

Synthesis of α -Methylene- δ -Valerolactone and its Selective Polymerization from a Product Mixture for Concurrent Separation and Polymer Production

Supporting Information

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S.1. Catalyst Characterization

S.2. Supplemental Reactivity Studies

S.3. Polymer Characterization

S.1. Catalyst Characterization

Table S.1. Metal weight loading and average particle size for each catalyst used in this study.

Catalyst	Metal weight loading / %
MgO/SiO₂	3.6
CaO/SiO₂	5.2
BaO/SiO₂	3.9

Imaging of Supported Catalysts

Figure S.1 presents a high-angle annular dark-field scanning transmission electron microscopy (STEM-HAADF) image of the CaO, MgO and BaO over SiO₂ catalyst, captured at a high resolution of 2048x2048 scan points with a magnification of 2.80 million times. On Figure S.1c, barium atoms are distinctly visible as bright white spots, indicating their dispersion across the amorphous silica support without any discernible aggregation into particles. In contrast, for the CaO and MgO catalysts, the metal atoms are not discernible against the SiO₂ background, as shown in Figure S.1a and S.1b. This is attributed to the atomic numbers (Z) of calcium and magnesium being relatively close to that of silicon, which results in insufficient contrast for clear visualization. Among all the collected STEM-HAADF images for the three catalyst samples, only one image, presented in Figure S.1a, reveals the presence of a visible crystalline particle. This particle, identified as a CaO crystal, measures approximately 5 nm in size. Aggregated particles contrasting with SiO₂ were also not observed in TEM (Figures S.2-S.4), precluding rigorous particle size distribution determinations.

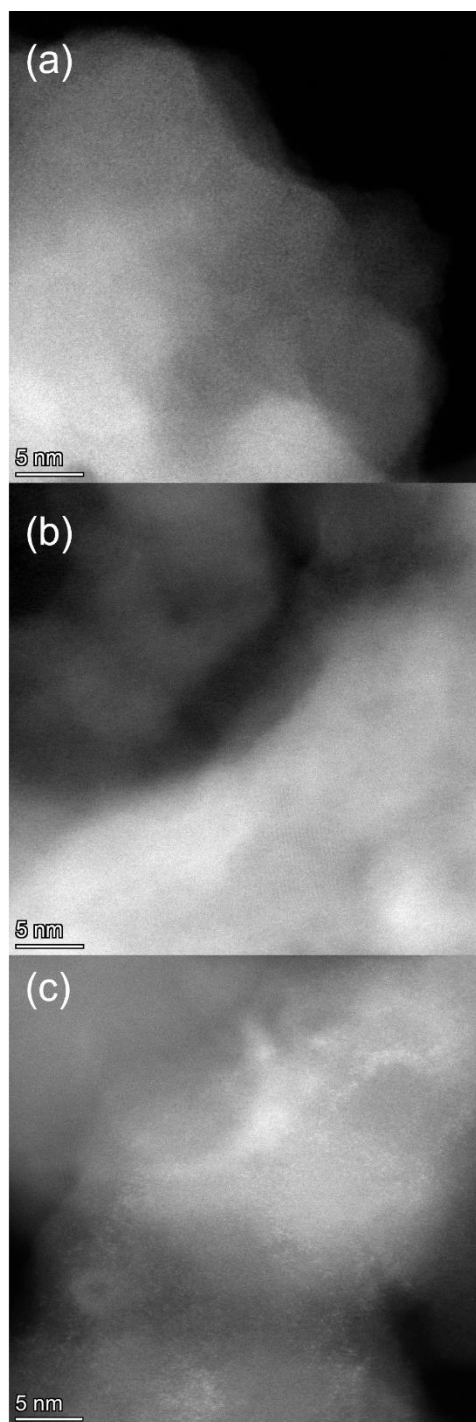


Figure S.1. STEM-HAADF images of SiO₂ supported (a) MgO, (b) CaO, and (c) BaO.

TEM Images of Supported Catalysts

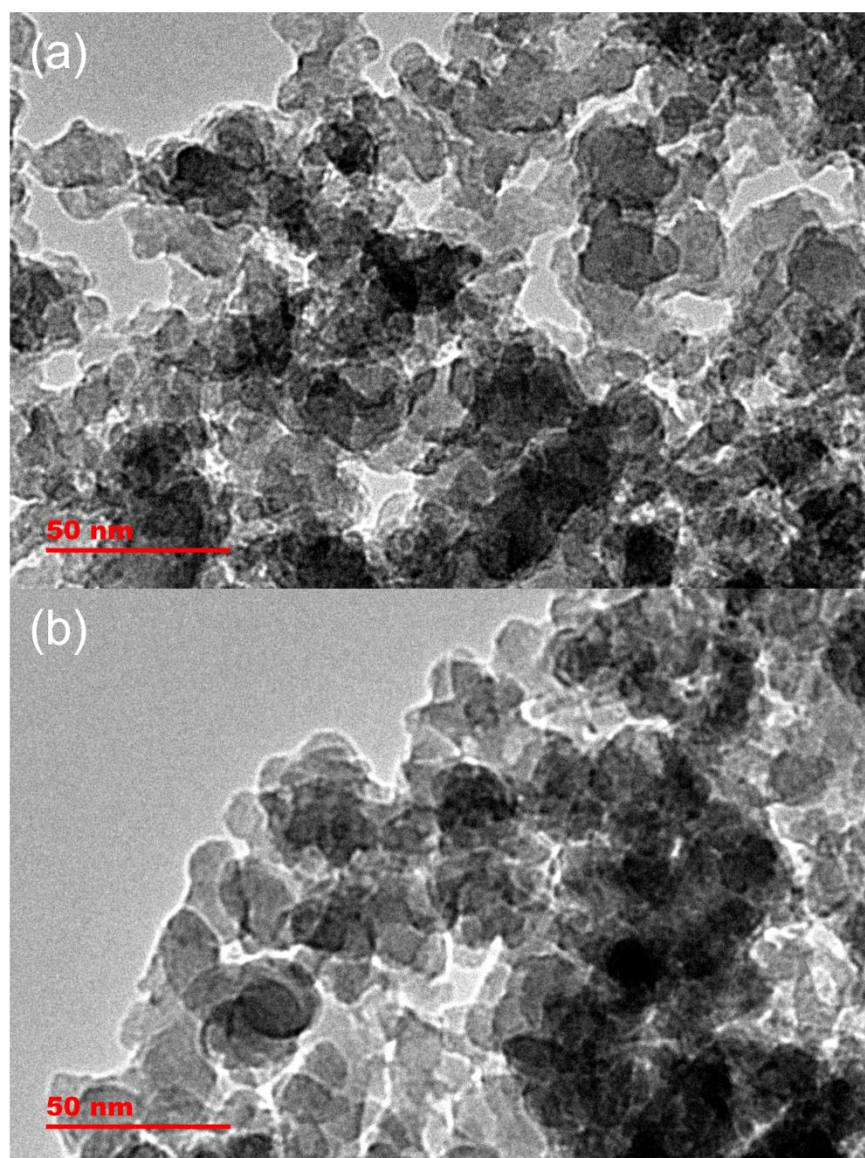


Figure S.2. Representative TEM images of the 5 wt% MgO/SiO₂ sample. Smaller dark points are MgO nanoparticles, while larger dark spots are stacked layers of SiO₂ support.

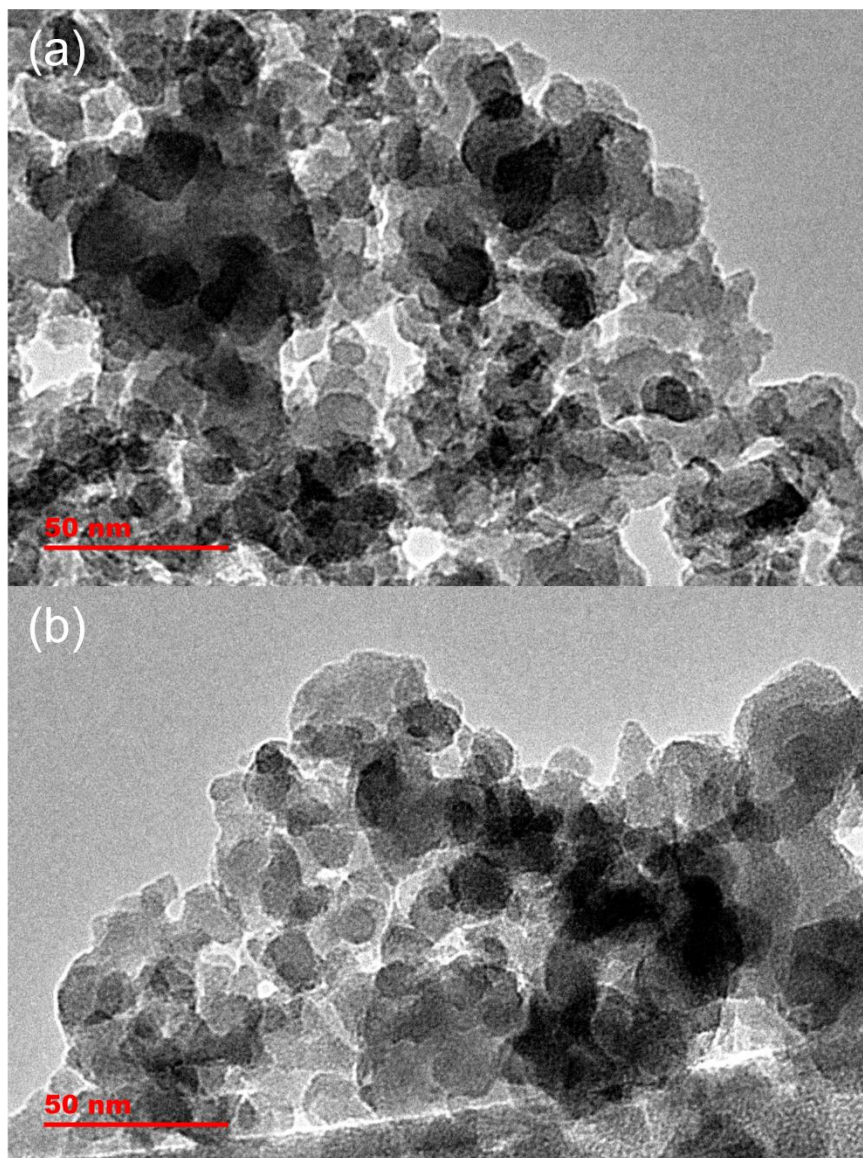


Figure S.3. Representative TEM images of the 5 wt% CaO/SiO₂ sample. Smaller dark points are CaO nanoparticles, while larger dark spots are stacked layers of SiO₂ support.

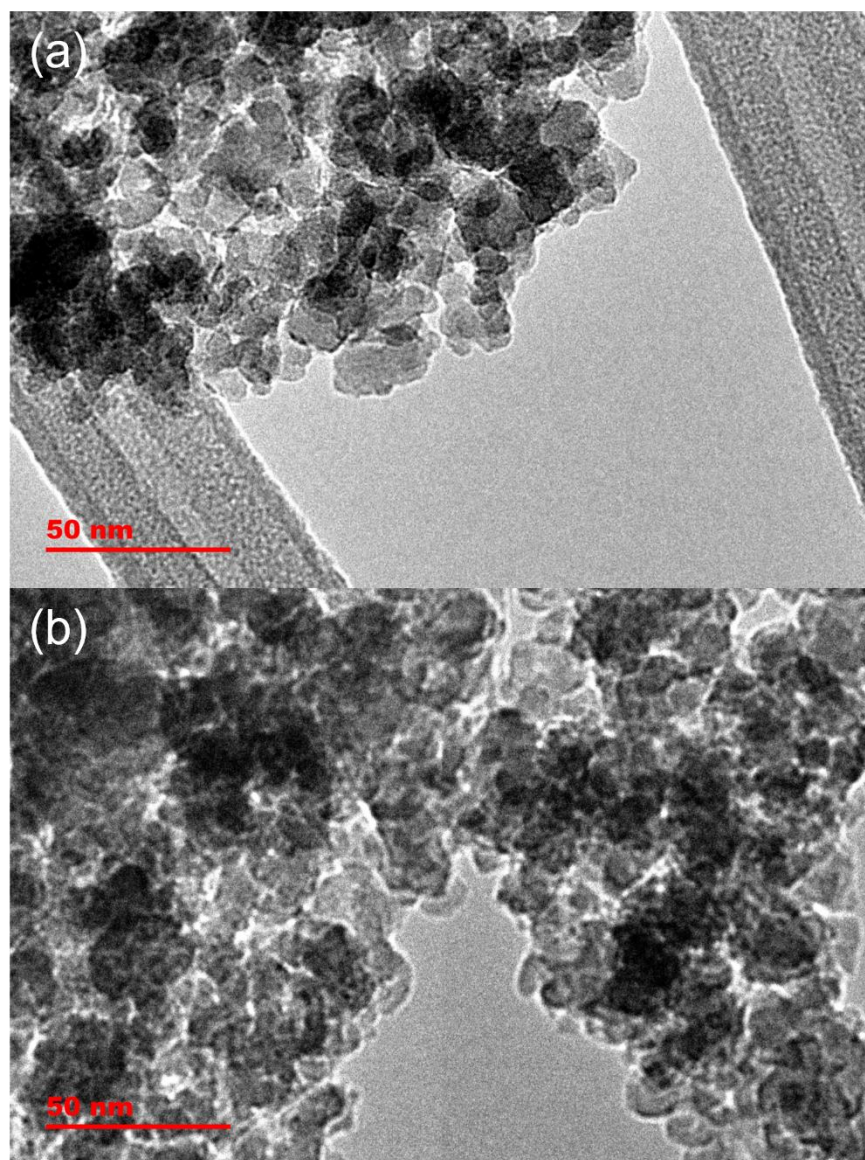


Figure S.4. Representative TEM images of the 5 wt% BaO/SiO₂ sample. Smaller dark points are BaO nanoparticles, while larger dark spots are stacked layers of SiO₂ support.

XRD Patterns of Supported Catalysts

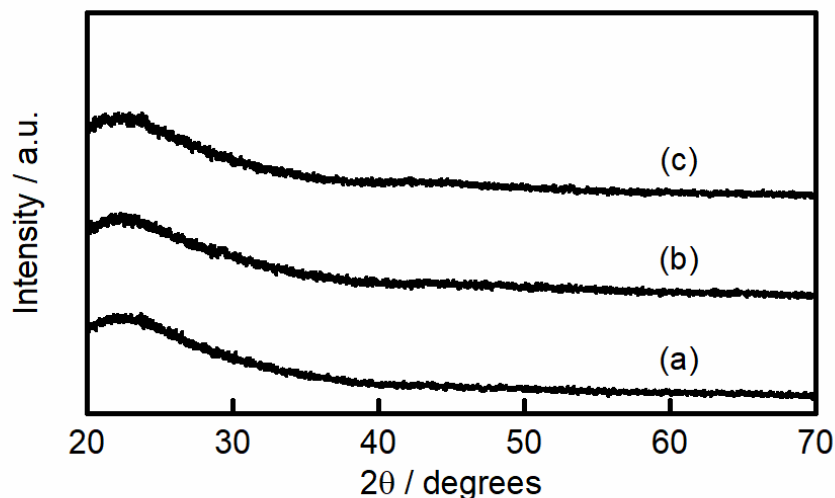


Figure S.5. XRD patterns of (a) MgO/SiO₂, (b) CaO/SiO₂, and (c) BaO/SiO₂. The only observable feature is a broad peak near 22° that comes from SiO₂.

CO₂ TPD of Supported Catalysts

CO₂ is able to bind to lattice oxygens on alkaline earth oxides, and the desorption temperature can be used to qualitatively determine the strength of these basic sites, where higher desorption temperatures correspond to more basic oxygens. Figure S.6 shows CO₂ TPD curves for each of the three catalysts used for this study. All three catalysts have weaker sites present with desorption temperatures at 400–450 K. On MgO, this is followed by one additional desorption peak at approximately 570 K. CaO shows a pair of overlapping peaks are centered near 570 K and 650 K, with an additional peak at 890 K. BaO shows a similar broad or overlapping set of peaks between 550 K and 700 K, similar to CaO. No further peaks were detected up to 1073 K.

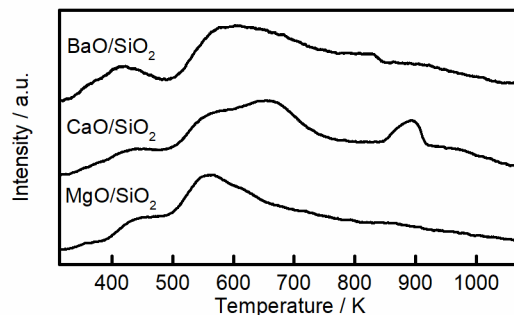


Figure S.6. CO₂ TPD of the three catalysts used in this study.

S.2. Supplemental Reactivity Data

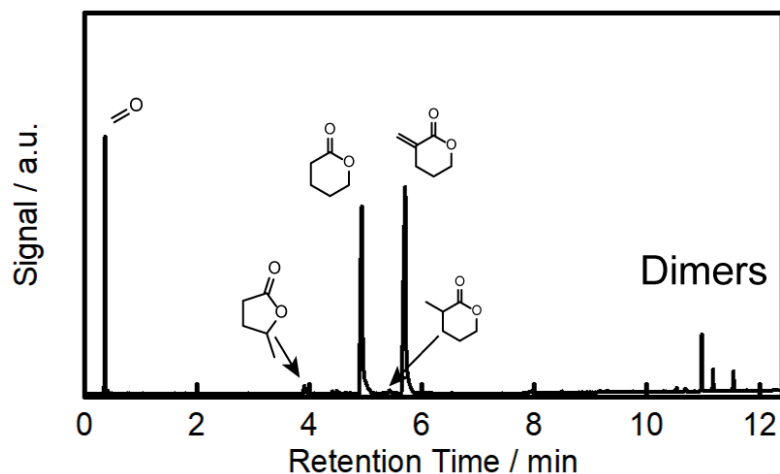


Figure S.7. Sample GC chromatogram from a typical gas-phase injection (0.1 g CaO, 613 K, 0.4 kPa DVL, 1.2 kPa FA, contact time of 0.60 h) showing the compounds and their retention times.

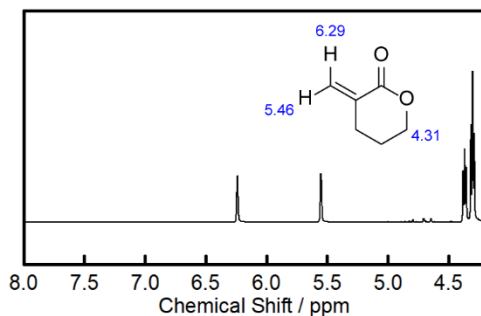


Figure S.8. HNMR of product mixture from CaO flow reaction in region of interest taken in deuterated acetone solvent. Labeled MVL molecule shows predicted chemical shifts from ChemDraw, which are consistent with the observed singlets at ~5.5 ppm and 6.3 ppm. One set of triplets near 4.4 ppm corresponds to protons from unreacted DVL.

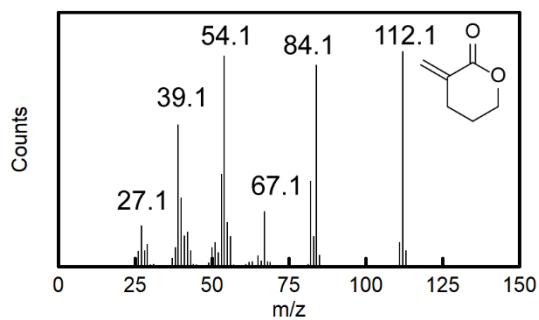


Figure S.9. GC-MS spectra of product observed at a retention time of 5.7 min, determined to be α-methylene-δ-valerolactone (MVL).

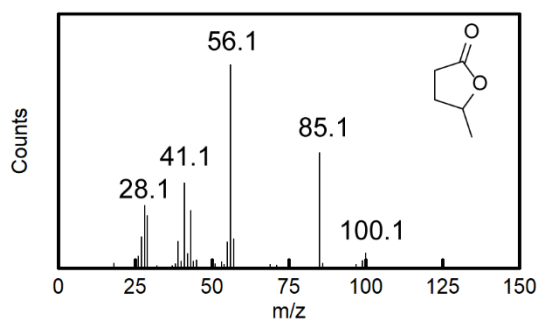


Figure S.10. GC-MS spectra of product observed at a retention time of 3.9 min, determined to be γ-valerolactone (GVL).

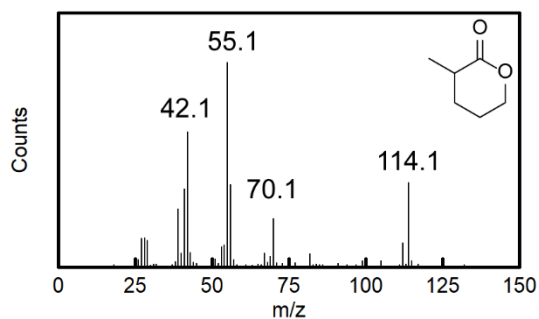


Figure S.11. GC-MS spectra of product observed at a retention time of 5.4 min, suspected to be α-methyl-δ-valerolactone (methyl-DVL).

Table S.2. Product distributions and DVL conversions, presented in tabulated form, as functions of contact time for the three catalysts studied in this work. Conditions: 613 K, 0.1 g catalyst, 0.4 kPa DVL, 1.2 kPa FA, 101 kPa, balance N₂.

Catalyst	Contact Time	DVL Conversion / %	MVL Selectivity / %	GVL Selectivity / %	Methyl-DVL Selectivity / %	Solids/Lost Carbon Selectivity / %
MgO/SiO₂	0.15	29.81	75.14	24.85	0	0.01
	0.30	45.53	50.18	17.92	0	31.91
	0.42	61.38	40.08	15.52	0	44.40
	0.64	73.61	27.56	12.11	0	60.33
CaO/SiO₂	0.14	19.10	100	0	0	0
	0.27	40.32	96.56	0	0	3.44
	0.60	58.74	86.55	2.44	0.35	10.65
	0.79	71.07	80.45	2.52	2.30	14.73
BaO/SiO₂	0.06	24.18	100	0	0	0
	0.16	42.71	95.28	0	0	4.72
	0.29	61.49	83.11	0	0.60	16.29
	0.78	68.13	76.70	0	1.89	21.41

Characterization of Spent Catalysts and Non-Volatiles

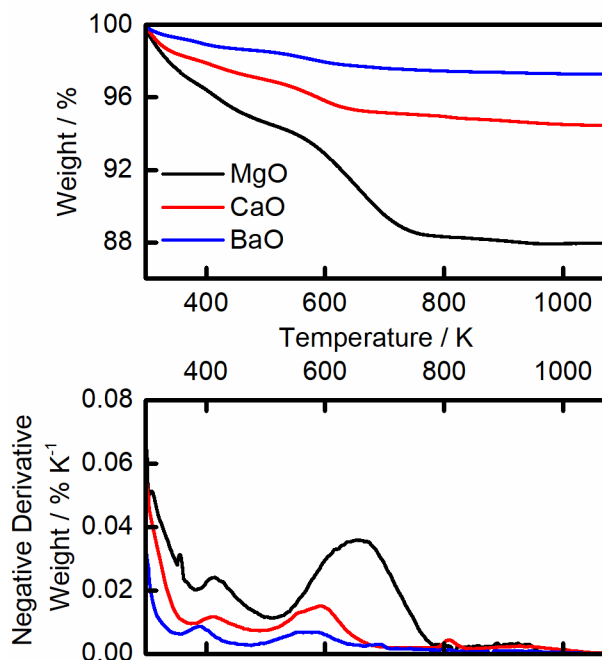


Figure S.12. TGA analysis (45 mL min⁻¹ air, 5 cm³ min⁻¹ N₂, 1 K/min ramp) of spent catalysts after 6-8 h on stream (reaction conditions: 613 K, 0.4 kPa DVL, 1.2 kPa FA, 101 kPa).

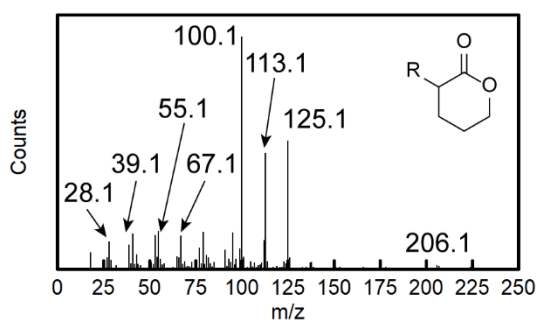


Figure S.13. Representative GC-MS spectra of product eluting at >10 min retention times that persist even in the absence of vaporized liquid feeds, indicating that they are significantly less volatile than any other compounds in the reaction system. Due to the similar features at $m/z \leq 100$ with DVL alongside the presence of larger peaks, these products are suspected to be dimers that are likely formed from the aldol condensation of DVL or MVL with other compounds.

Table S.3. Product distribution and DVL conversion over CaO/SiO₂ as a function of reaction temperature, presented in tabulated form. Conditions: contact time of 0.27 h, 0.4 kPa DVL, 1.2 kPa FA, 0.1 g catalyst, 101 kPa.

Temperature	DVL Conversion / %	MVL Selectivity / %	GVL Selectivity / %	Methyl-DVL Selectivity / %	Solids/Lost Carbon Selectivity / %
573	23.72	100	0	0	0
613	40.32	96.56	0	0	3.44
653	54.25	73.72	3.90	0	22.38

Table S.4. Product distribution and DVL conversion over CaO/SiO₂ as a function of FA:DVL ratio, presented in tabulated form. Conditions: 613 K, contact time of 0.27 h, 0.4 kPa DVL, 100 mg catalyst, 101 kPa.

FA:DVL Molar Ratio	DVL Conversion / %	MVL Selectivity / %	GVL Selectivity / %	Methyl-DVL Selectivity / %	Solids/Lost Carbon Selectivity / %
1:1	24.55	80.14	0	0	19.86
3:1	40.32	96.56	0	0	3.44
5:1	41.34	97.45	0	0	2.55

S.3. Polymer Characterization

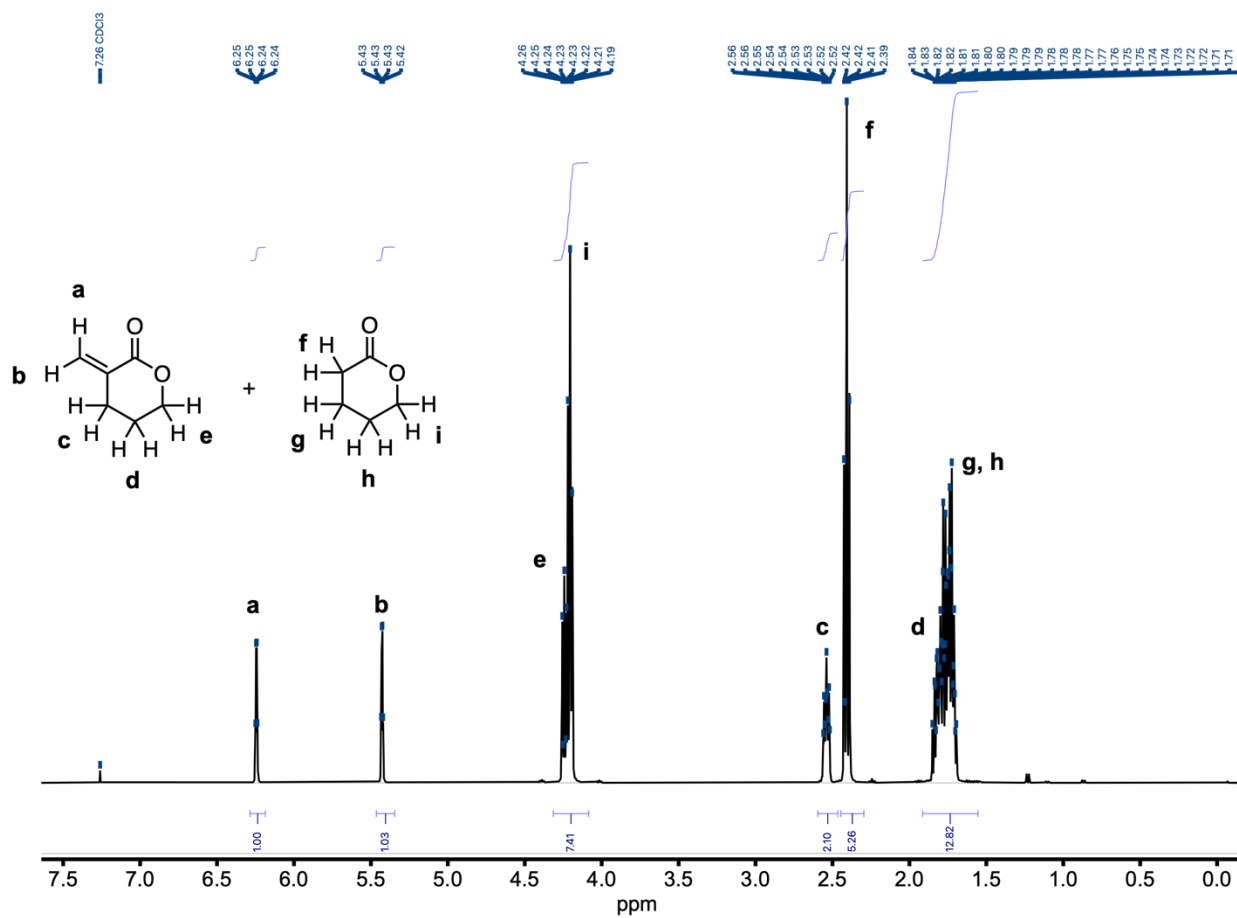


Figure S.14. ^1H NMR spectrum (CDCl_3 , 23 °C) of initial monomer mixture of 30 wt% MVL in DVL used for polymerization studies.

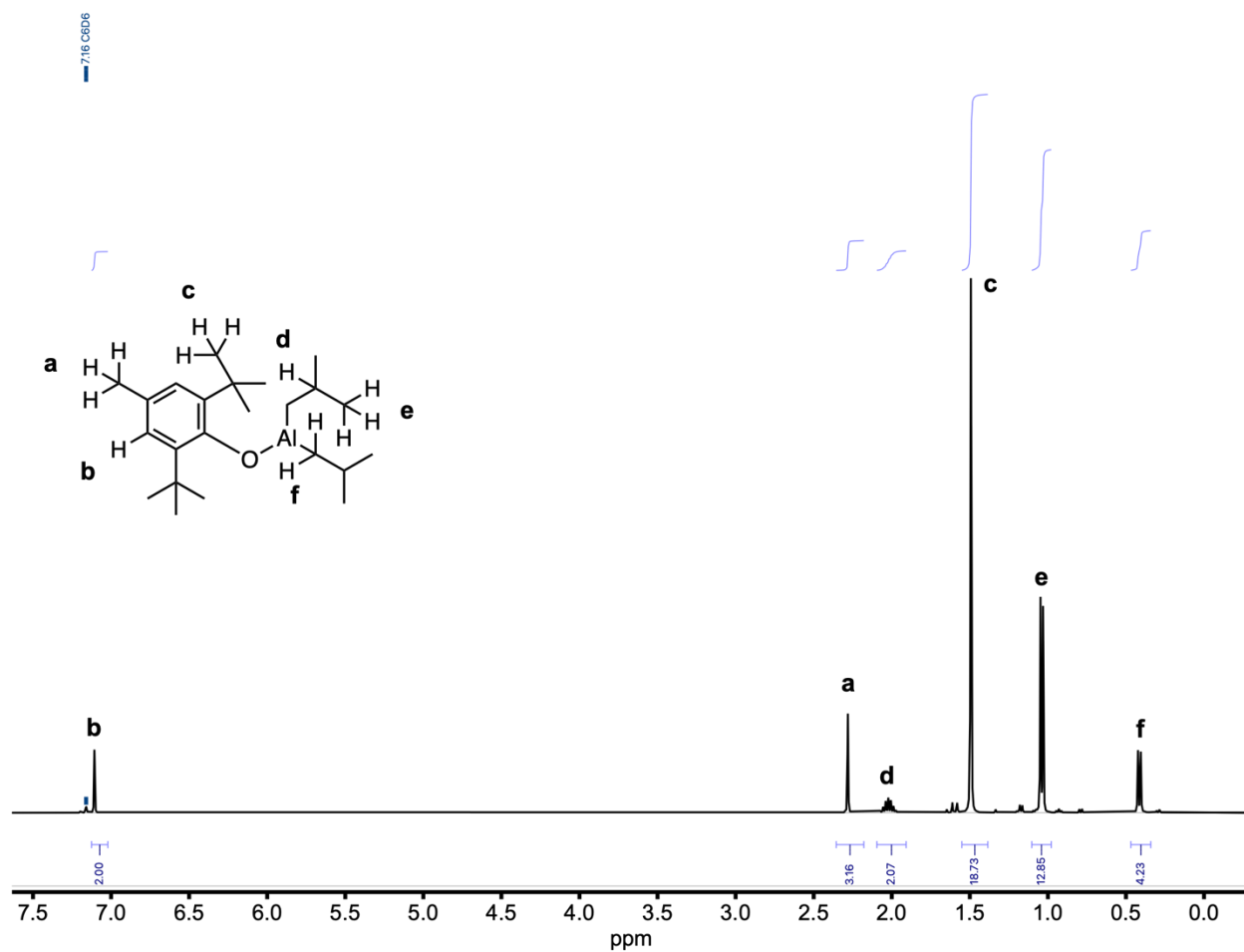


Figure S.15. ^1H NMR spectrum (C $_6\text{D}_6$, 23 °C) of purified $\text{Al}(\text{iBu})_2\text{BHT}$. Equivalent hydrogens are omitted from the structure for clarity.

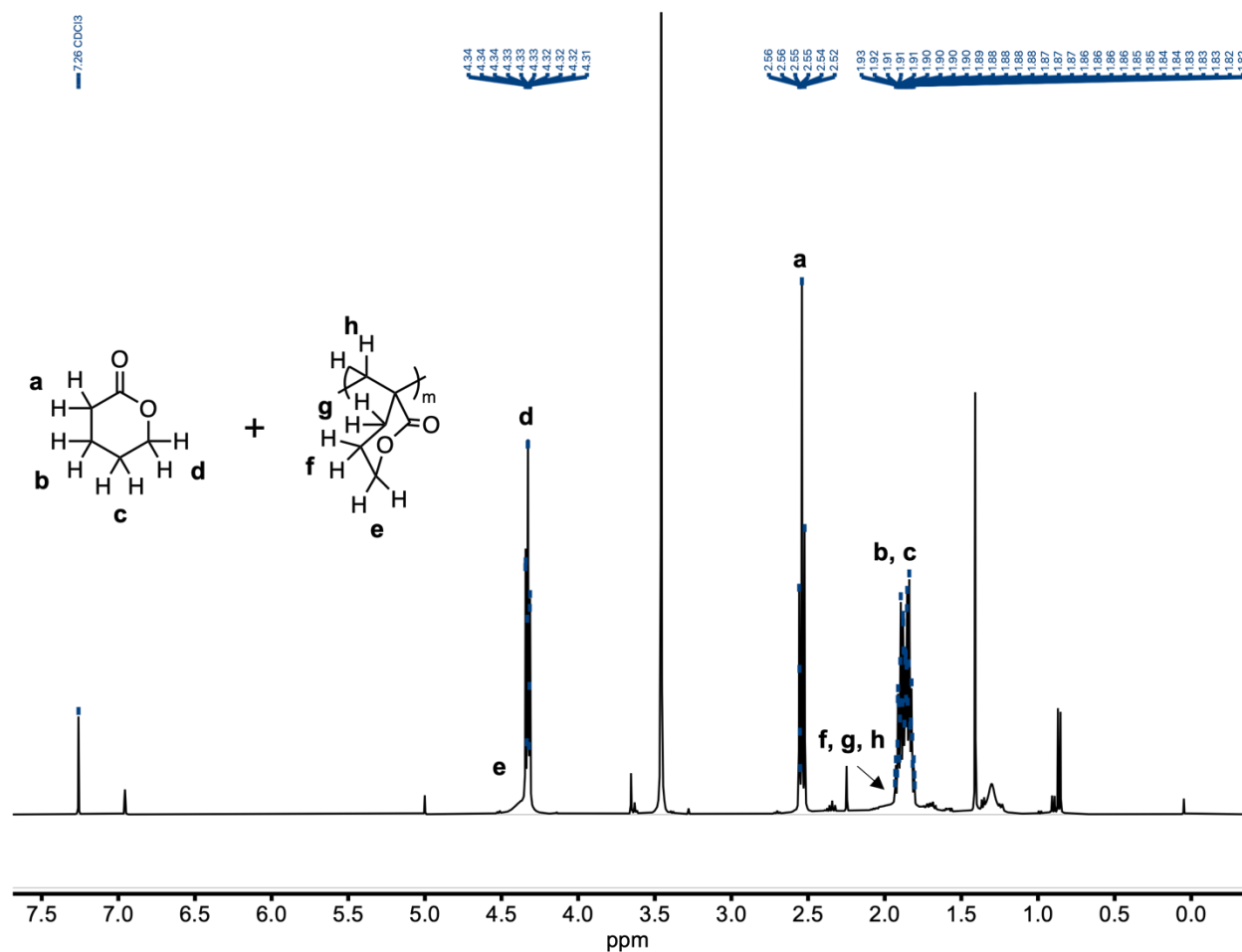


Figure S.16. ^1H NMR spectrum (CDCl_3 , 23 °C) of crude VAP reaction mixture ($[\text{MVL}]:[\text{Al}(\text{iBu})_2\text{BHT}] = 100:1$) at -30 °C prior to distillation, showing $\text{P}(\text{MVL})_{\text{VAP}}$ produced in DVL. $\text{P}(\text{MVL})_{\text{VAP}}$ peaks are seen as broad signals overlapping DVL monomer signals. Integrations omitted.

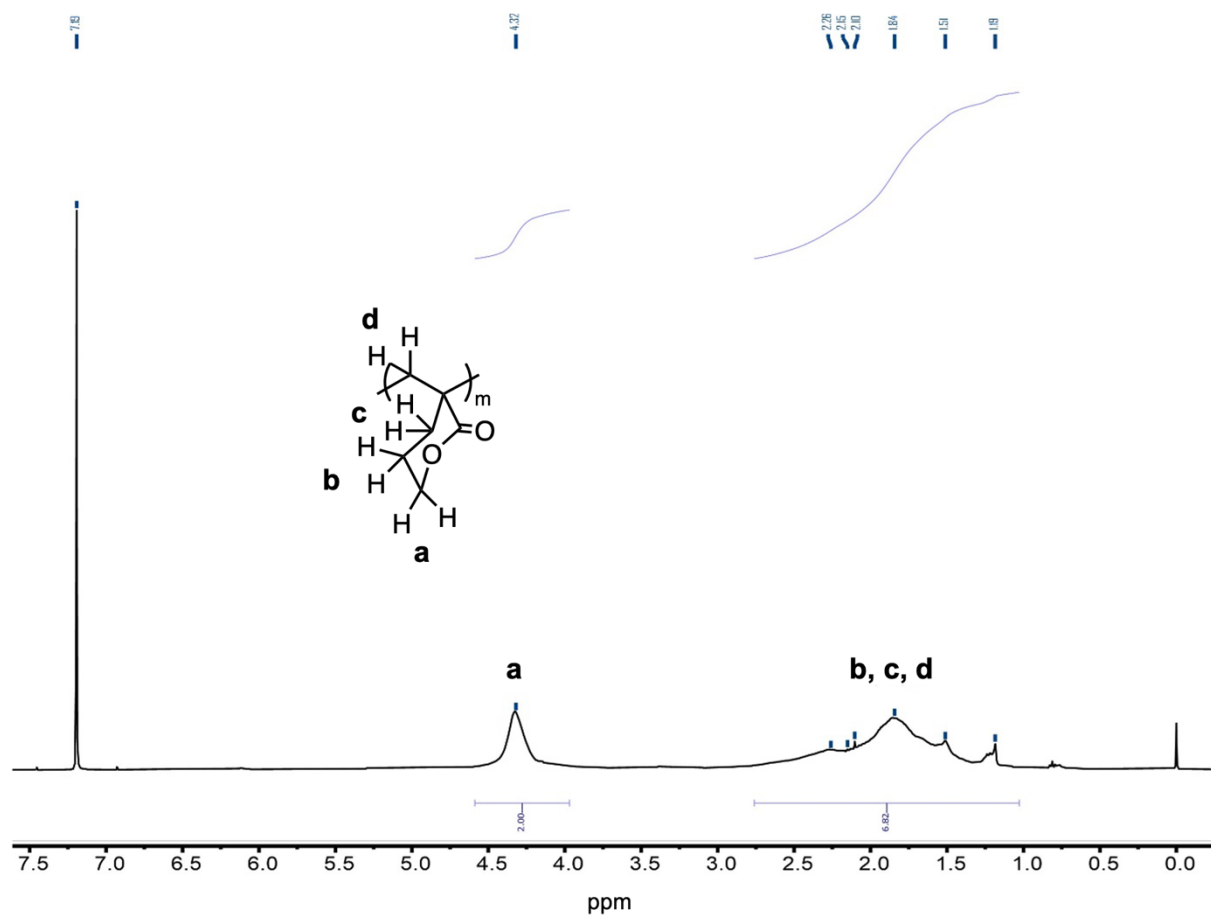


Figure S.17. ^1H NMR spectrum (CDCl_3 23 $^\circ\text{C}$) of $\text{P(MVL)}_{\text{VAP}}$ post-distillation from the VAP in a ratio of $[\text{MVL}]:[\text{Al}(\text{iBu})_2\text{BHT}] = 100:1$ at $-30\text{ }^\circ\text{C}$ ($M_n = 25.3\text{ kDa}$, $\bar{D} = 1.54$).

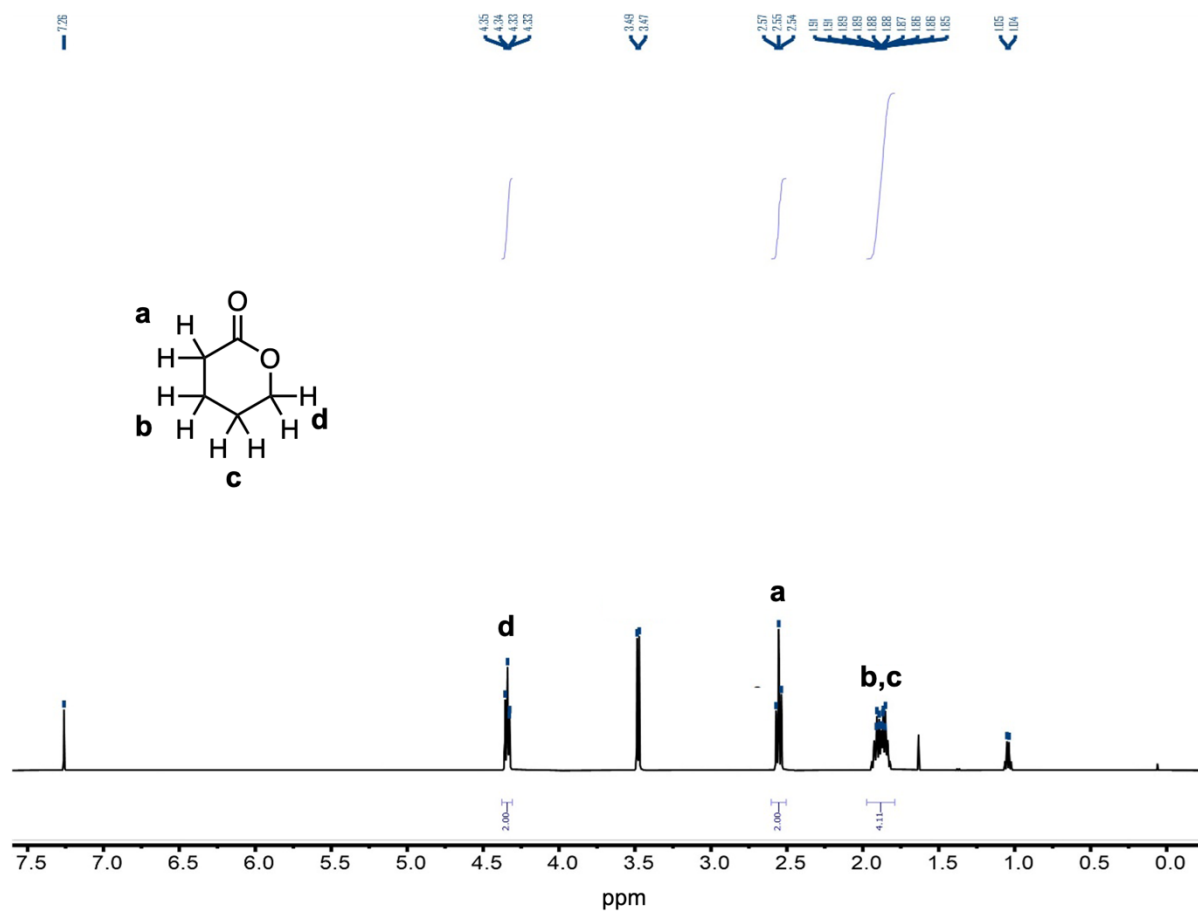


Figure S.18. ^1H NMR spectrum (CDCl_3 , 23 °C) of the recovered DVL post-distillation from the VAP reaction mixture. Peaks at 3.49 and 1.56 ppm are for MeOH and water, respectively. Peak around 1.00 ppm is unidentified. All residual peaks were removed after drying.

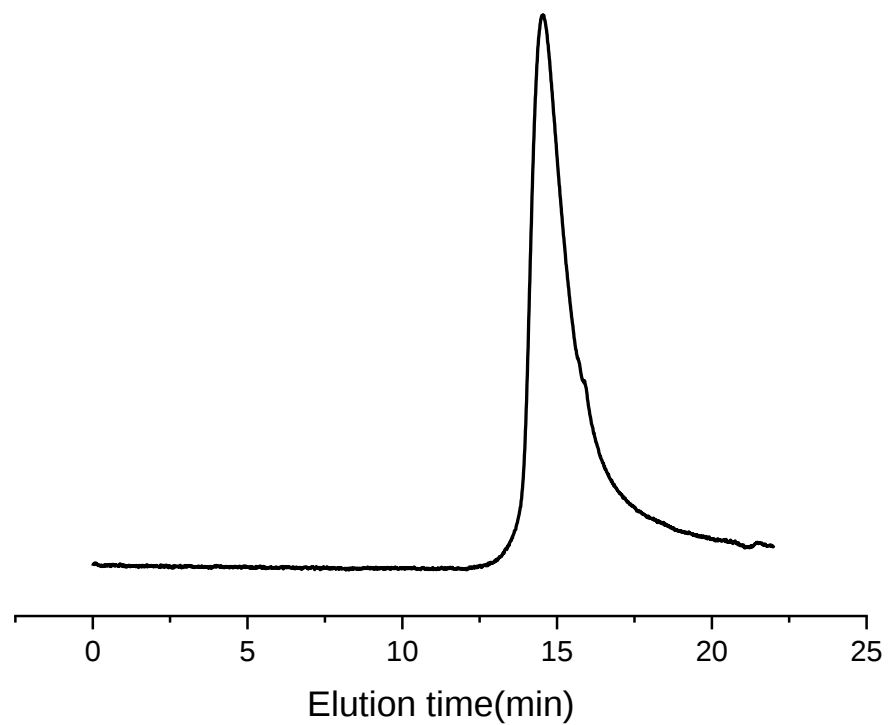


Figure S.19. SEC trace of P(MVL)_{VAP} produced from a ratio of [MVL]:[Al(^{*i*}Bu)₂BHT] = 100:1 at -30 °C ($M_n = 25.3$ kDa, $\bar{D} = 1.54$).

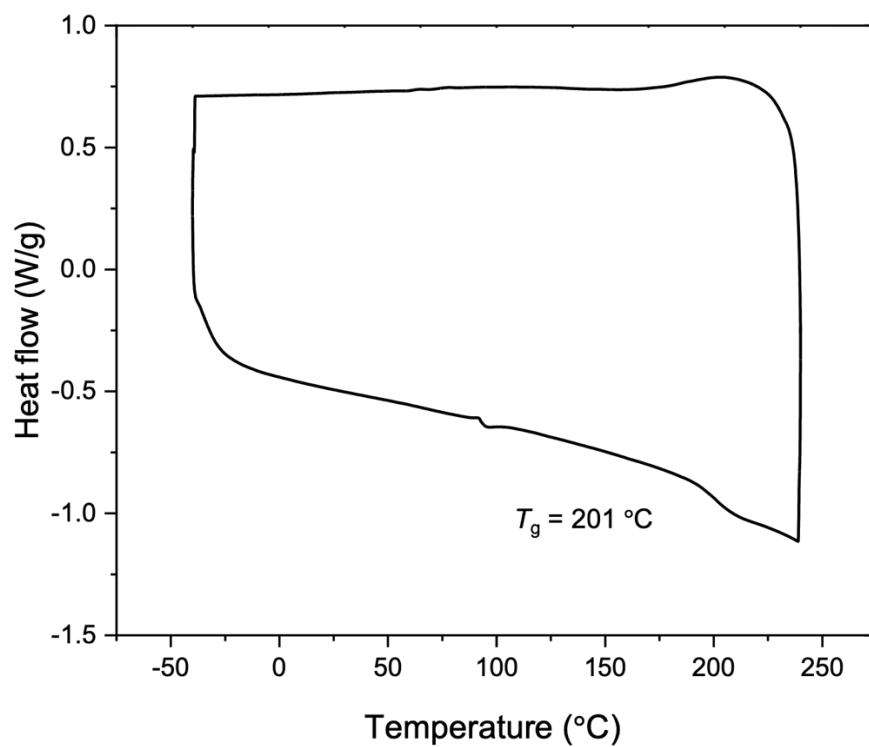


Figure S.20. DSC curve of P(MVL)_{VAP} produced from a ratio of [MVL]:[Al(*i*Bu)₂BHT] = 100:1 at -30 °C (*M*_n = 25.3 kDa, Đ = 1.54).

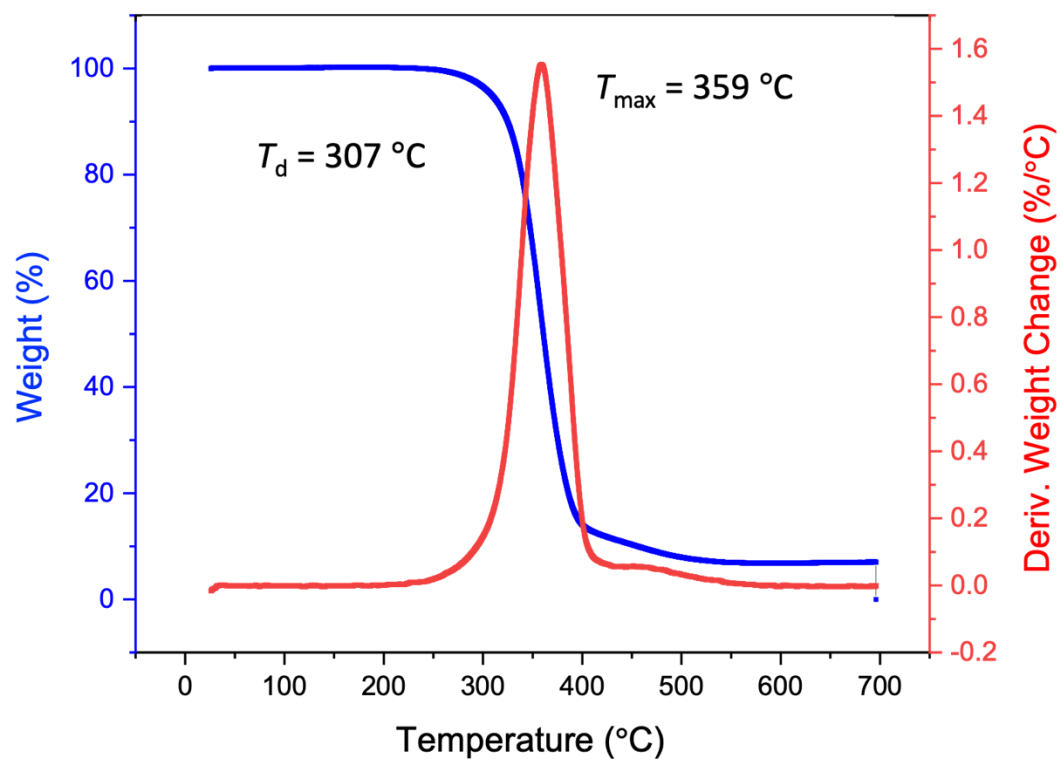


Figure S.21. TGA and DTA curves of P(MVL)_{VAP} produced from a ratio of [MVL]:[Al(*i*Bu)₂BHT] = 100:1 at -30 °C (*M*_n = 25.3 kDa, *Đ* = 1.54).

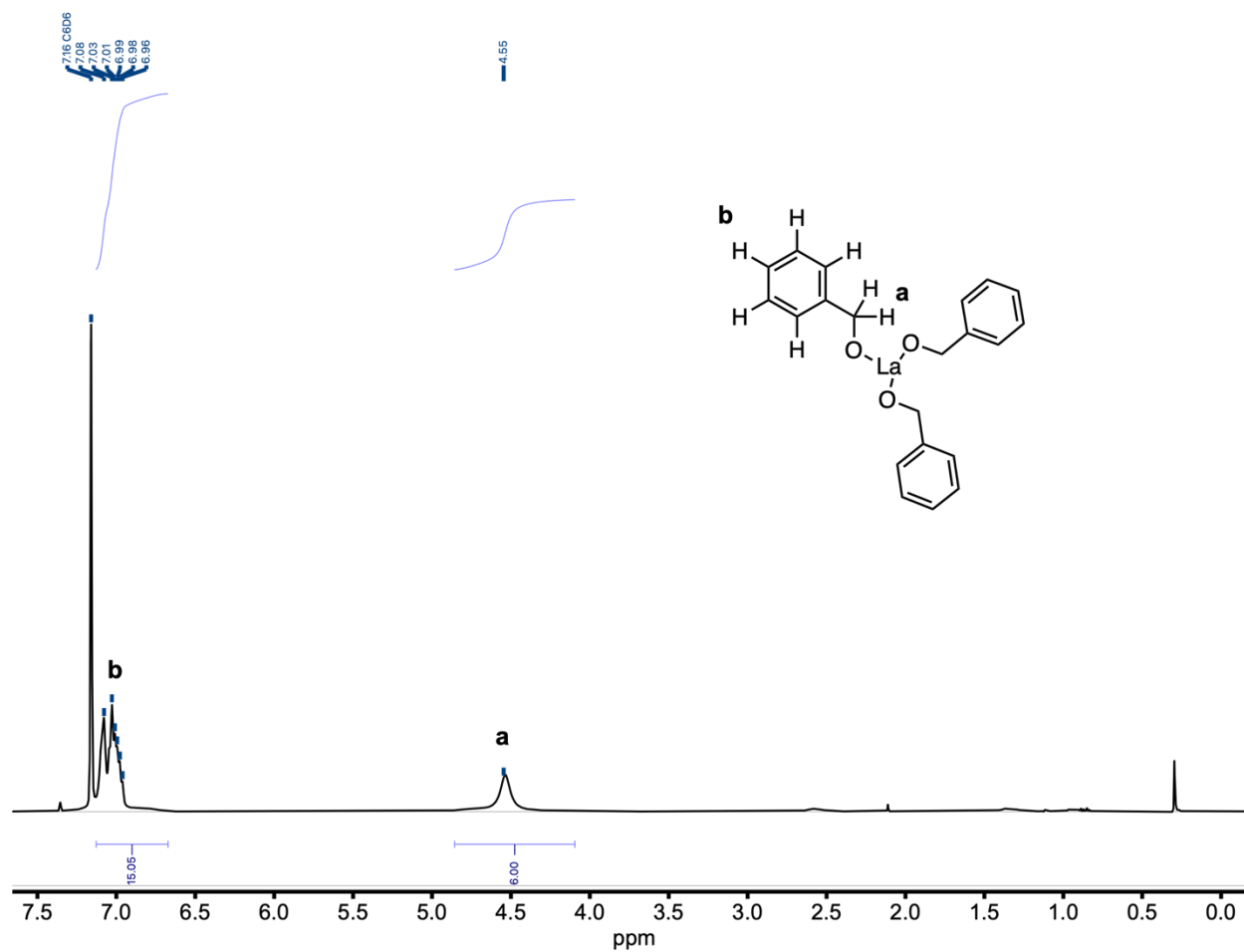


Figure S.22. ^1H NMR spectrum (C_6D_6 , 23°C) of purified $[\text{La}(\text{OBn})_3]_x$. Residual peaks between 1.5 and 0.0 ppm attributed to hexanes and grease.

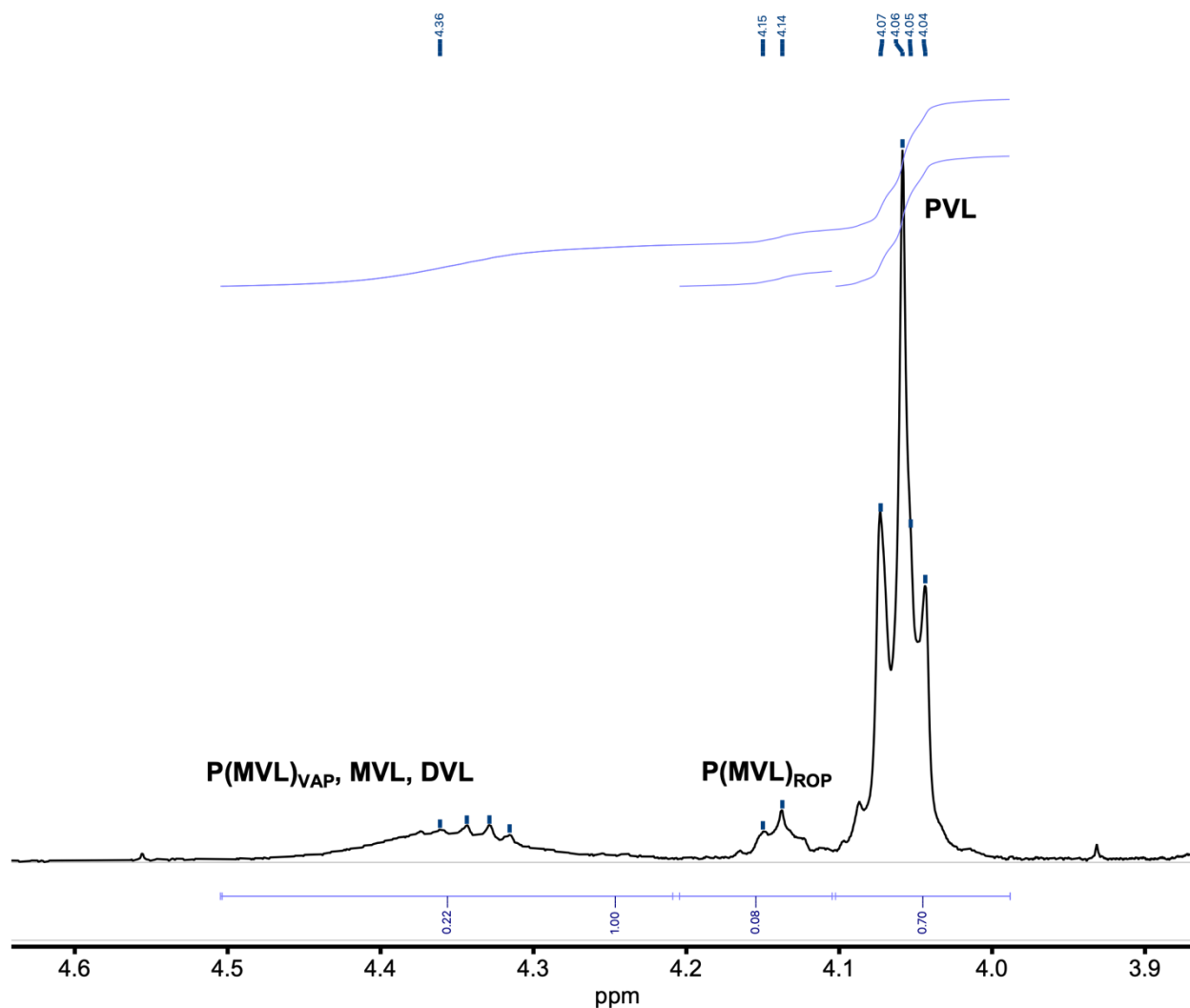


Figure S.23. ^1H NMR spectrum (CDCl_3 , 23 $^\circ\text{C}$) of crude polyester reaction mixture of the polymerization in toluene at the ratio $[\text{M}]:[\text{La}(\text{OBn})_3]_x = 1500:1$ containing PVL, $\text{P(MVL)}_{\text{ROP}}$, $\text{P(MVL)}_{\text{VAP}}$, MVL, and DVL. Zoomed region depicts the initial ratio of products, with $\text{P(MVL)}_{\text{VAP}}$ visible as a broad peak around 4.36 ppm. Final product distributions and conversions were calculated accounting for the overlapping peaks of $\text{P(MVL)}_{\text{VAP}}$ and the two monomers but are not indicated in this figure.

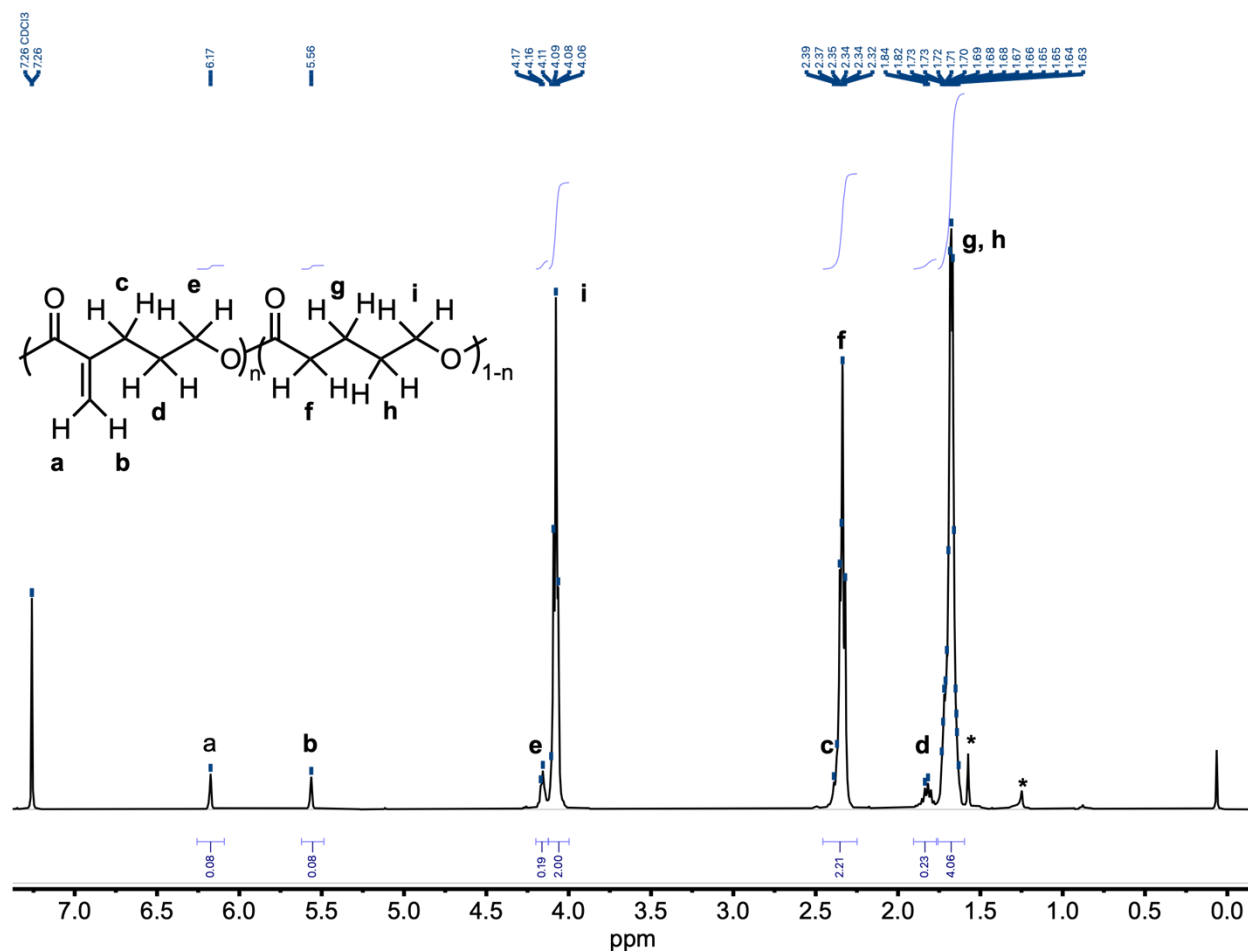


Figure S.24. ^1H NMR spectrum (CDCl_3 , 23 $^\circ\text{C}$) of purified P(MVL-co-VL) produced from a ratio of $[\text{M}]:\{[\text{La}(\text{OBn})_3]_x\} = 1500:1$ ($M_n = 124$ kDa, $\bar{D} = 1.39$). Asteriks indicate water and grease at 1.56 and 1.24 ppm, respectively.

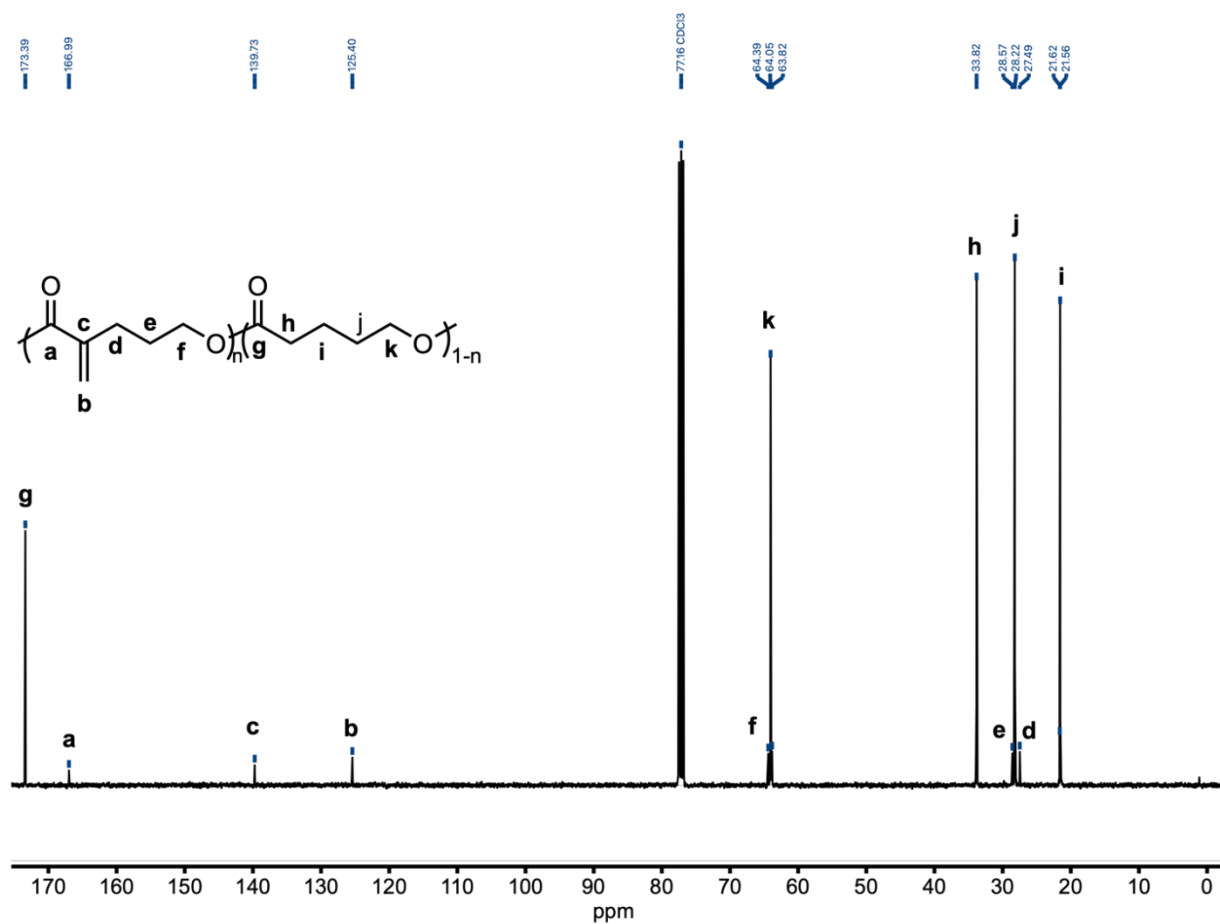


Figure S.25. ^{13}C NMR spectrum (CDCl_3 , 23 °C) of purified P(MVL-co-VL) produced from a ratio of $[\text{M}]:\{[\text{La}(\text{OBn})_3]_x\} = 1500:1$ ($M_n = 124$ kDa, $\bar{D} = 1.39$).

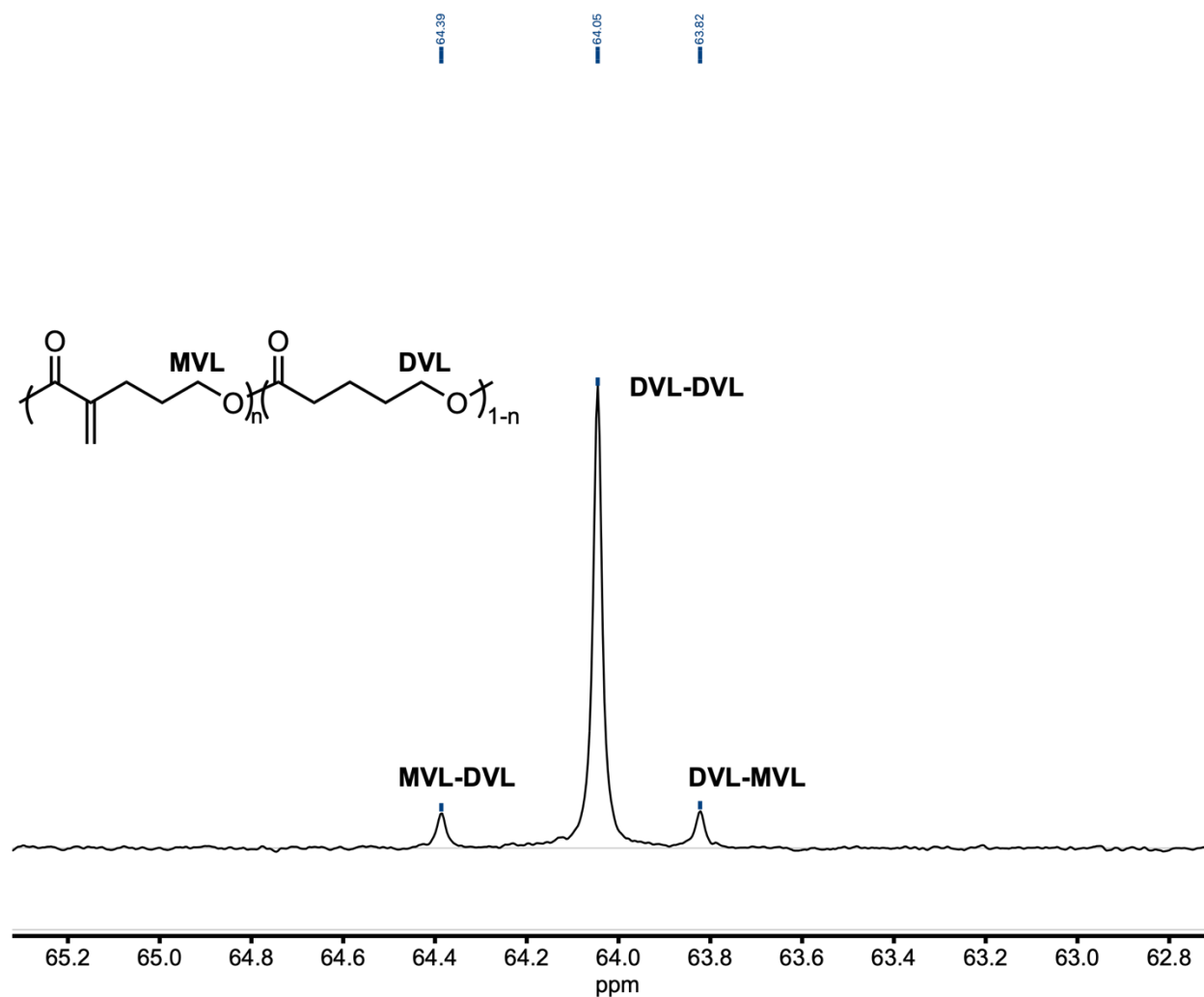


Figure S.26. ^{13}C NMR spectrum (CDCl_3 , 23 °C) of purified P(MVL-co-VL) produced from a ratio of $[\text{M}]:\{[\text{La}(\text{OBn})_3]_x\} = 1500:1$ ($M_n = 124$ kDa, $\bar{D} = 1.39$). Zoomed region of signal adjacent to linking oxygen groups. As expected, the main signal is attributed to homopolymer linkages between DVL units (DVL-DVL). DVL-MVL and MVL-DVL signals indicate DVL to MVL and MVL to DVL linkages, respectively. Assignments were made based on a report of a similar copolymer product.⁵ These data support the conclusion that MVL units are incorporated randomly throughout PVL.

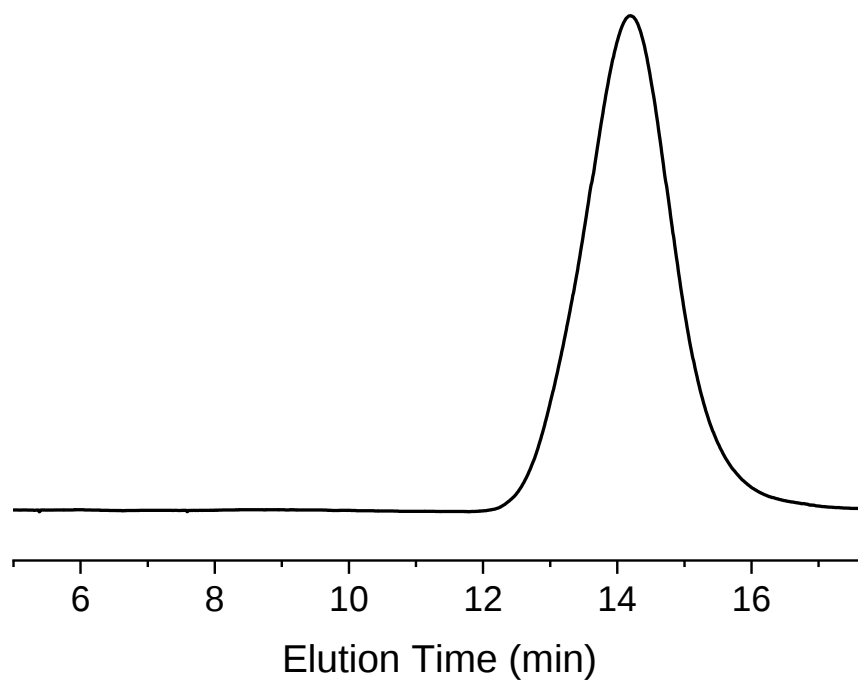


Figure S.27. SEC trace of P(MVL-co-VL) produced from a ratio of $[M]:\{[La(OBn)_3]_x\} = 1500:1$ ($M = 30$ wt% MVL in DVL) ($M_n = 124$ kDa, $\bar{D} = 1.39$).

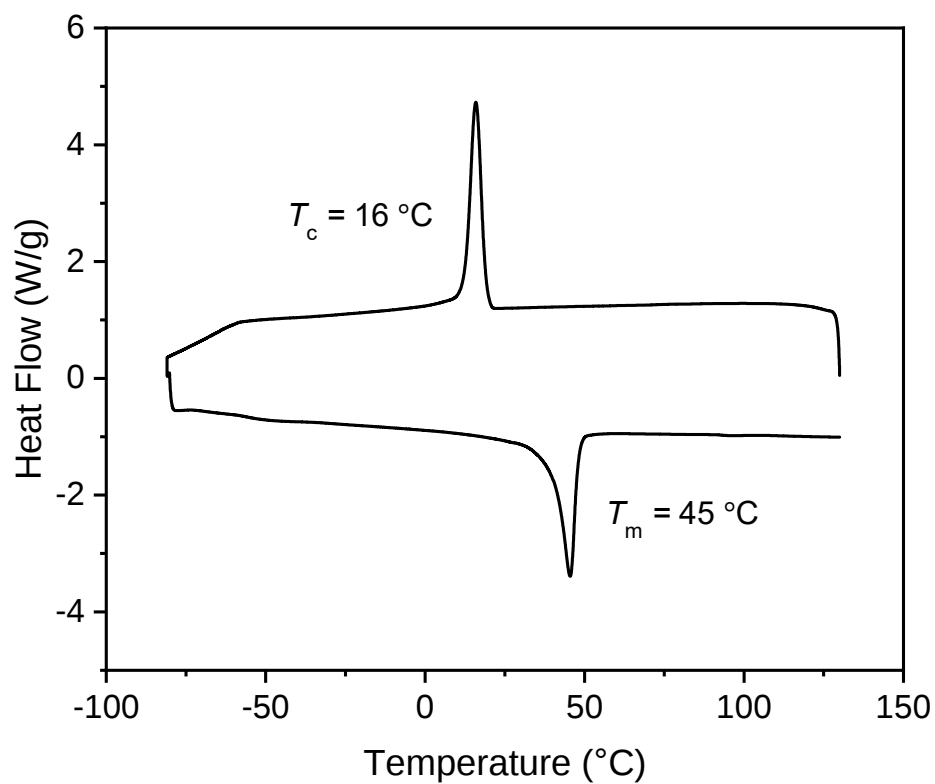


Figure S.28. DSC curve of P(MVL-*co*-VL) produced from a ratio of $[M]:\{[La(OBn)_3]_x\} = 1500:1$ ($M_n = 124\text{ kDa}$, $\bar{D} = 1.39$, $\Delta H_f = 51.50\text{ J/g}$).

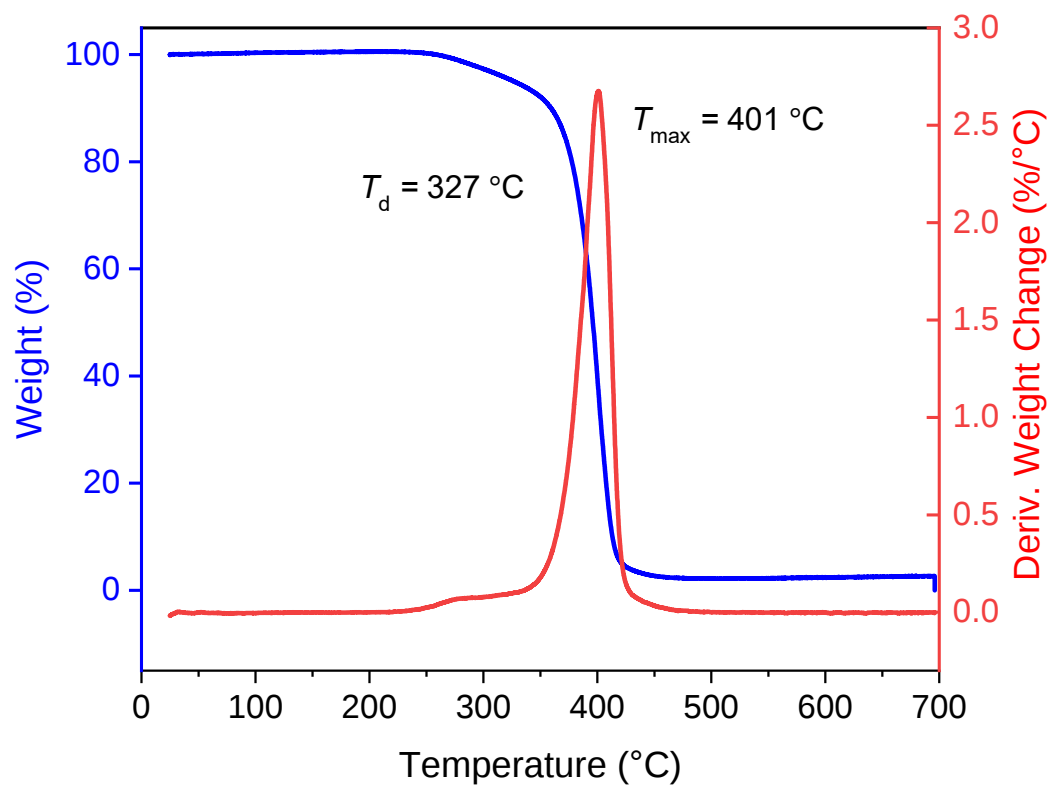


Figure S.29. TGA and DTA curves of P(MVL-co-VL) produced from a ratio of $[M]:\{[\text{La}(\text{OBn})_3]_x\} = 1500:1$ ($M_n = 124\text{ kDa}$, $\bar{D} = 1.39$).

References

- (1) Xu, T. Q.; Yu, Z. Q.; Zhang, X. M. Recyclable Vinyl-Functionalized Polyesters via Chemoselective Organopolymerization of Bifunctional α -Methylene- δ -Valerolactone. *Macromol. Chem. Phys.* **2019**, *220* (12), 1900150. <https://doi.org/10.1002/macp.201900150>.
- (2) Healy, M. D.; Power, M. B.; Barron, A. R. Sterically Crowded Aryloxide Compounds of Aluminum. *Coord. Chem. Rev.* **1994**, *130* (1–2), 63–135. [https://doi.org/10.1016/0010-8545\(94\)80003-0](https://doi.org/10.1016/0010-8545(94)80003-0).
- (3) Hong, M.; Chen, E. Y. X. Completely Recyclable Biopolymers with Linear and Cyclic Topologies via Ring-Opening Polymerization of γ -Butyrolactone. *Nat. Chem.* **2015**, *8* (1), 42–49. <https://doi.org/10.1038/nchem.2391>.
- (4) Manzer, L. E. Catalytic Synthesis of α -Methylene- γ -Valerolactone: A Biomass-Derived Acrylic Monomer. *Appl. Catal. A Gen.* **2004**, *272*, 249–256. <https://doi.org/10.1016/j.apcata.2004.05.048>.
- (5) Liu, Y.; Kou, X.; Xu, C.; Zhou, W.; Zhang, H.; Liu, F.; Shen, Y.; Li, Z. Chemoselective and Controlled Ring-Opening Copolymerization of Biorenewable α -Methylene- δ -Valerolactone with ϵ -Caprolactone toward Functional Copolyesters. *Polym. Chem.* **2023**, *14* (19), 2326–2332. <https://doi.org/10.1039/d3py00188a>.