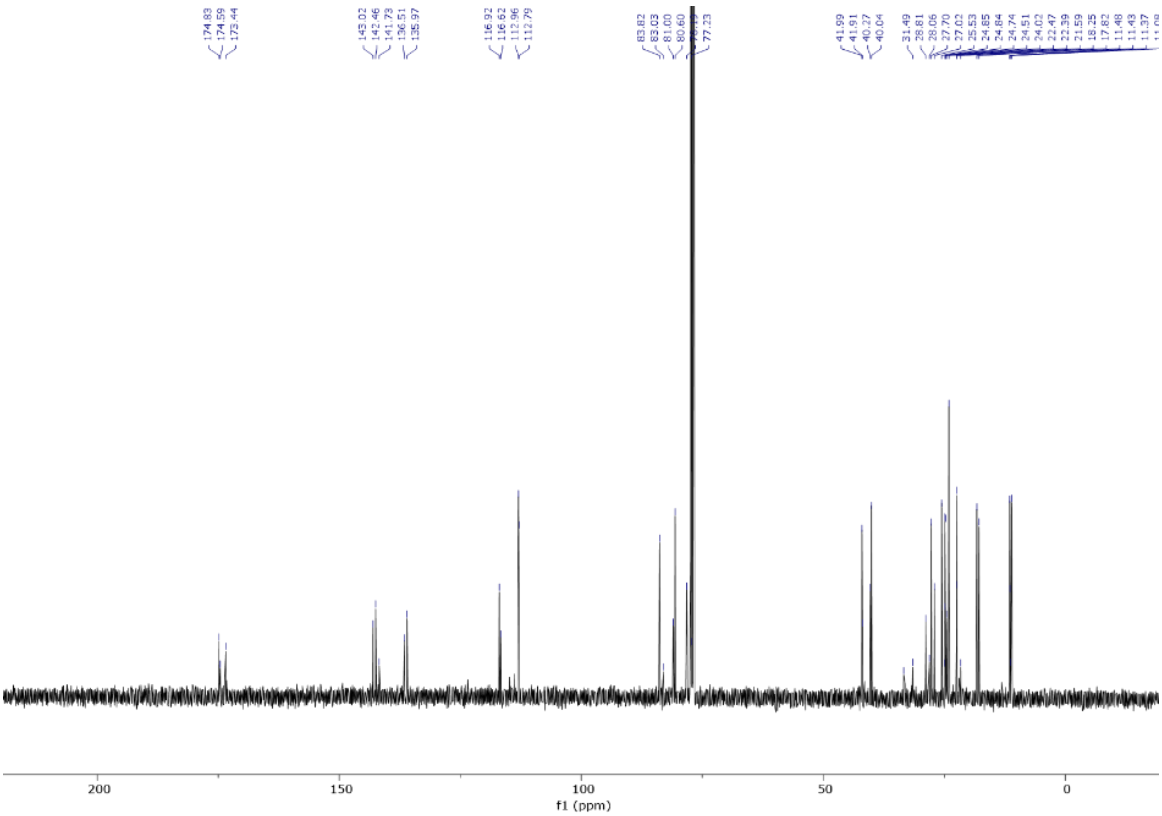
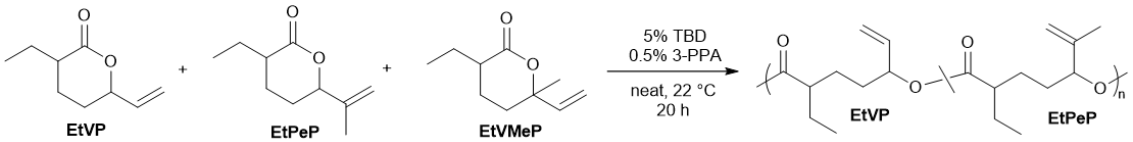



**Figure S15.** Typical $^{13}C$ NMR of purified EtPeP: EtVMeP:EtVP in $CDCl_3$. Mixtures vary depending on catalyst system and reaction conditions (see stepwise synthesis for labelled NMR).

## Synthesis of EtPeP Copolymers

All monomer mixtures were allowed to stir in the presence of calcium hydride ($CaH_2$) overnight before being distilled and put into a nitrogen glovebox. Mixtures were then allowed to dry over 3Å molecular sieves for at least 1 day before use. In a typical polymerization, monomer mixture was weighed into a 2 mL vial equipped with a football-shaped stir bar. Occasionally, EtVP was doped in, in order to access a wider range of EtPeP incorporation. 250 mg of monomer mixture was used for each reaction. 3-phenyl-1-propanol (3-PPA), (0.005 eq.) was then added to the vial followed by triazabicyclodecene (TBD), (0.05 eq.). Reactions were allowed to stir overnight (20 h) before being taken out, quenched with benzoic acid, and analyzed *via* $^1H$ NMR for monomer conversion. Polymers were then dissolved using 70:30 DCM:MeCN and filtered through silica to remove residual TBD. The solvent was then removed *on vacuo* and excess monomer was extracted via vacuum distillation at 165 °C. Typical yields were between 40-70% depending on molar ratios and total monomer conversion. $^1H$ NMR (400 MHz, $CDCl_3$, δ, ppm) 5.79-5.67 (m, 1H, pEtVP), 5.29-5.10 (m, 3H, pEtVP, 1H pEtPeP), 4.93 (s, 1H, pEtPeP), 4.87 (s, 1H, pEtPeP), 2.69 (t, 2H, initiator), 2.33-2.20 (m, 2H, pEtVP and pEtPeP), 1.68 (s, 3H, pEtPeP), 1.71-1.39 (m, 12H, pEtVP and pEtPeP), 0.93-0.82(m, 6H, pEtVP and pEtPeP); $^{13}C$ NMR (101 MHz, CDCl3, δ, ppm) 175.0, 174.8, 142.9, 136.3, 128.5, 128.4, 117.2, 77.2, 74.4, 73.9, 47.4, 47.0, 46.7, 32.1, 31.9, 30.4, 27.8, 27.5, 25.6, 25.5, 18.0, 11.7.

**Table S6.** Copolymerization results for varying monomer mixtures




| Entry | EtVP/**EtPeP**/EtVMeP (mol/mol/mol)[b] | Polymer **EtPeP** (%)[c] | Total Conversion (%)[c] | **EtPeP** Conversion (%)[c] | $M_{n,SEC}$ (kDa)[d] | $Đ$ | $T_g$(°C) |
|---|---|---|---|---|---|---|---|
| 1[e] | 100/**0**/0 | 0 | 80 | - | 13.6 | 1.3 | -39.2 |
| 2 | 73/**19**/8 | 20 | 72 | 75 | 12.7 | 1.4 | -35.5 |
| 3 | 67/**30**/3 | 32 | 71 | 68 | 9.5 | 1.2 | -33.0 |
| 4 | 56/**40**/4 | 42 | 70 | 71 | 8.9 | 1.4 | -28.6 |
| 5[f] | 51/**44**/5 | 48 | 67 | 70 | 17.9 | 1.9 | -27.2 |
| 6 | 39/**52**/9 | 56 | 64 | 67 | 7.4 | 1.2 | -28.1 |
| 7 | 17/**70**/13 | 76 | 54 | 63 | 5.5 | 1.3 | -27.5 |
| 8 | 7/**79**/14 | 93 | 48 | 56 | 7.4 | 1.4 | -23.2 |

[a]Reaction conditions: 5.0 mol% TBD, 0.5 mol% 3-PPA, neat, 22 °C, 20 h. [b]initial molar ratios. [c]calculated from $^1$H NMR spectroscopy. [d]determined by THF SEC using polystyrene standards. [e]taken from reference 1. [f]2.5% KHMDS, 2.5% Ph,Cy-urea used instead of 5% TBD.

## Characterization EtPeP Copolymers

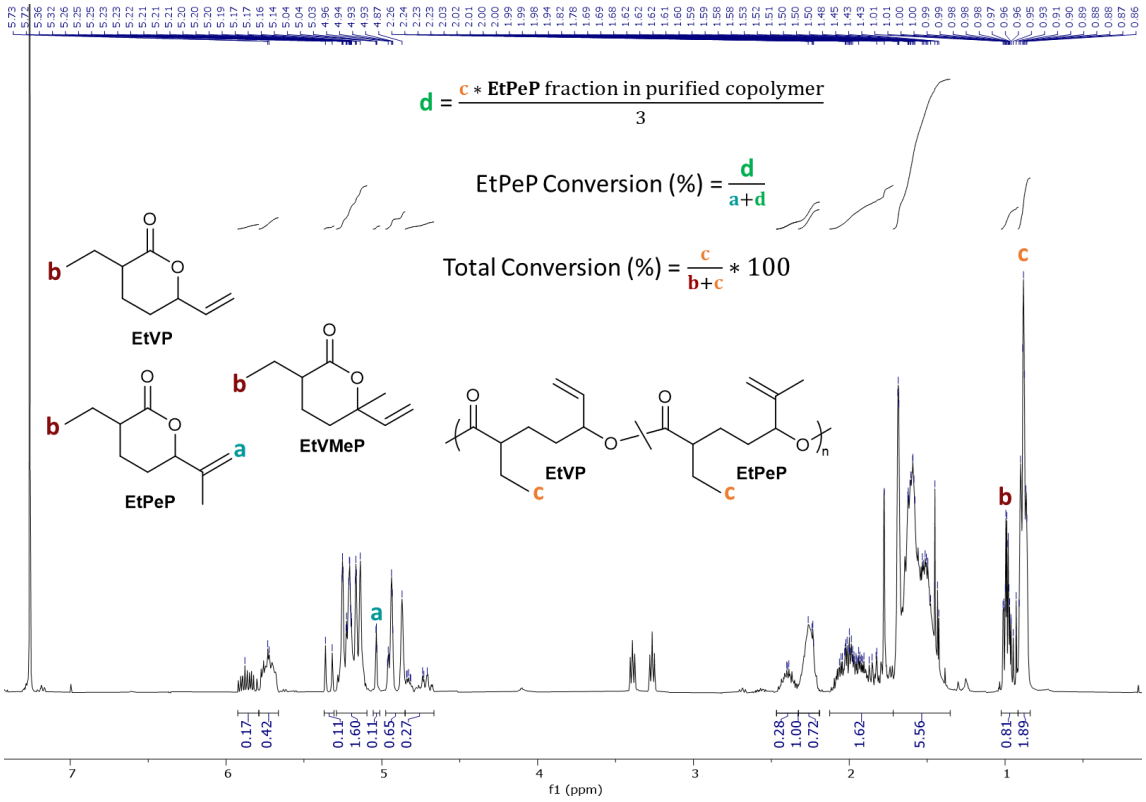



**Figure S16.** Typical $^1$H NMR spectrum of crude polymerization to determine conversion (Table S6, entry 4) in $CDCl_3$.

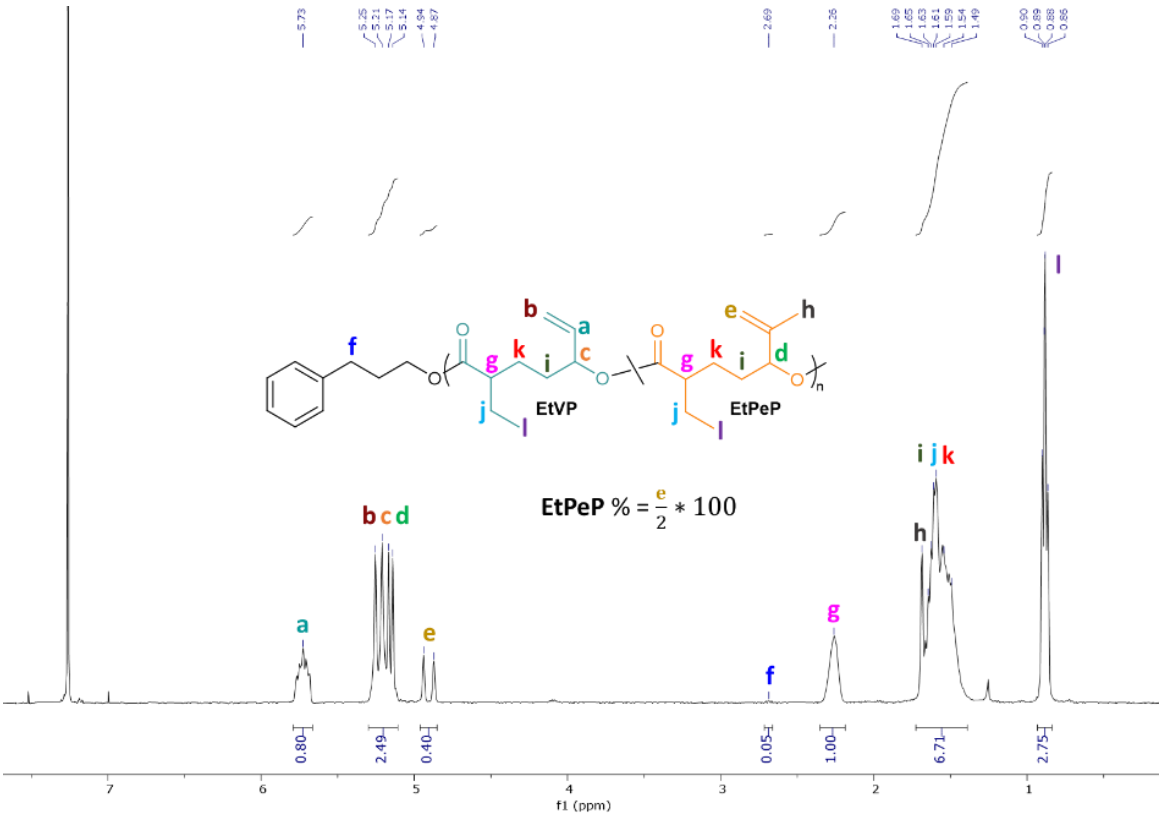



**Figure S17.** $^{1}$H NMR spectrum of 20% EtPeP incorporation (Table S6, entry 2) in $CDCl_3$. Monomer ratios are determined as rough estimates by setting the $\alpha$-H (g) to 1.0.

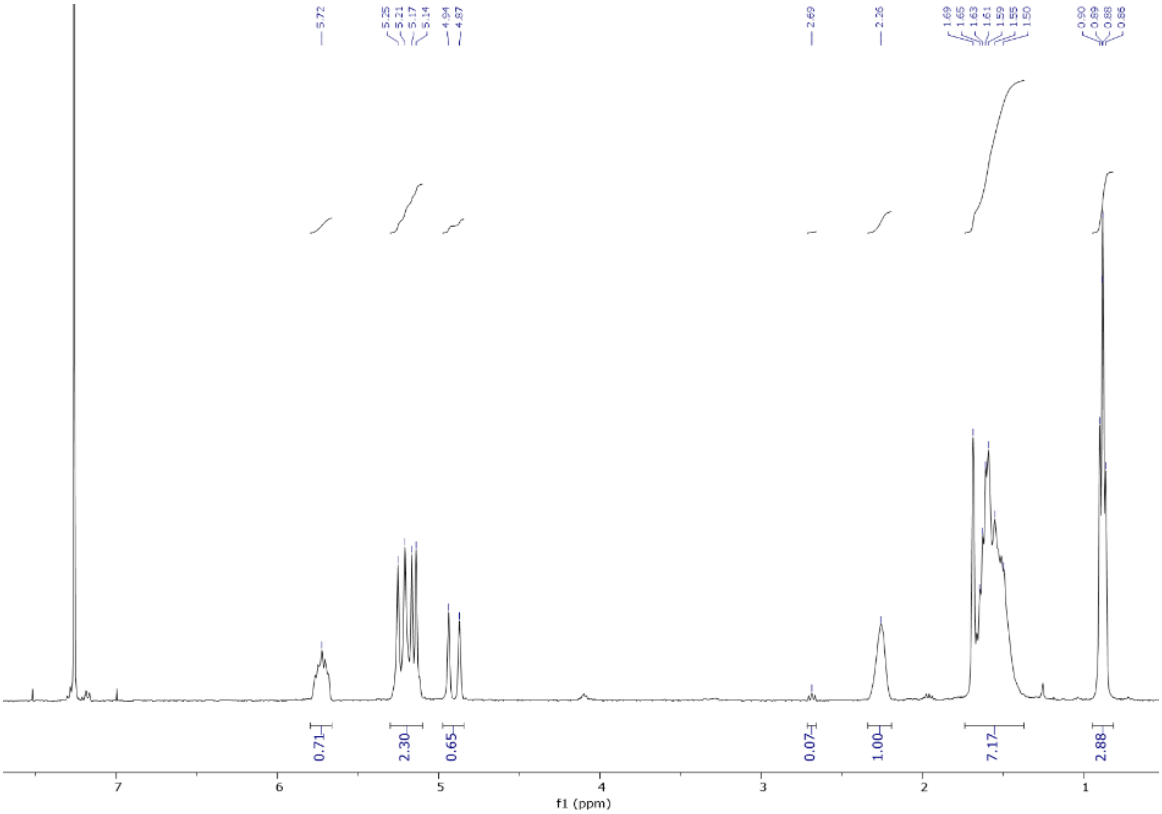



**Figure S18.** $^{1}H$ NMR spectrum of 32% EtPeP incorporation (Table S6, entry 3) in $CDCl_3$.

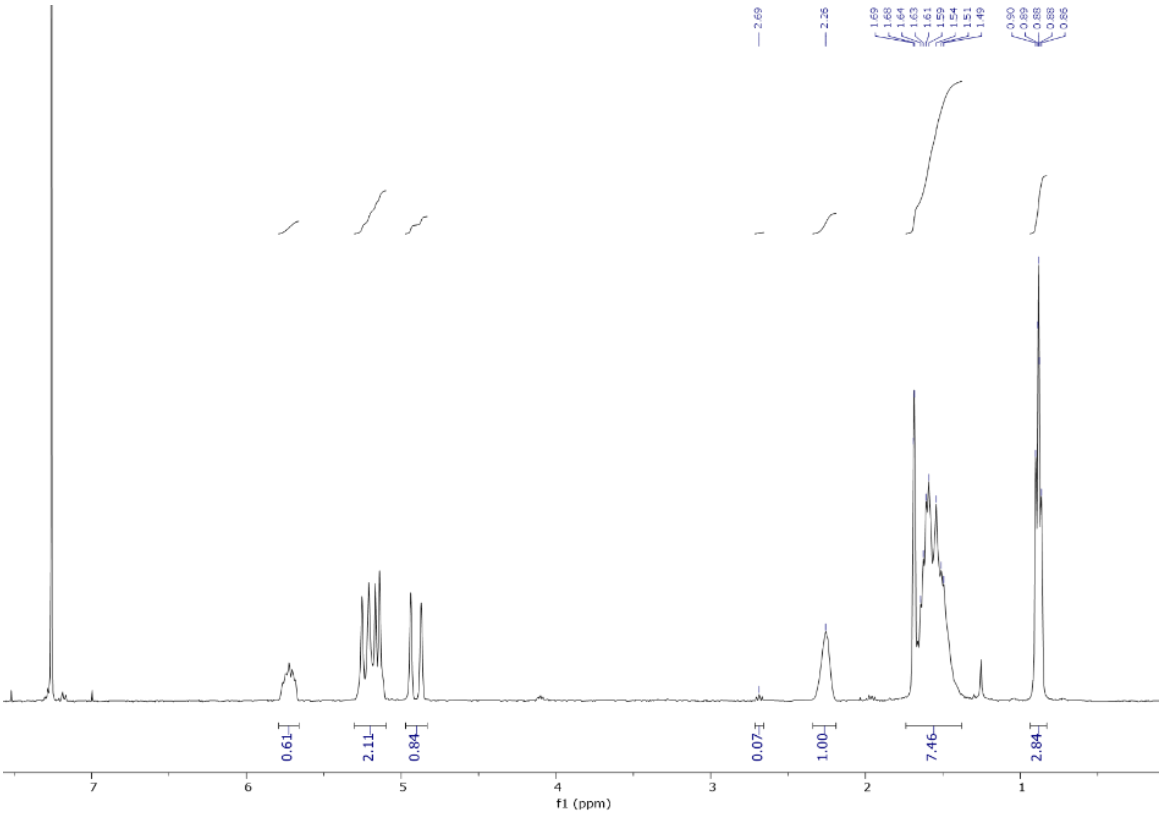


**Figure S19.** $^{1}$H NMR of 42% EtPeP incorporation (Table S6, entry 4) in $CDCl_3$.

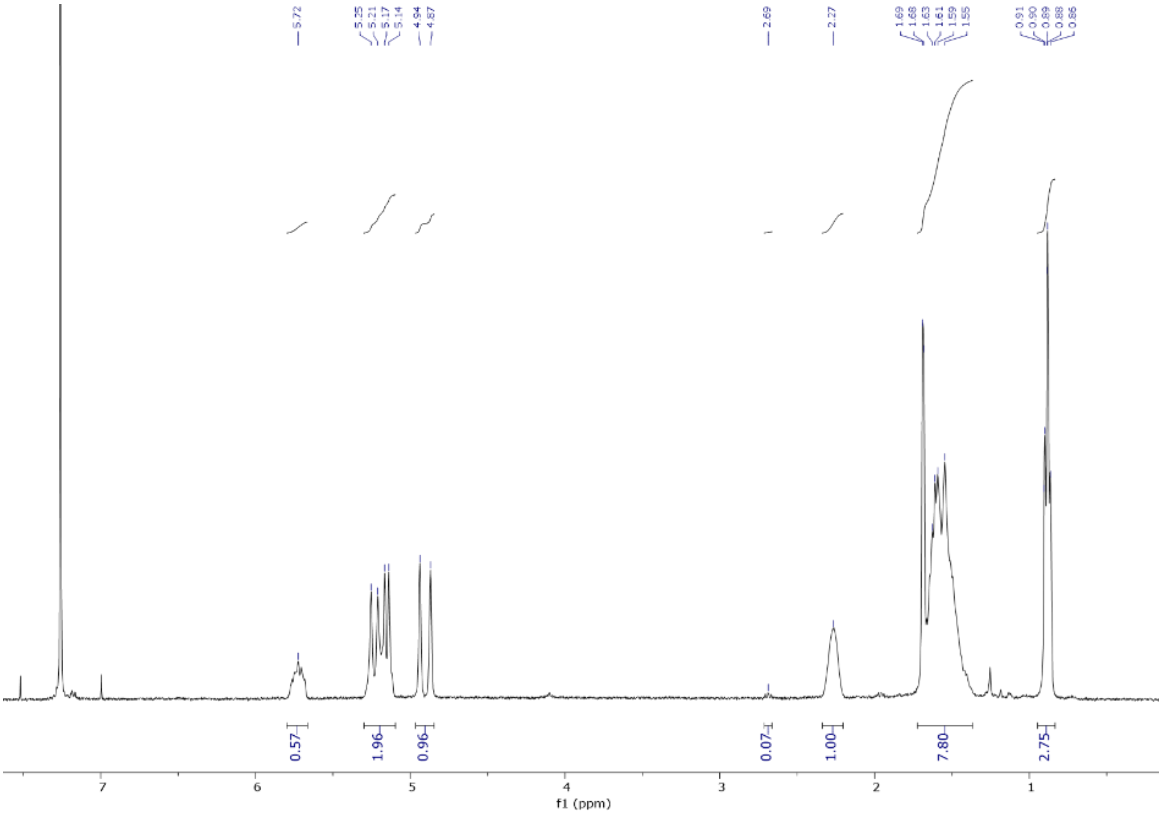



**Figure S20.** $^{1}$H NMR of 48% EtPeP incorporation using KHMDS and Ph,Cy-Urea (Table S6, entry 5) in $CDCl_3$.

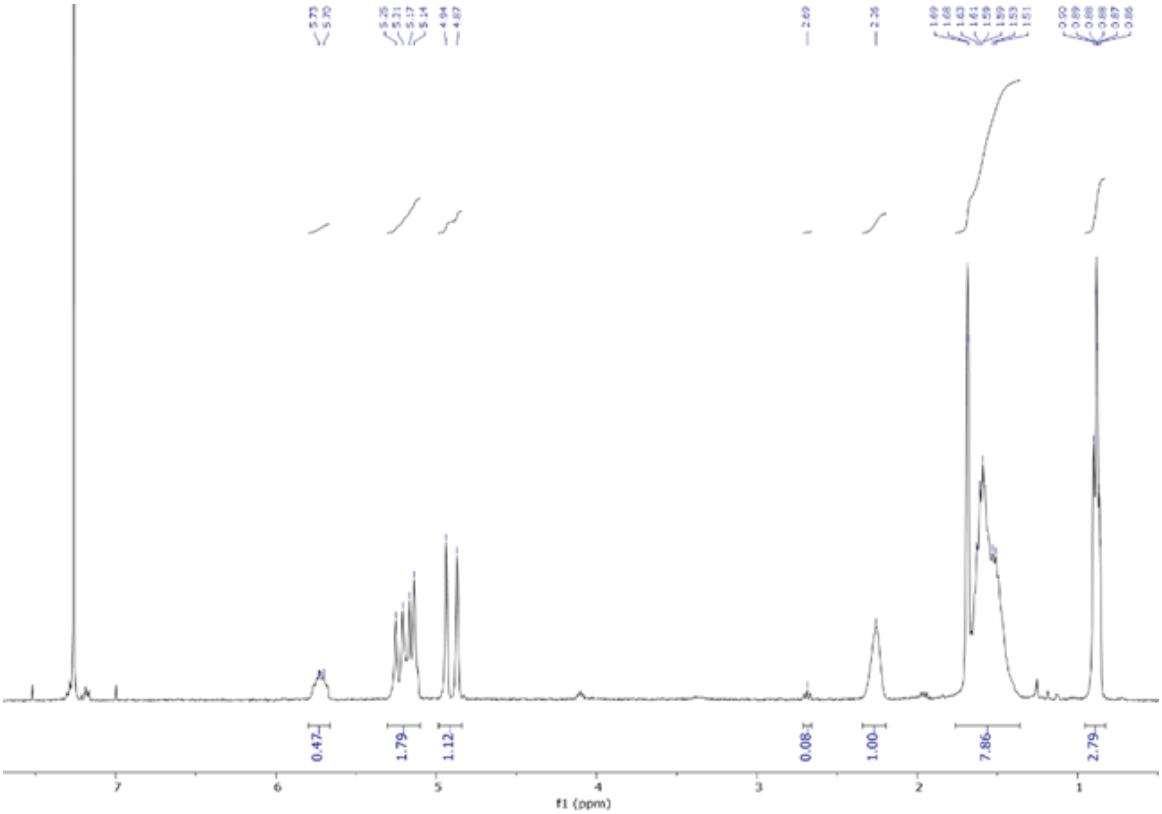



**Figure S21.** $^{1}H$ NMR of 56% EtPeP incorporation (Table S6, entry 6) in $CDCl_3$.

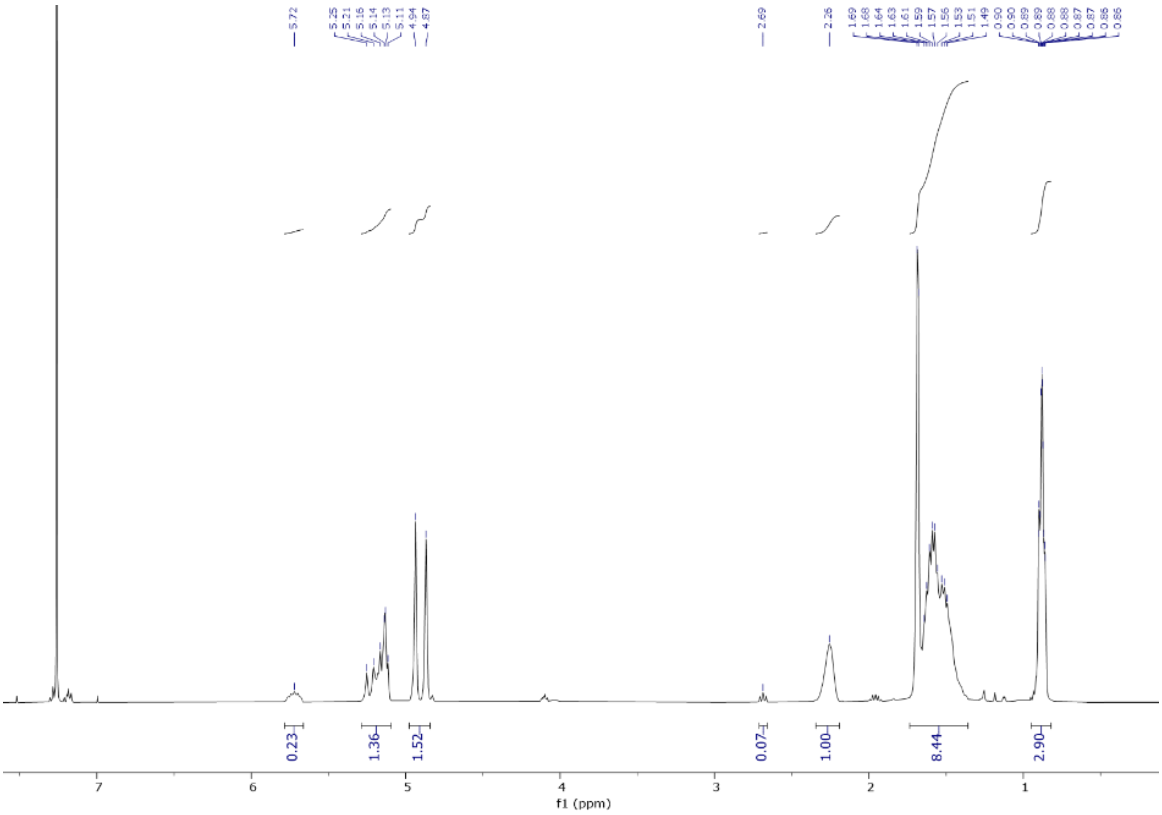


**Figure S22.** $^{1}$H NMR of 76% EtPeP incorporation (Table S6, entry 7) in $CDCl_3$.

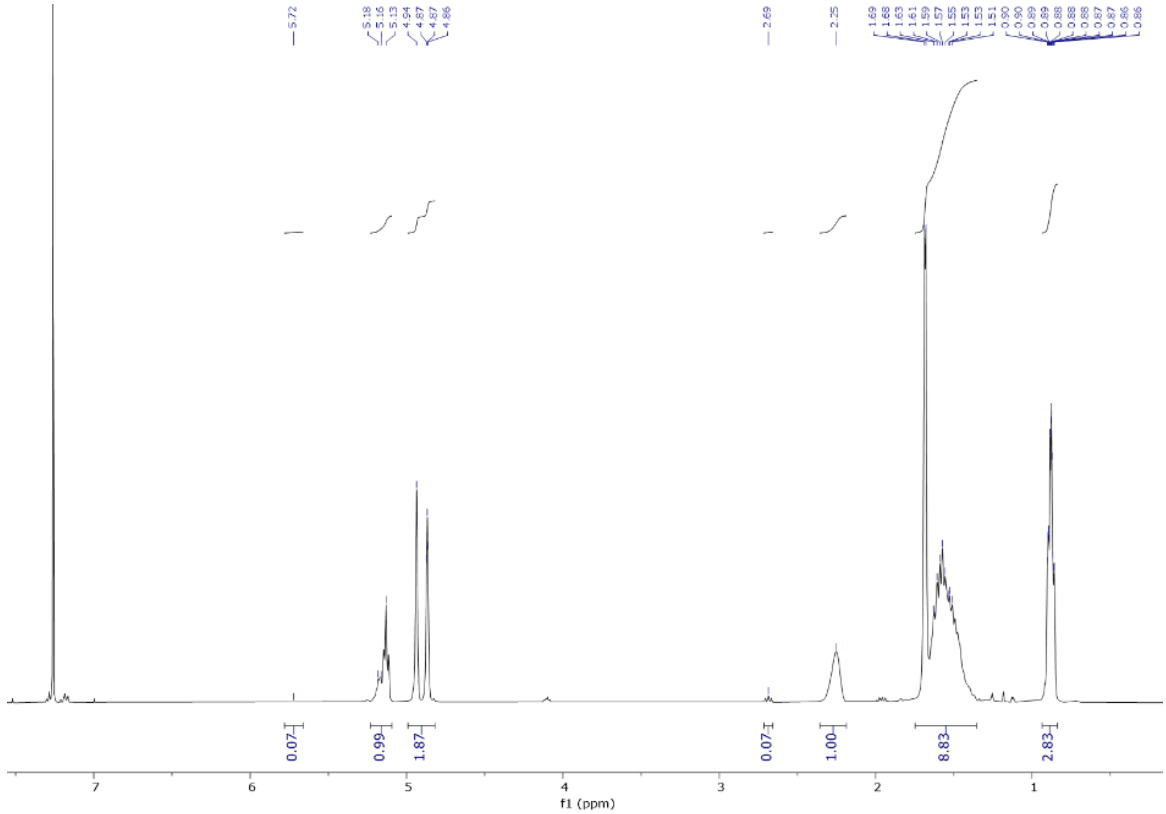



**Figure S23.** $^{1}$H NMR of 93% EtPeP incorporation (Table S6, entry 8) in $CDCl_3$.

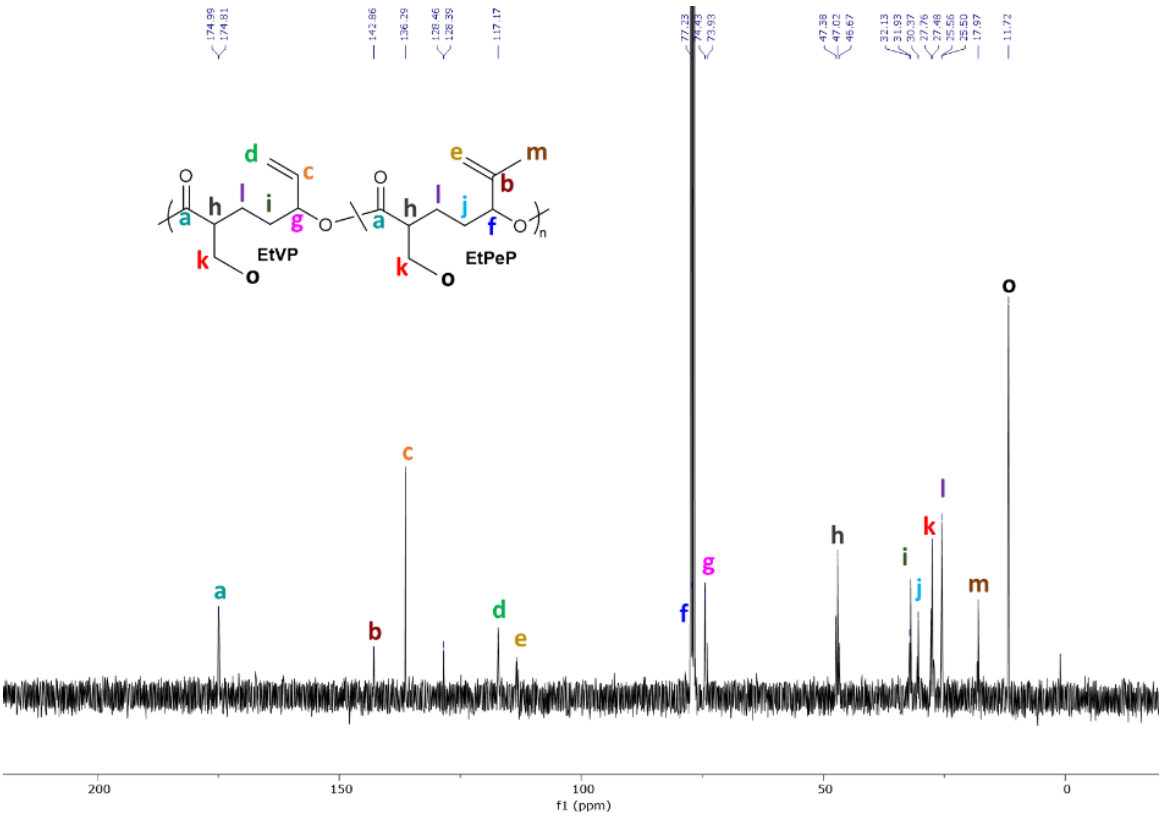



**Figure S24.** Typical $^{13}C$ NMR of EtPeP copolymers (Table S6, entry 4) in $CDCl_3$.

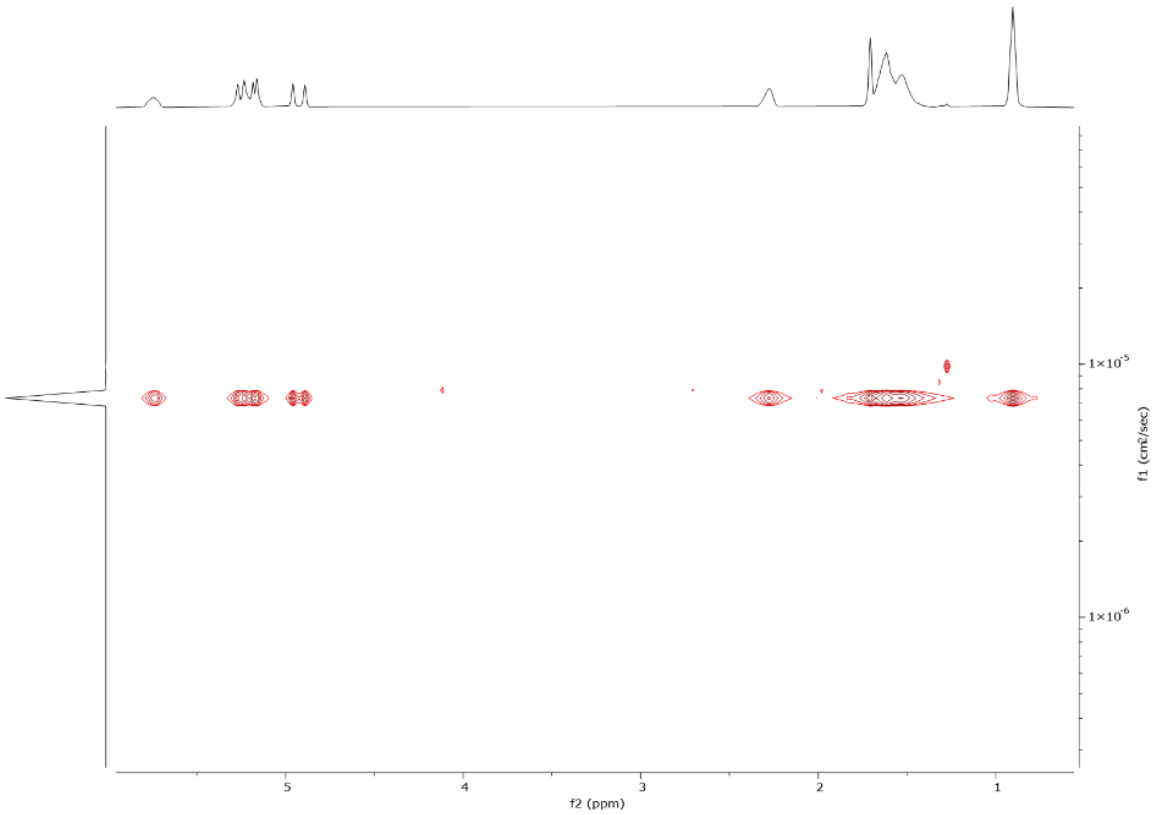


**Figure S25.** Typical DOSY NMR of EtPeP copolymers (Table S6, entry 6) in $CDCl_3$.

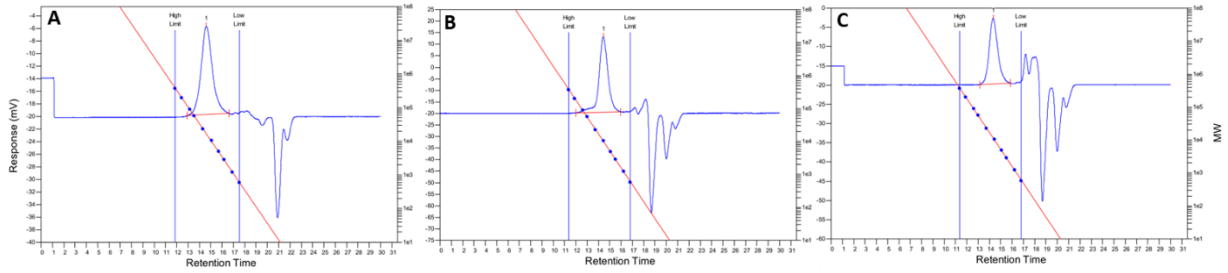



**Figure S26.** SEC dRI of 20% (A), 32% (B), and 44% (C) EtPeP incorporation (Table S6, entries 2-4)

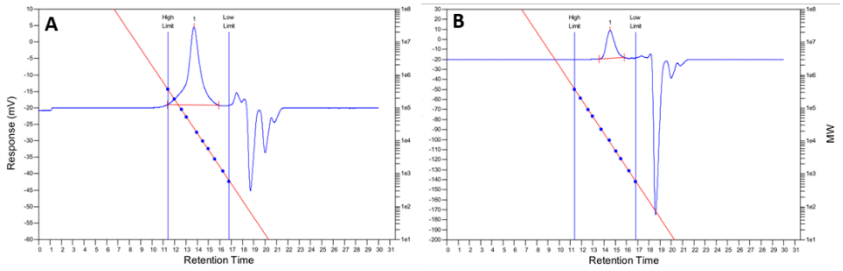



**Figure S27.** SEC dRI of 48% (A) and 58% (B) EtPeP incorporation (Table S6, entries 5-6)

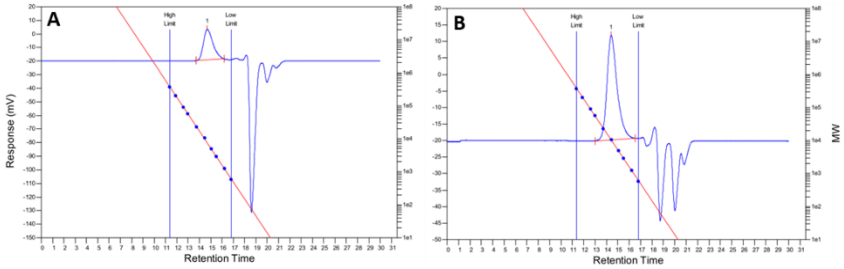



**Figure S28.** SEC dRI of 76 and 95% EtPeP incorporation (Table S6, entries 7-8)

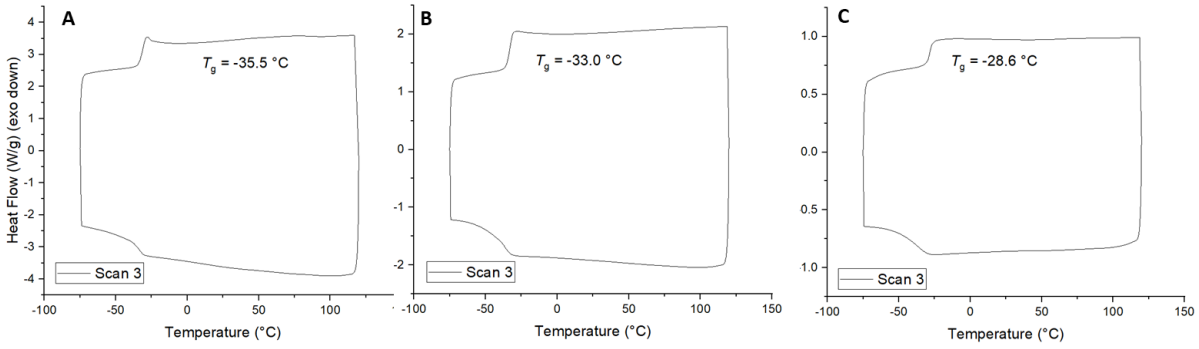



**Figure S29.** DSC of 20, 32, and 44% EtPeP incorporation (Table S6, entries 2-4)

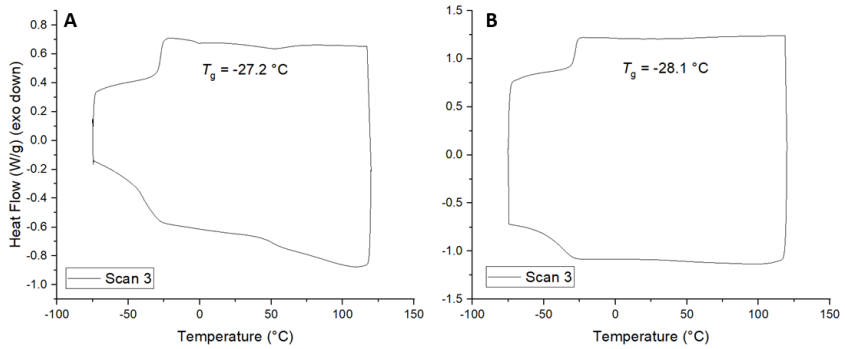



**Figure S30.** DSC of 48 and 58% EtPeP incorporation (Table S6, entries 5-6)

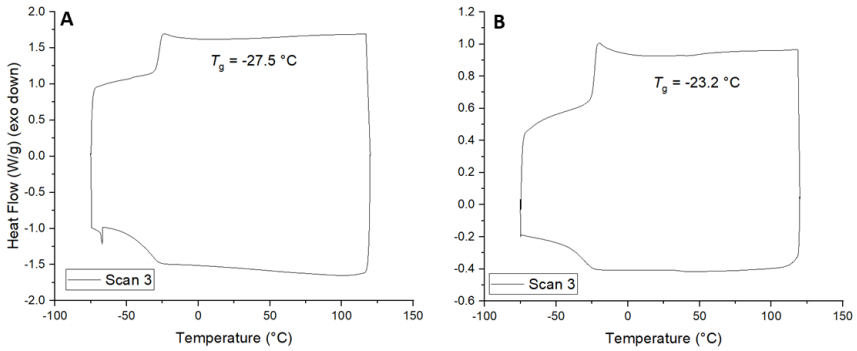



**Figure S31.** DSC of 76 and 93% EtPeP incorporation (Table S6, entries 7-8)

## Determination of Reactivity Ratios

TBD (21.7 mg, 0.16 mmol, 0.05 eq.), 54:41:5 EtVP:EtPeP:EtVMeP (500 mg, 3.11 mmol, 1 eq. ), and 3-PPA (4.24 mg, 0.031 mmol, 0.01 eq) were added to a 20 mL scintillation vial equipped with a stir bar. Aliquots were removed and quenched with benzoic acid in $CDCl_3$ at t = 0, 10, 20, 30, 60, 120, 240 and 360 min. Individual monomer conversion was plotted vs. total monomer conversion (**Figure S33**) and the data set for each monomer was fit using a non-terminal model **(Eq. S1-2)**.[5]

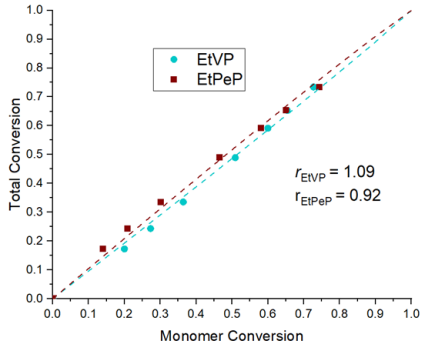



**Figure S32.** Reactivity ratios for *poly*(EtVP-*co*-EtPeP) determined from BSL method.

$$p_{AB}(p_A) = 1 - n_A(1 - p_A) - (1 - n_A)(1 - p_A)^{r_B} \quad \textbf{Eq. S1}$$

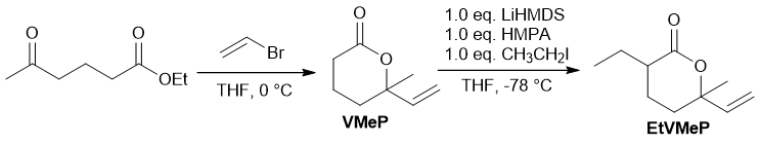
$$p_{AB}(p_B) = 1 - n_A(1 - p_B)^{r_A} - (1 - n_A)(1 - p_B) \quad \textbf{Eq. S2}$$

where,

$p_{AB}$ = total monomer conversion, $p_A$ = EtVP conversion, $p_B$ = EtPeP conversion, $n_A$ = initial EtVP molar ratio, $r_A$ = EtVP reactivity ratio, $r_B$ = EtPeP reactivity ratio

## Stepwise Synthesis of EtVMeP and EtPeP

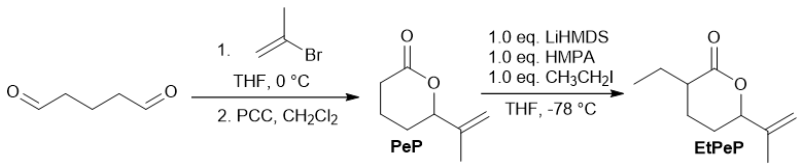
**EtVMeP Synthesis**




**Scheme 3.** Stepwise synthesis of EtVMeP

**6-methyl-6-vinyltetrahydro-2*H*-pyran-2-one (VMeP)** was synthesized following a modified literature protocol for a similar lactone.[6] Ethyl 5-oxohexanoate (13.0 g, 82.2 mmol, 1.0 eq.) was added to a 3-neck round-bottomed flask equipped with a stir bar. The RBF was cycled onto the Schlenk line before 55 mL of anhydrous THF was added *via* cannula. The flask was place in an ice bath before vinyl magnesium bromide (30 mL, 90.4 mmol, 1.1 eq) was added dropwise. The reaction mixture was allowed to stir at 0 °C for 3 h before being quenched with excess saturated $NH_4Cl$. The product was extracted three times with 20 mL $Et_2O$, washed with brine 3x20 mL, and dried over $Na_2SO_4$. The resulting solution was dried on vacuo before being columned with 4:1 hexanes:ethyl acetate. The desired product, VMEP, was obtained in 23% yield. $^1$H NMR (400 MHz, $CDCl_3$, δ, ppm) 5.86-5.77 (m, 1H), 5.29-5.15 (m, 2H), 2.58-2.37 (m, 2H), 1.92-1.69 (m, 4H), 1.46 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$, δ, ppm) 171.3, 141.2, 114.6, 83.6, 32.8, 29.2, 28.4, 16.6.

**3-ethyl-6-methyl-6-vinyltetrahydro-2H-pyran-2-one (EtVMeP)** was synthesized following a modified α-alkylation procedure.[7] Lithium bis(trimethylsilyl)amide (LiHMDS) (4.77 g, 28.5 mmol, 1.0 eq.) was weighed into a 100 mL 3-neck round-bottom flask (RBF) equipped with a stir bar inside a nitrogen-filled glovebox. RBF was taken out of the glovebox and cycled onto a Schlenk line using $N_2$. 30 mL dry THF was added, solution was stirred until all the LiHMDS had dissolved before being cooled to -78 °C in a dry ice/acetone bath. VMeP (4.00 g, 28.5 mmol, 1.0 eq.) was dissolved in 20 mL THF and added dropwise to LiHMDS solution via cannula. The reaction mixture was allowed to stir for 30 minutes before hexamethylphosphoramide (HMPA) (4.96 mL, 28.5 mmol, 1.0 eq.) was added followed by iodoethane (EtI) (2.29 mL, 28.5 mmol, 1.0 eq.) dropwise. The reaction mixture was then stirred at -78 °C for 3 h before being quenched with 50 mL of saturated $NH_4Cl$ at -78 °C. The quenched solution was filtered through a glass frit before the organic layer was extracted with 50 mL of $Et_2O$ three times. The layer was then dried once with 30 mL brine before being dried over $Na_2SO_4$ and concentrated *on vacuo*. The resulting product was purified *via* column chromatography using 4:1 hexanes:EtOAc. The desired product was obtained in 23% yield as a mixture of diastereomers. $^1$H NMR (400 MHz, $CDCl_3$, δ, ppm) δ 5.91-5.73 (m, 1H), 5.27-5.13 (m, 2H), 2.39-2.24 (m, 1H), 2.02-1.74 (m, 4H), 1.68-1.53 (m, 2H), 1.45-1.41 (two s, 1H), 1.00-0.89 (two t, 3 H); $^{13}$C NMR (101 MHz, $CDCl_3$, δ, ppm) 174.2, 173.9, 141.7, 141.6, 114.8, 113.9, 83.5, 83.0, 41.4, 40.2, 33.4, 31.5, 28.9, 28.1, 24.9, 24.5, 21.9, 11.4, 11.0. ESI-HRMS (m/z): calcd. for $C_{10}H_{16}O_2$, 169.1223; found, 169.1219 (diff. 0.0004)




**Scheme 4.** Stepwise synthesis of EtPeP.

**6-(prop-1-en-2-yl)tetrahydro-2H-pyran-2-one (PeP)** was synthesized following a reported protocol for a similarly substituted valerolactone.[8] Mg turnings (15.3 g, 629 mmol, 1.8 eq.) was weighed into a 250 mL 3-neck RBF equipped with a stir bar. The RBF was equipped with a condenser and cycled onto the Schlenk line under $N_2$. 250 mL of dry THF was added and the mixture was heated to reflux while stirring. 2-bromopropene (37.3 mL, 420 mmol, 1.2eq.) was then slowly added starting with a small amount (1-2 mL) to active the Mg turnings. Once a clear color change occurred, the remaining 2-bromopropene was added dropwise while retaining reflux. The reaction mixture was stirred for 1 h while refluxing before being cooled to room temperature. Freshly purified glutardialdehyde (35.0 g, 350 mol, 1.0 eq.) was weighed into a 1 L RBF equipped with a stir bar and cycled onto the Schlenk line using $N_2$. 500 mL THF was added and mixture was manually agitated until all of the dialdehyde dissolved. The RBF was placed in an ice bath at 0 °C before the synthesized Grignard was added dropwise while stirring. Upon complete addition of the Grignard, the reaction mixture was allowed to stir at 0 °C for 2 h before being quenched with x mL of saturated $NH_4Cl$. The resulting solids were filtered off and washed with $Et_2O$. The filtrate was then transferred to a separatory funnel before being extracted with 100 mL $Et_2O$ three times and washed with 100 mL brine three times. The organic layer was then dried over $Na_2SO_4$ before being pumped down. All of the obtained material (25 g) was used in the next step without further purification.

Pyridinium chlorochromate (PCC) (46 g, 213 mol, 1.2 eq.) and 50 g of partially powdered molecular sieves were added to a 1 L 3-neck RBF equipped with a stir bar. The RBF was cycled onto the Schlenk line using $N_2$ before 500 mL of dry DCM was added *via* cannula. The reaction mixture was allowed to stir until the PCC had fully dissolved before the RBF was cooled to 0 °C in an ice bath. The crude cyclized product was dissolved in 100 mL DCM and added dropwise to the PCC mixture. The dark brown solution was allowed to stir at 0 °C for 30 min before being warmed to room temperature and stirring for another 1.5 h. More PCC (20 g, 93 mmol, 0.5 eq.) was then added and the mixture was allowed to stir for another 2 h. The solution was filtered through celite and pumped down *on vacuo*. Excess $Et_2O$ was added and the thick mixture was triturated several times before being filtered through a short plug of silica. The filtrate was then pumped down and then purified via column chromatography using DCM. PeP was obtained in 7% yield from the starting aldehyde. $^1$H NMR (400 MHz, $CDCl_3$, δ, ppm) 5.04 (s, 1H), 4.96 (s, 1H), 4.76-4.70 (m, 1H), 2.66-2.43 (m, 2H), 2.00-1.67 (m, 4H), 1.78 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$, δ, ppm) δ 171.3, 142.6, 113.0, 83.0, 29.5, 26.7, 18.3, 18.1.

**3-ethyl-6-(prop-1-en-2-yl)tetrahydro-2H-pyran-2-one (EtPeP)** was synthesized from PeP following the identical α-alkylation procedure to EtVMeP. EtPeP was isolated in 21% yield. $^1$H NMR (400 MHz, $CDCl_3$, δ, ppm) δ 5.03 (s, 1H), 4.97-4.91 (2, 1H), 4.75-4.66 (m, 1H), 2.46-2.31 (m, 1H), 2.11-1.44 (m, 6H), 1.77 (s, 1H), 1.01-0.95 (m, 3 H); $^{13}$C NMR (101 MHz, $CDCl_3$, δ, ppm) δ 174.0, 173.4, 143.0, 142.5, 113.0, 112.8, 83.8, 80.6, 42.0, 40.0, 27.7, 25.5, 24.9, 24.7, 24.0, 22.5, 18.3, 17.8, 11.5, 11.1. ESI-HRMS (m/z): calcd. for $C_{10}H_{16}O_2$, 169.1223; found, 169.1217 (diff. 0.0006)

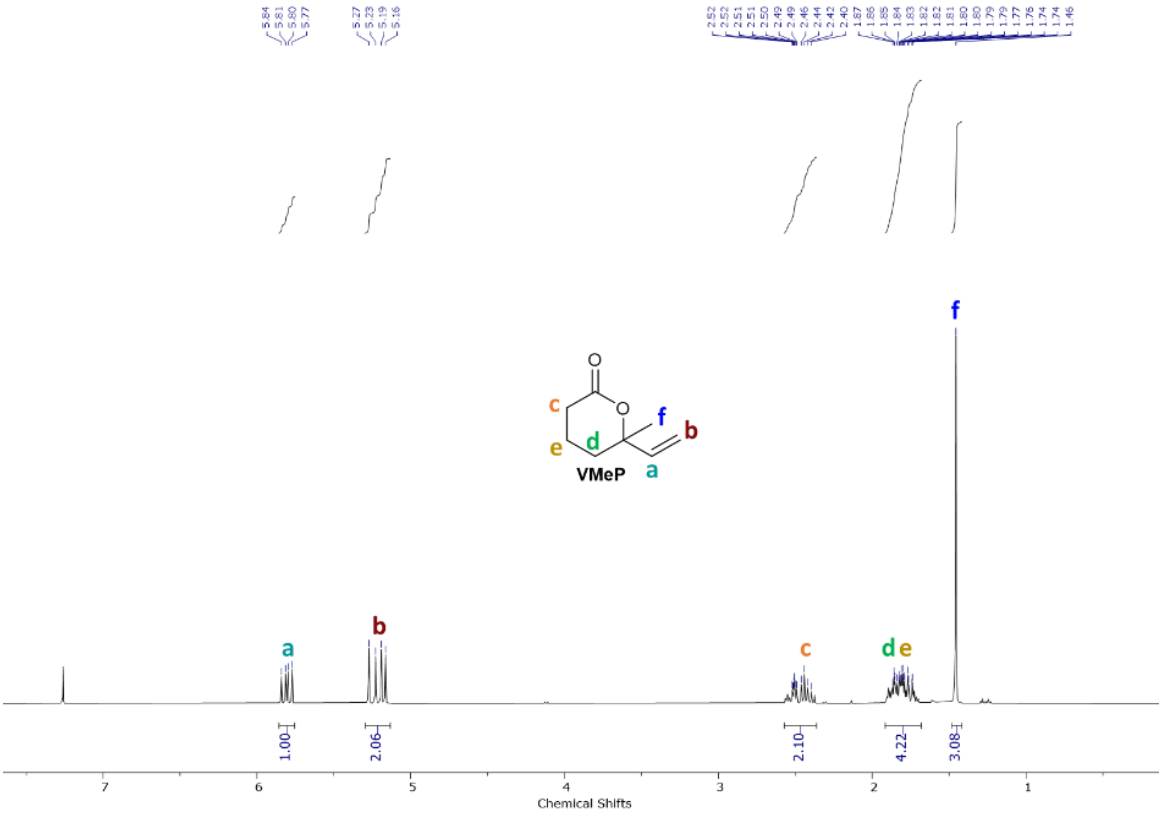



**Figure S33.** $^{1}H$ NMR spectrum of VMeP in $CDCl_3$.

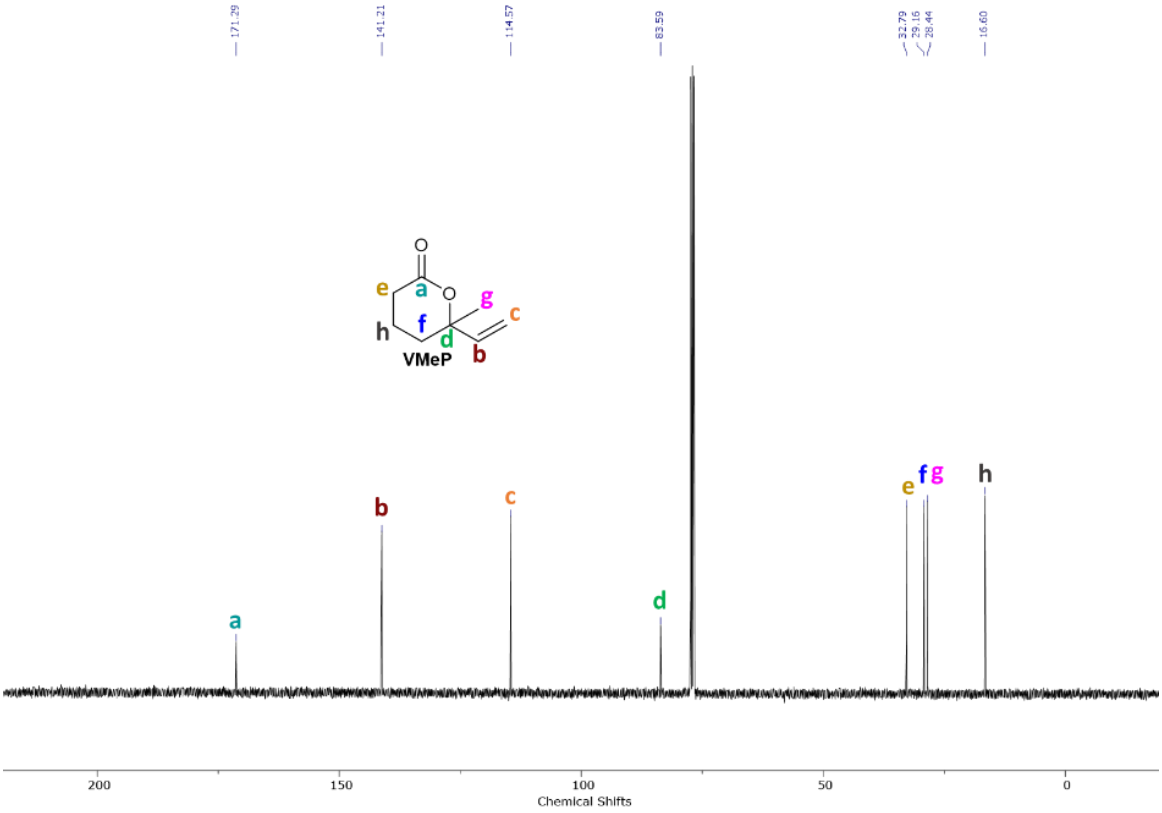


**Figure S34.** $^{13}C$ NMR spectrum of VMeP in $CDCl_3$.

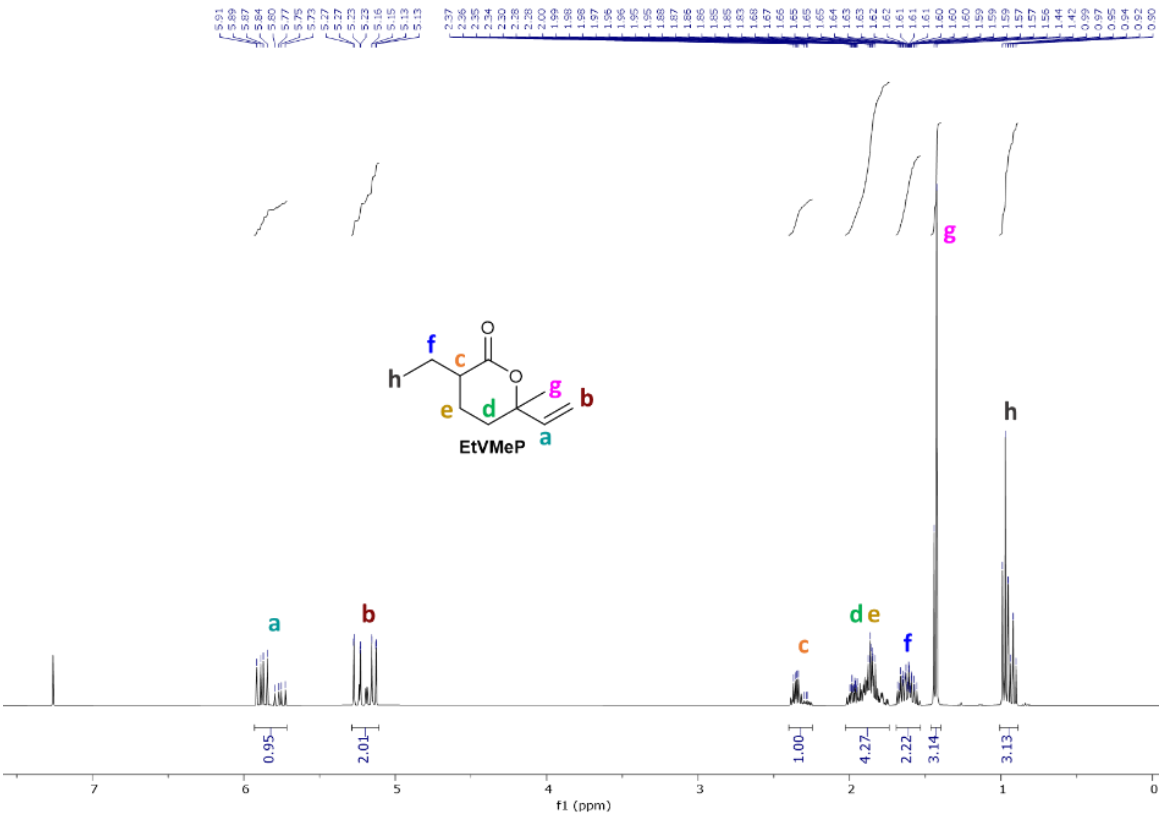



**Figure S35.** $^{1}H$ NMR spectrum of EtVMeP in $CDCl_3$.

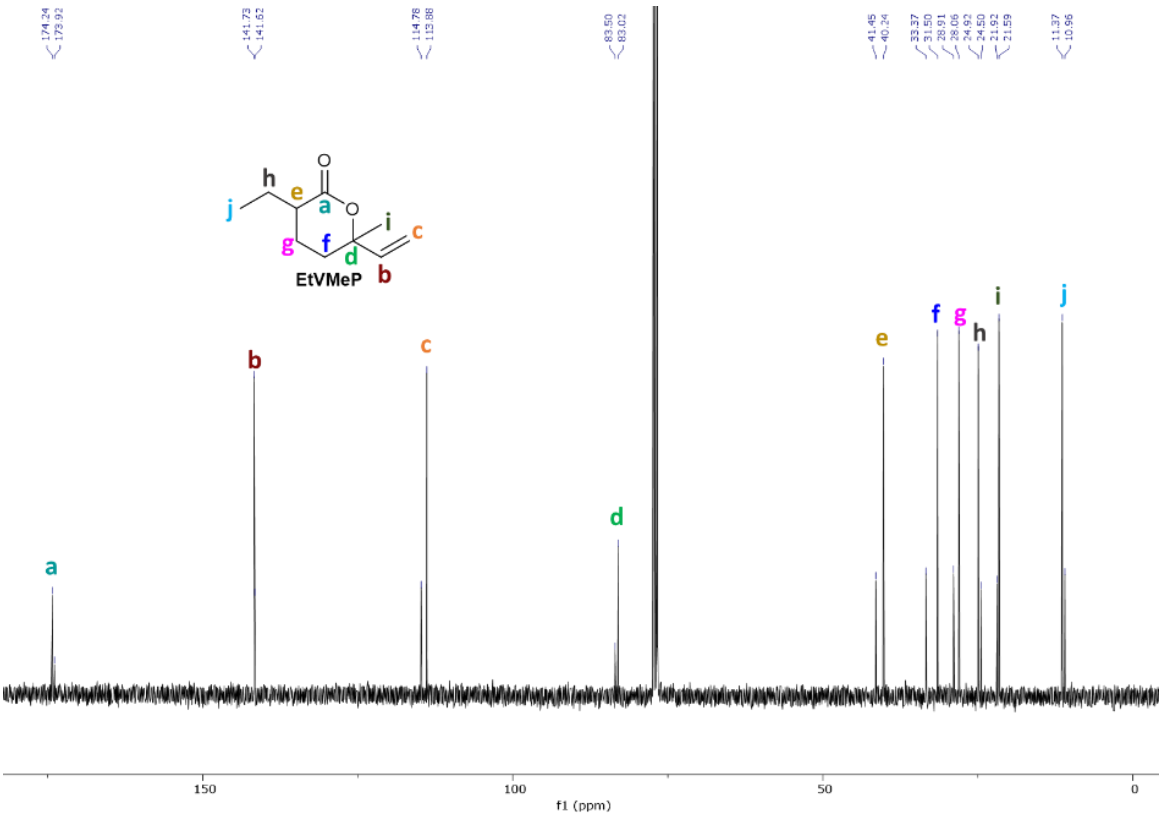



**Figure S36.** $^{13}C$ NMR spectrum of EtVMeP in $CDCl_3$.

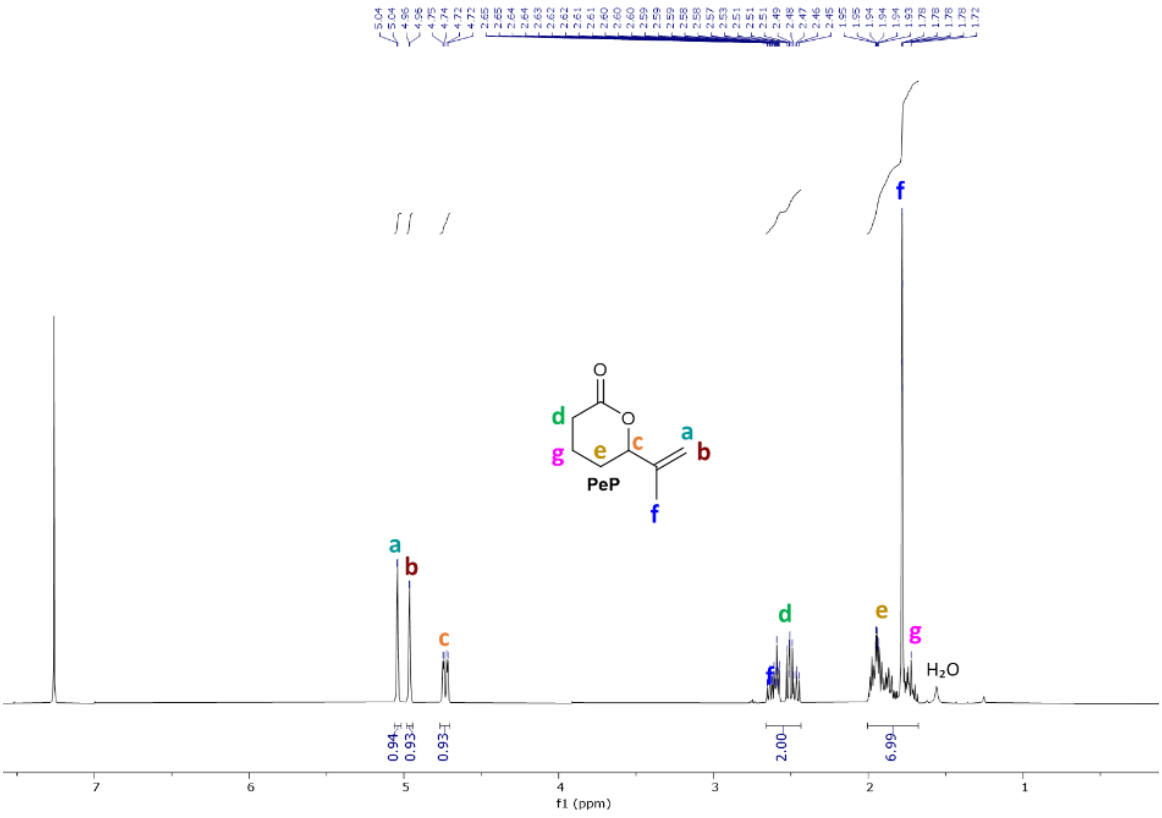


**Figure S37.** $^{1}H$ NMR spectrum of PeP in $CDCl_3$.

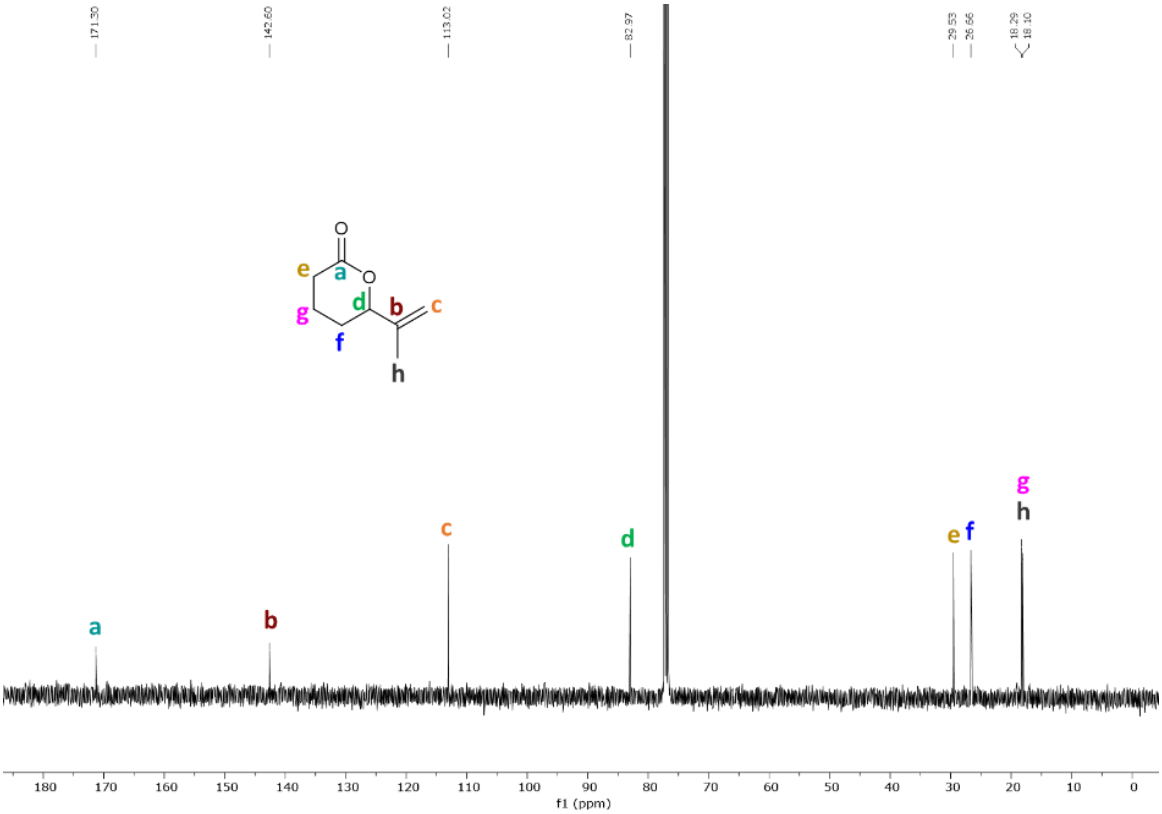



**Figure S38.** $^{13}C$ NMR spectrum of PeP in $CDCl_3$.

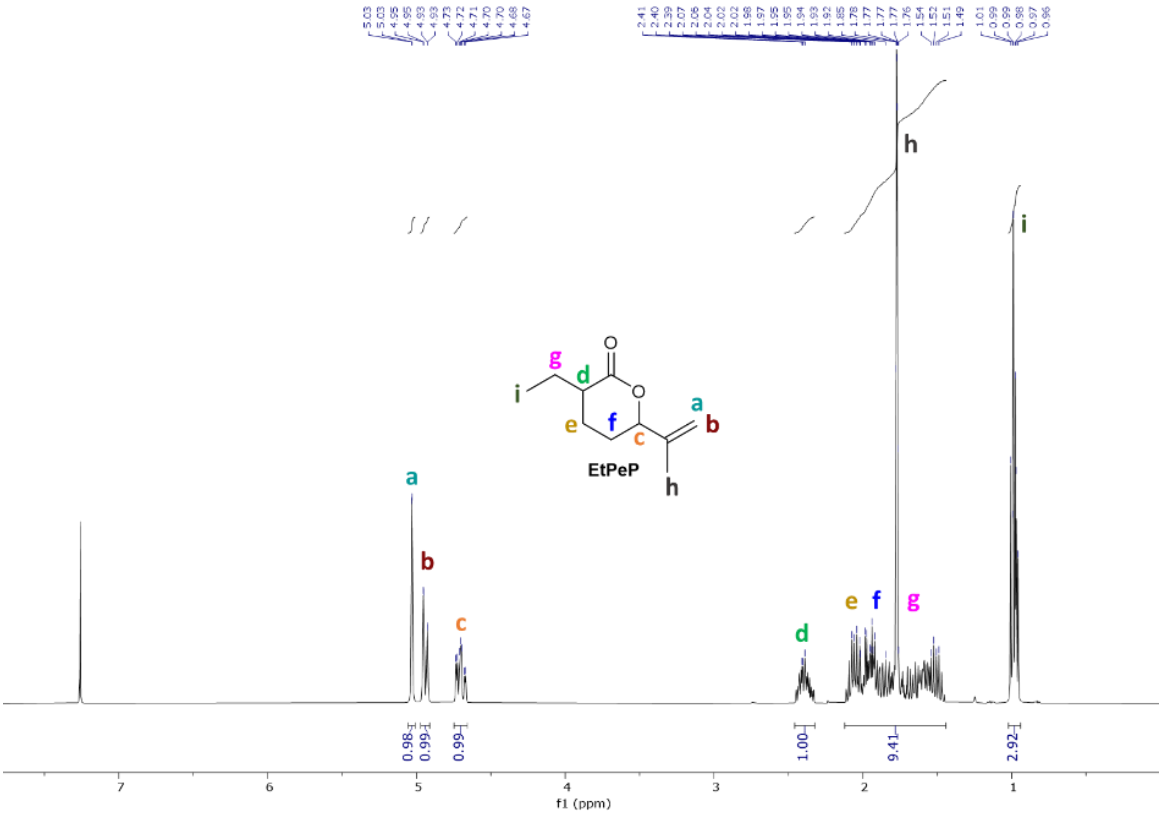



**Figure S39.** $^{1}H$ NMR spectrum of EtPeP in $CDCl_3$.

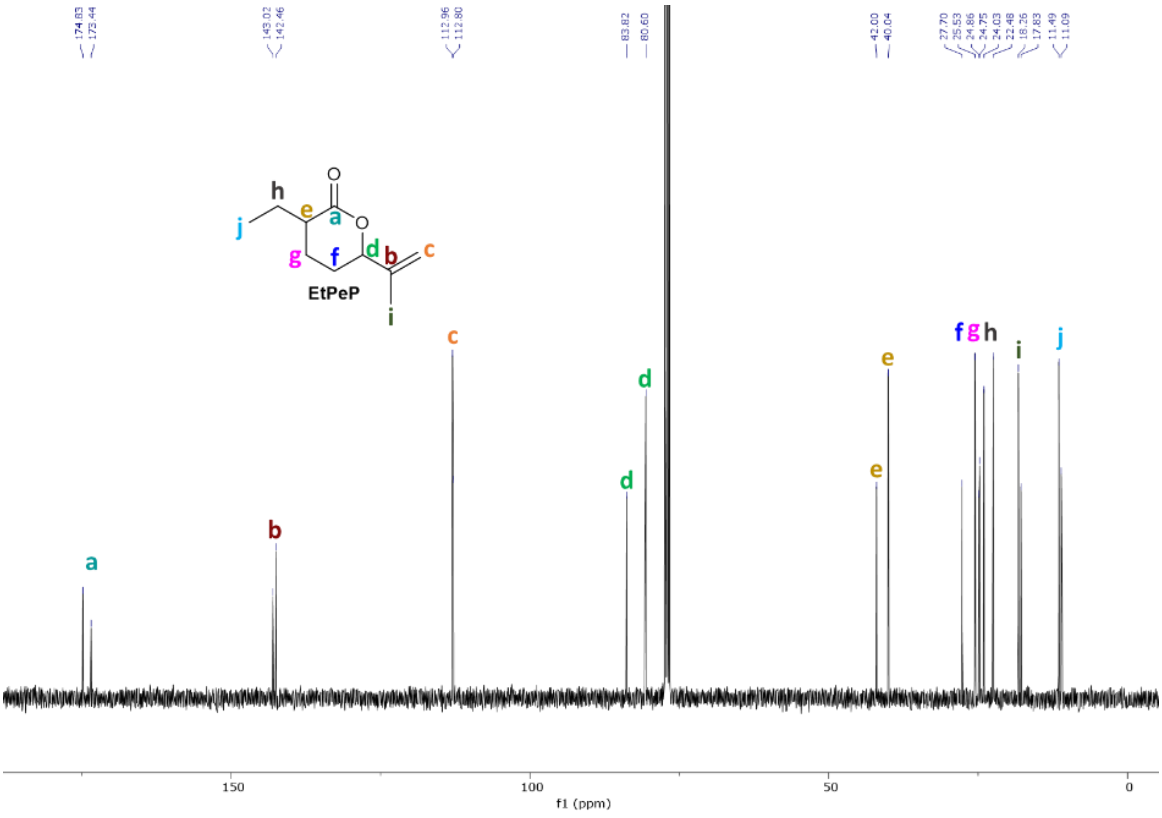
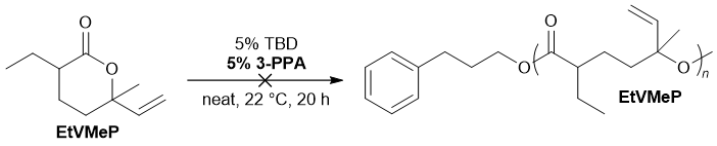


**Figure S40.** $^{13}C$ NMR spectrum of EtPeP in $CDCl_3$.

## Investigation of EtVMeP and EtPeP Reactivity

### EtVMeP Homopolymerization




**Scheme 5.** Attempted homopolymerization of EtVMeP

In a nitrogen-filled glove box, EtVMeP (250 g, 1.48 mmol, 1.0 eq.), 3-PPA (10.1 mg, 0.074 mmol, 0.05 eq.) and TBD (10.3 mg, 0.074 mmol, 0.05 eq.) were weighed into a 4 mL vial equipped with a small, football-shaped stir bar. The mixture was allowed to stir at room temperature for 20 h before being taken out and quenched with benzoic acid. $^1H$ NMR from an aliquot of the resulting mixture was collected.

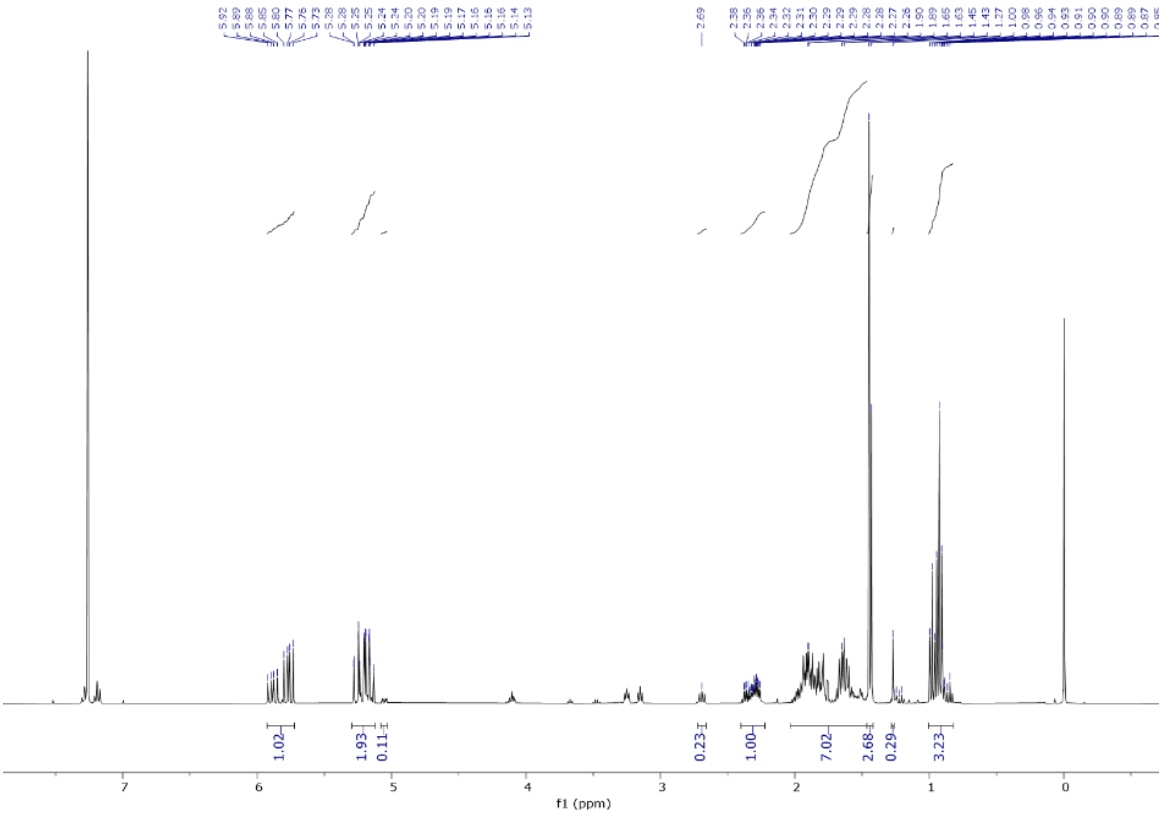
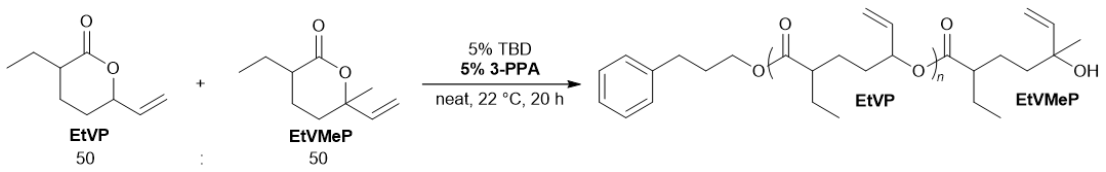



**Figure S41.** Crude $^1H$ NMR spectrum of attempted EtVMeP homopolymerization in $CDCl_3$.

### EtVMeP Copolymerization with EtVP




**Scheme 6.** Attempted copolymerization of EtVP and EtVMeP

The above copolymer was synthesized according to the general procedure for EtPeP synthesis, but with an increased loading in 3-PPA (0.05 eq. instead of 0.05). $^{1}$H NMR (400 MHz, $CDCl_3$, δ, ppm) 7.25-7.08 (m, 5H, 3-PPA) 5.92-5.66 (m, 2H, pEtVP and EtVMeP), 5.31-5.00 (m, 3H pEtVP and 2H EtVMeP), 4.16-4.03 (m, 2H, 3-PPA), 2.72-2.65 (t, 2H, 3-PPA), 2.35-2.20 (m, 2H, pEtVP and EtVMeP), 2.00-1.90 (quint, 2H, 3-PPA), 1.76-1.39 (m, 12H, pEtVP and EtVMeP), 1.29-1.24 (two s, 3H, EtVMeP), 0.94-0.83 (m, 6H, pEtVP and EtVMeP).

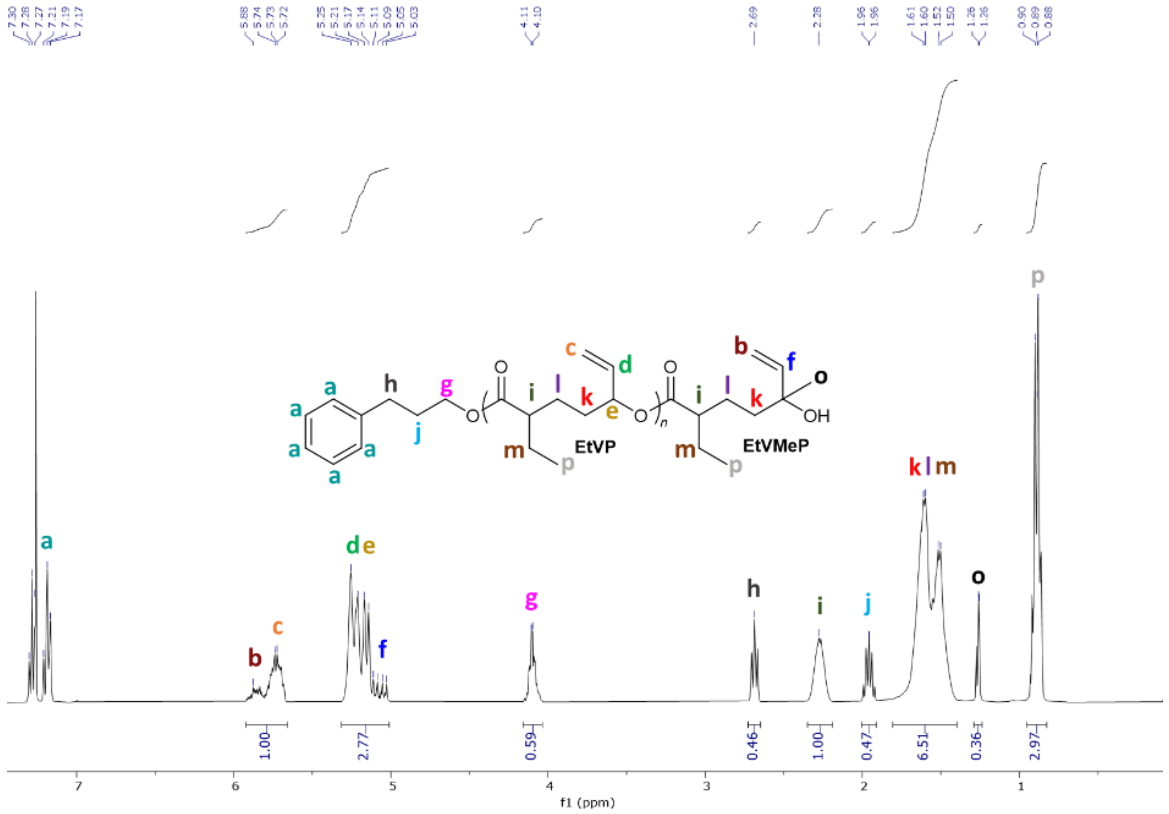



**Figure S42.** $^{1}$H NMR spectrum of EtVP/EtVMeP copolymerization in $CDCl_3$.

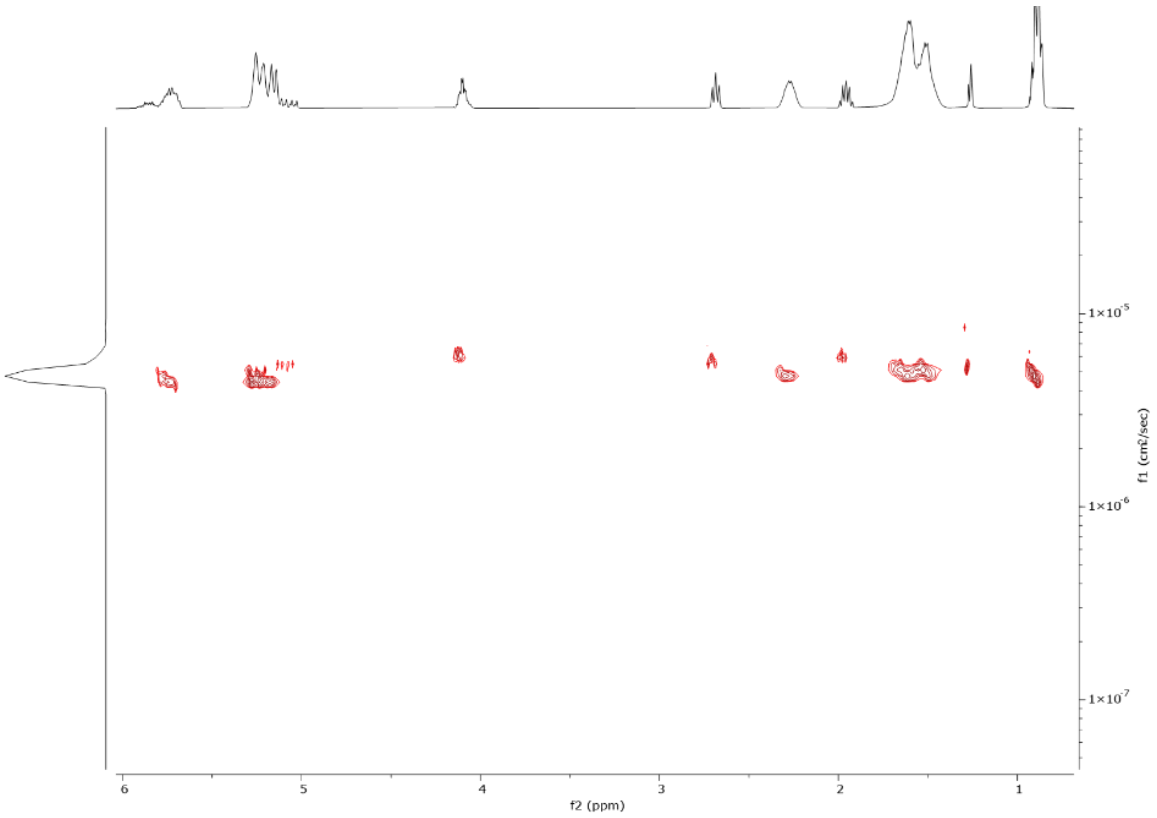



**Figure S43.** DOSY NMR spectrum of EtVP/EtVMeP copolymerization in $CDCl_3$.

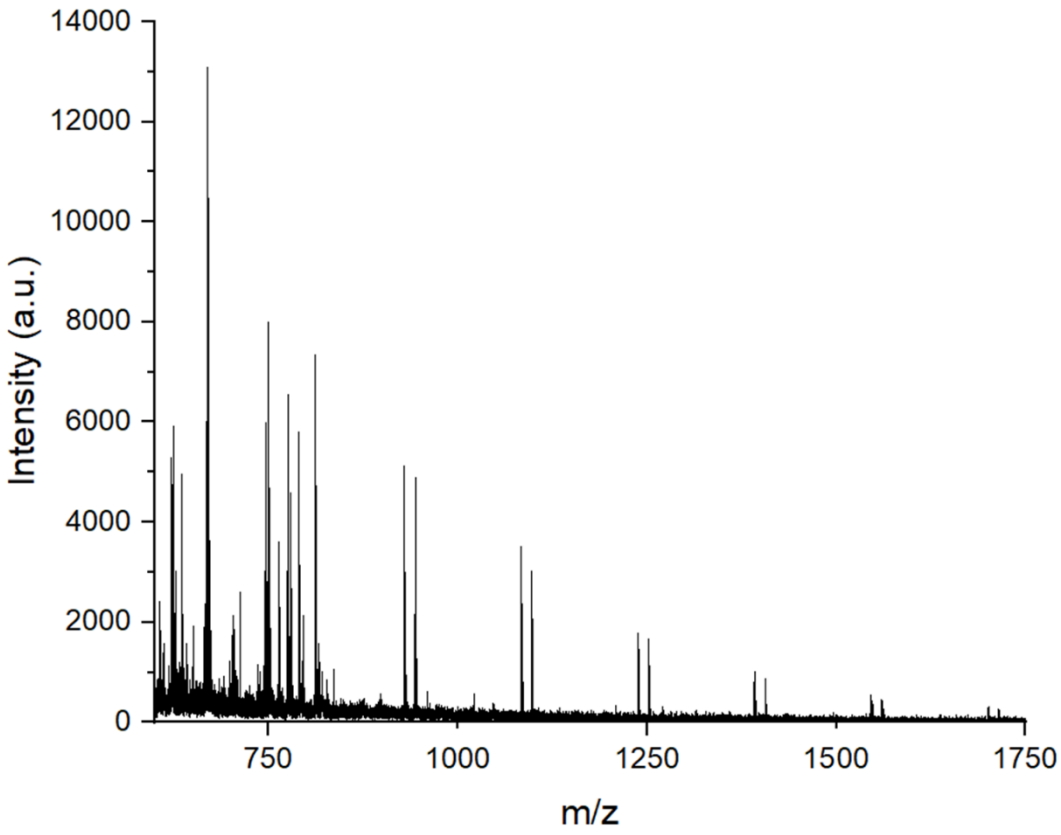
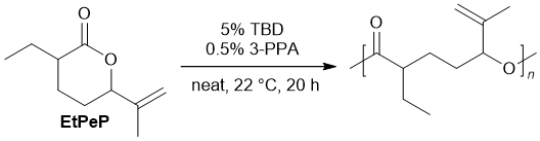



**Figure S44.** Fully zoomed out MALDI-TOF of EtVP/EtVMeP copolymerization

**EtPeP Homopolymerization**




**Scheme 7.** Synthesis of *poly*(**EtPeP**)

The polymer was synthesized according to the standard procedure for EtPeP copolymers. $^{1}$H NMR (400 MHz, $CDCl_3$, δ, ppm) 5.21-5.09 (m, 1H), 4.93 (s, 1H), 4.87 (s, 1H), 2.69 (t, 2H, initiator), 2.34-2.10 (m, 1H), 1.68 (s, 3H), 1.73-1.36 (m, 6H), 0.93-0.83 (m, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$, δ, ppm) 175.0, 174.5, 142.9, 142.9, 142.8, 142.8, 113.5, 113.4, 113.3, 113.2, 77.2, 77.1, 47.6, 47.1, 47.0, 30.7, 30.4, 27.8, 27.5, 25.6, 25.6, 25.5, 18.1, 18.0, 18.0, 17.9, 17.8, 11.7.

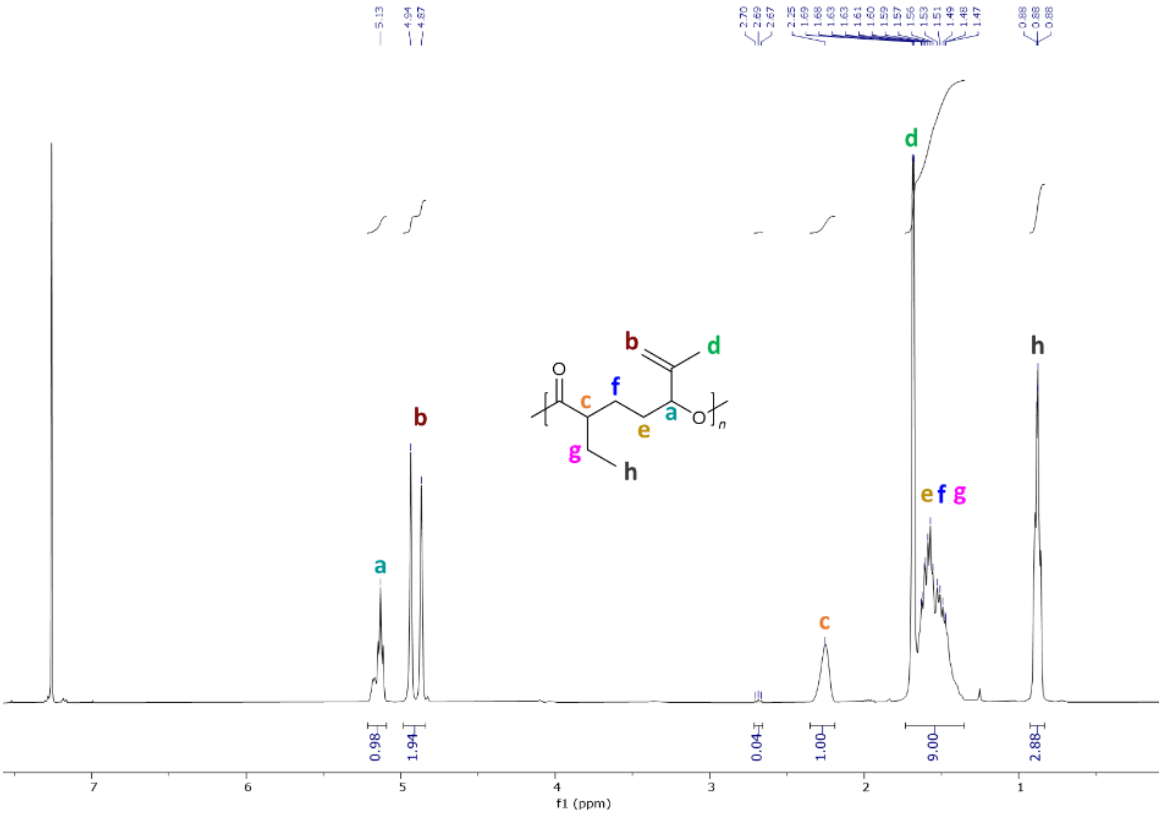



**Figure S45.** $^{1}$H NMR spectrum of *poly*(EtPeP) in $CDCl_3$.

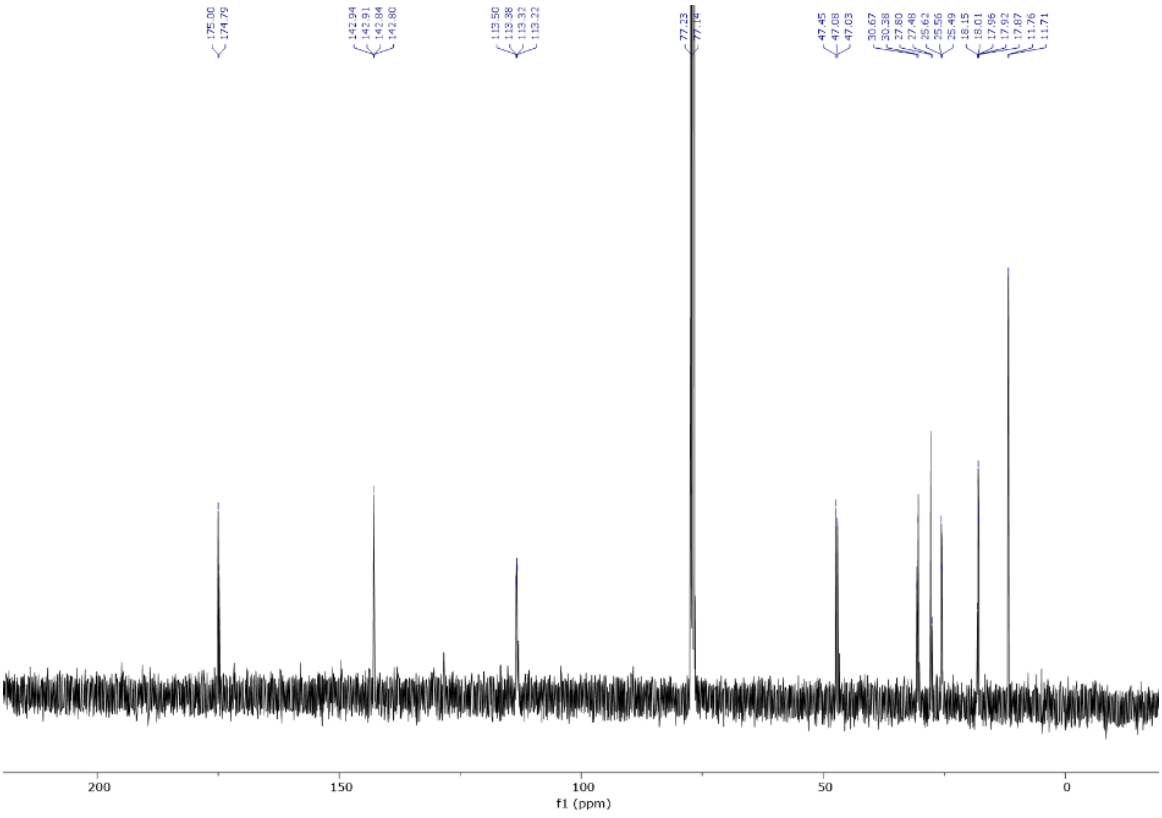


**Figure S46.** $^{13}C$ NMR spectrum of *poly*(EtPeP) in $CDCl_3$.

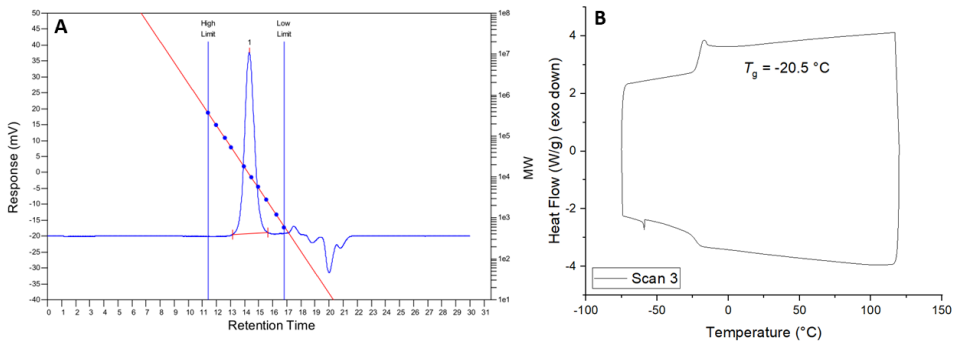



**Figure S47.** (A) SEC dRI and (B) DSC of *poly*(EtPeP)

## End-Capping of EtVMeP and EtPeP Polymers

End-capping was done following a modified reported procedure.[9] 0.0050 g of polymer was weighed into an 8 mL vial equipped with a stir bar. 0.50 mL $CDCl_3$ was added and the polymer was stirred until all of it dissolved. 0.10 mL trifluoroacetic anhydride (TFAA) was added and the reaction mixture was allowed to stir for 1 h before the solvent and excess TFAA was removed *on vacuo*. 0.55 mL CDCl3 was added along with trifluorotoluene (TFT) as an external standard. $^{19}F$ NMR was collected for each polymer.

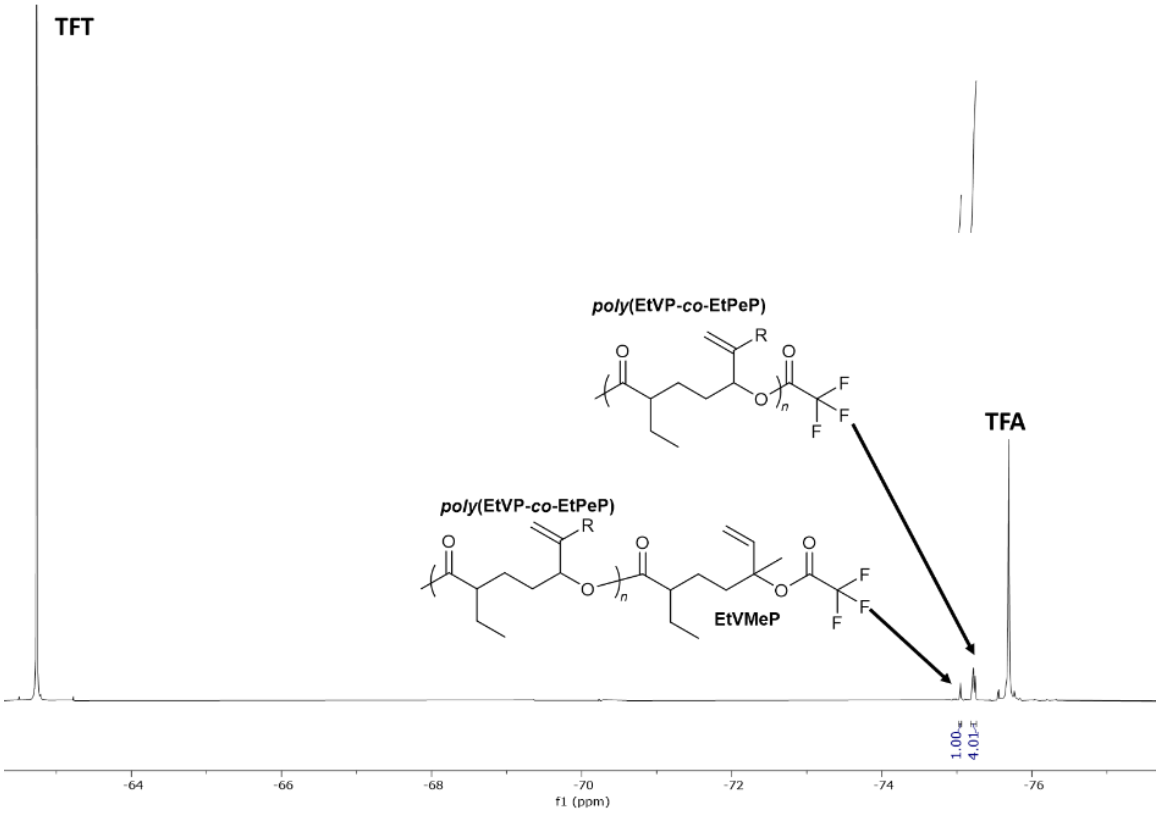



**Figure S48.** $^{19}F$ NMR spectrum of *poly*(EtVP-co-EtPeP), (Table S4, entry 6), and trifluorotoluene in $CDCl_3$.

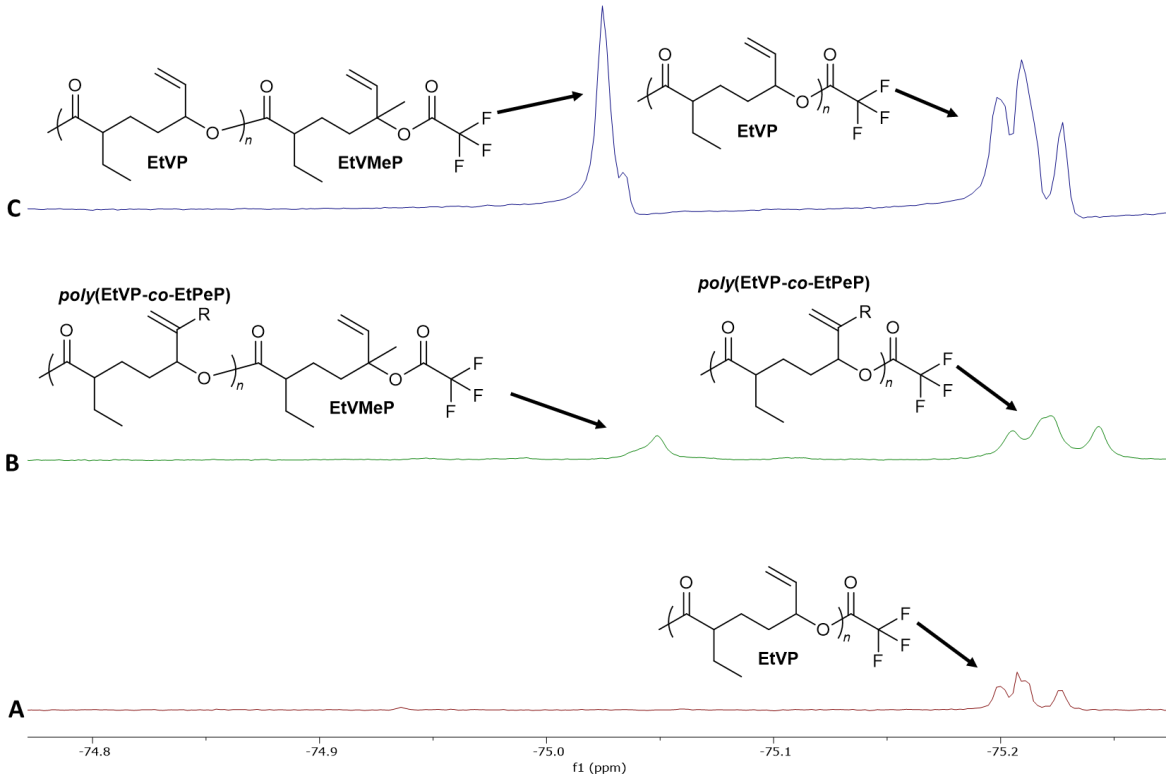
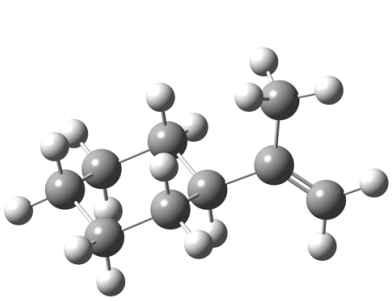


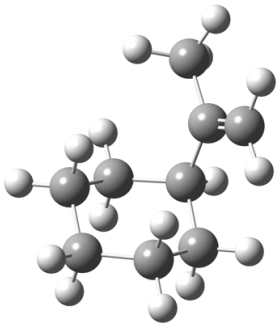

**Figure S49.** $^{19}$F NMR spectrum of three polymers end-capped with trifluoroacetic anhydride in $CDCl_3$. (A) *poly*(EtVP), (B) *poly*(EtVP-co-EtPeP), (Table S4, entry 6), (C) EtVP and EtVMeP copolymerization attempt.

## Computational Investigation of Cotelomerization

All DFT calculations were performed with Gaussian 16.[10] Geometry optimizations for **INT-1**, **INT-2**, **TS-A**, **TS-B**, **TS-C**, **TS-D**, **INT-3A**, **INT-3B**, **INT-3C**, and **INT-3D** were carried out at M06L functional[11] with SDD basis set and the corresponding ECP[12,13] for Pd and 6-311+G(d,p) basis set[14,15] for other elements (C, H, O, P). Geometry optimization for **EPeP**, **EVMeP**, **PeVP** and **VMeVP** were carried out by the following two levels of theory: (i) MP2[16]/cc-pVTZ[17], and (ii) wB97XD[18]/def2-QZVP[19]. The vibrational frequencies were calculated at the corresponding level of theory to the optimizations to evaluate the Gibbs free energy corrections at 298.15 K. The solvation effects of acetonitrile were evaluated using the CPCM model.[20,21] The intrinsic reaction coordinate (IRC)[22] analysis was carried out to confirm that all saddle points (transition states) are smoothly connected to two minima. NCI analysis[23] was performed by using Multiwfn 3.8[24] and visualized by using VMD.[25]



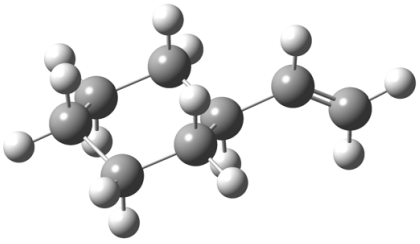
Electronic energy: -351.804878 (Hartree)
Enthalpy: -351.561840 (Hartree)
Gibbs free energy: -351.607289 (Hartree)



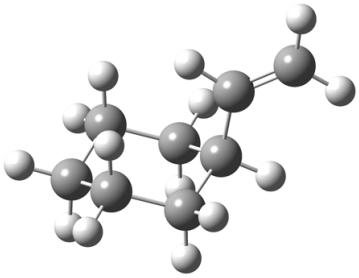
Electronic energy: -351.802546 (Hartree)
Enthalpy: -351.559344 (Hartree)
Gibbs free energy: -351.602655 (Hartree)

A value = 2.91

**Figure S50.** A-value of calculation propenyl group computed at MP2/aug-cc-pVTZ at 298.15 K (gas phase)



Electronic energy: -351.574769 (Hartree)
Enthalpy: -351.361537 (Hartree)
Gibbs free energy: -351.402808 (Hartree)



Electronic energy: -312.572247 (Hartree)
Enthalpy: -351.358792 (Hartree)
Gibbs free energy: -351.399905 (Hartree)

A value = 1.82

**Figure S51.** A-value calculation of vinyl group computed at MP2/aug-cc-pVTZ at 298.15 K (gas phase)

Electronic, free energies, and enthalpy (Hartree) for all computed structures are listed below.

$CO_2$ (M06L)
Electronic energy = -188.633936
Enthalpy = -188.618601
Gibbs free energy = -188.643521

$CO_2$ (MP2)
Electronic energy = -188.310261
Enthalpy = -188.295192
Gibbs free energy = -188.320142

$CO_2$ (ωB97XD)
Electronic energy = -188.618034
Enthalpy = -188.602700

Gibbs free energy = -188.627588

Butadiene (MP2)
Electronic energy = -155.630068
Enthalpy = -155.539015
Gibbs free energy = -155.571120

Butadiene (ωB97XD)
Electronic energy = -156.006231
Enthalpy = -155.915070
Gibbs free energy = -155.947118

Isoprene (MP2)
Electronic energy = -194.857874
Enthalpy = -194.737099
Gibbs free energy = -194.772416

Isoprene (ωB97XD)
Electronic energy = -195.330102
Enthalpy = -195.209342
Gibbs free energy = -195.244485

**INT-1**
Electronic energy = -1859.407418
Enthalpy = -1858.796215
Gibbs free energy = -1858.906208

**INT-2**
Electronic energy = -1859.412057
Enthalpy = -1858.800890
Gibbs free energy = -1858.910803

**TS-A**
Electronic energy = -2048.015920
Enthalpy = -2047.389253
Gibbs free energy = -2047.504735

**TS-B**
Electronic energy = -2048.012969
Enthalpy = -2047.386175
Gibbs free energy = -2047.500696

**TS-C**
Electronic energy = -2048.004190
Enthalpy = -2047.377524
Gibbs free energy = -2047.491942

**TS-D**
Electronic energy = -2048.016362
Enthalpy = -2047.389511
Gibbs free energy = -2047.503766

**INT-3A**

Electronic energy = -2048.067729
Enthalpy = -2047.437044
Gibbs free energy = -2047.553257

**INT-3B**
Electronic energy = -2048.065048
Enthalpy = -2047.434299
Gibbs free energy = -2047.550468

**INT-3C**
Electronic energy = -2048.064398
Enthalpy = -2047.433821
Gibbs free energy = -2047.548510

**INT-3D**
Electronic energy = -2048.058859
Enthalpy = -2047.428783
Gibbs free energy = -2047.544476

**EPeP** (MP2)
Electronic energy = -538.844618
Enthalpy = -538.608966
Gibbs free energy = -538.662194

**EPeP** (ωB97XD)
Electronic energy = -540.000758
Enthalpy = -539.765186
Gibbs free energy = -539.818289

**EVMeP** (MP2)
Electronic energy = -538.843979
Enthalpy = -538.608889
Gibbs free energy = -538.660644

**EVMeP** (ωB97XD)
Electronic energy = -539.998619
Enthalpy = -539.763398
Gibbs free energy = -539.815037

**PeVP** (MP2)
Electronic energy = -538.840304
Enthalpy = -538.604852
Gibbs free energy = -538.657709

**PeVP** (ωB97XD)
Electronic energy = -539.995568
Enthalpy = -539.760132
Gibbs free energy = -539.812715

**VMeVP** (MP2)
Electronic energy = -538.831727
Enthalpy = -538.596396
Gibbs free energy = -538.647864

**VMeVP** (ωB97XD)
Electronic energy = -539.985125
Enthalpy = -539.749537
Gibbs free energy = -539.800801

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