

Electronic Supporting Information (ESI)

Effect of Macromonomer Chemical Structure on the Rate of Grafting-Through Ring Opening Metathesis Polymerization

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Abbreviations

ROP, ring opening polymerization
ROMP, ring opening metathesis polymerization
MM, macromonomer
BB, bottlebrush
M1, exo-5-norbornene-2-methanol
M2, N-ethoxy-exo-5-norbornene-2,3-dicarboximide
PO, propylene oxide
PPO, poly(propylene oxide)
LA, D,L-lactide
PLA, poly(lactic acid)
TEB, triethyl borane
tBuP4, P4-tertbutyl phosphazene base
DBU, 1,8-diazabicyclo[5.4.0]undec-7-ene
THF, tetrahydrofuran
G3, Grubbs 3rd generation catalyst
SEC, size exclusion chromatography
RI, refractive index
M_n, average molecular weight
MWD, molecular weight distribution
D, dispersity
DP, degree of polymerization
RSD, relative standard deviation

I. General Methods and Materials

All reactions were performed in oven dried glassware in an argon-filled glovebox ($O_2 < 2$ ppm, $H_2O < 0.5$ ppm) at room temperature. All solvents were dried using a solvent purification system. All commercially obtained reagents were used as received unless otherwise stated. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) was distilled over CaH_2 and stored under argon at -20 °C. Boric acid solution (10 mg/mL in THF) was prepared by heating the solution to ~ 80 - 90 °C until all of the boric acid dissolved and then the solution was allowed to cool back to room temperature before use (avoid rapid cooling of the solution, as it will cause boric acid to precipitate).

Size Exclusion Chromatography (SEC) was performed using a Tosoh ECOSEC HLC-8320GPC at 40 °C fitted with a guard column (6.0 mm ID x 4.0 cm) and two analytical columns (TSKgel GMHHR-H, 7.8 mm ID x 30 cm x 5 μ m). A flow rate of 1 mL*min⁻¹ was used for both the analytical columns and the reference flow. THF (HPLC grade) was used as the eluent, and polystyrene standards (15 points ranging from 500 g/mol to 8.42 million g/mol) were used as the

general calibration (Figure S1 and S2). Standards were rerun periodically to ensure accurate fit with samples.

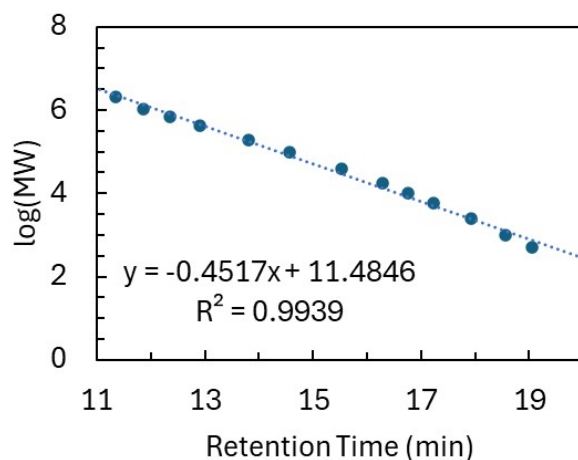


Figure S1. Calibration of PS standards from RI traces measured from SEC in THF used to determine the M_n and \mathcal{D} of SEC traces of ROMP kinetic experiments in figures S5-S16.

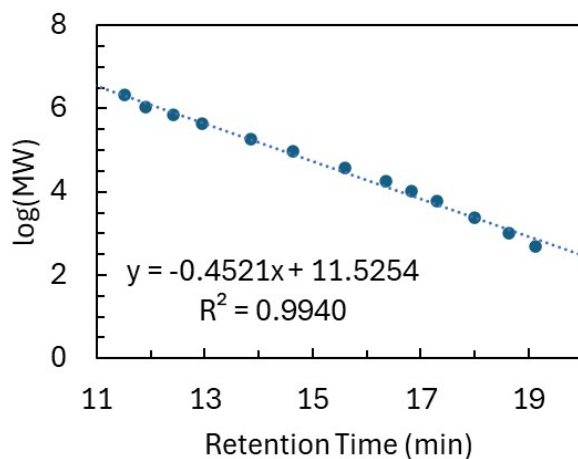
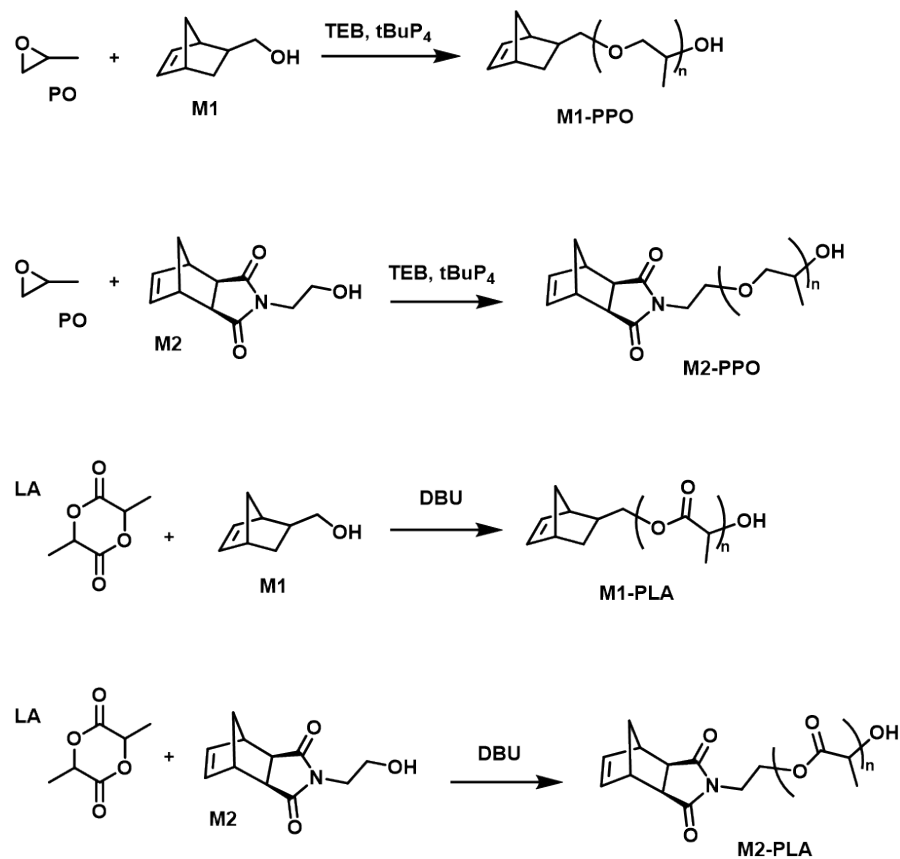


Figure S2. Calibration of PS standards from RI traces measured from SEC in THF used to determine the M_n and \mathcal{D} of SEC traces of control experiments in figures S18-S25 and of the isolated PLA experiments in figures S26 and S28.

II. Synthesis of Macromonomers via Ring Opening Polymerization (ROP)**Exo-5-norbornene-2-methanol (M1)**

M1 was synthesized according to previously reported procedure.¹

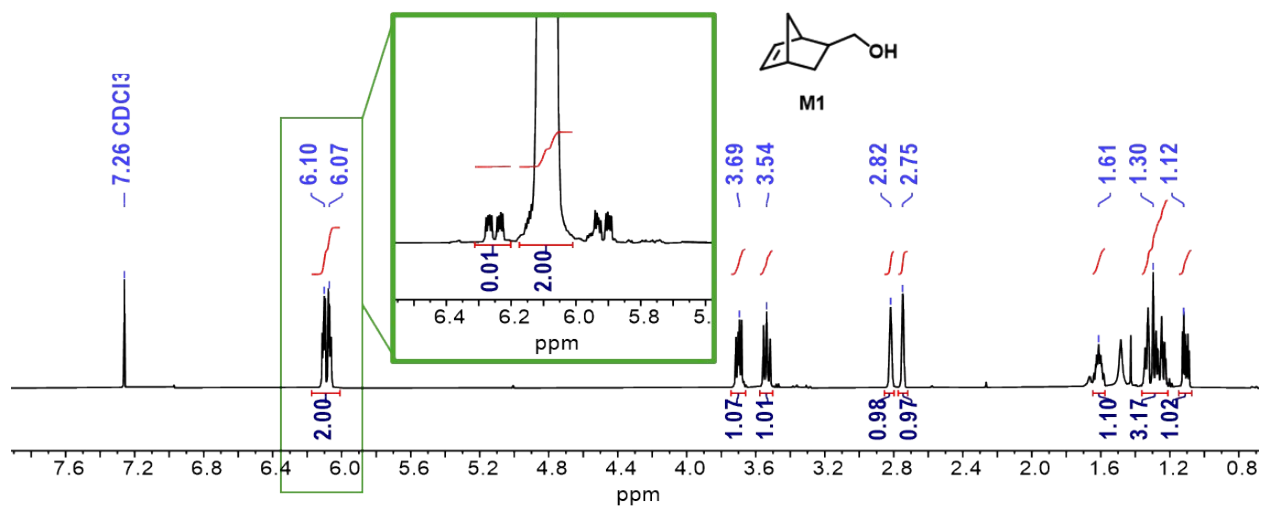


Figure S3. ¹H NMR spectrum of compound exo-5-norbornene-2-methanol (M1).

N-ethoxy-exo-5-norbornene-2,3-dicarboximide (M2)

M2 was synthesized according to previously reported procedure.²

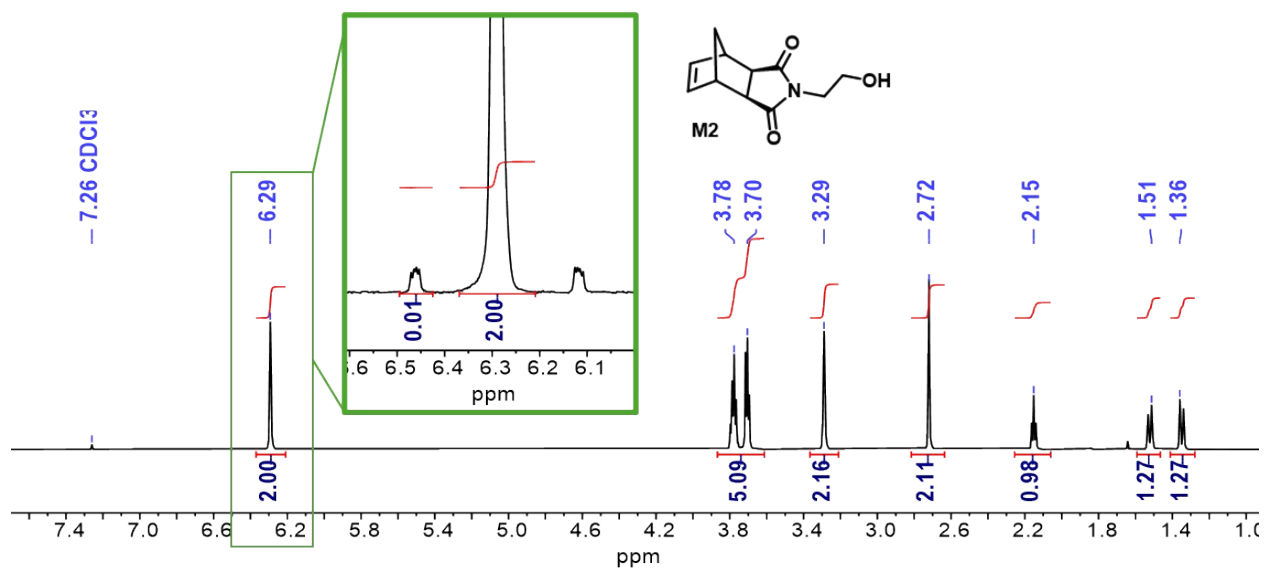


Figure S4. ¹H NMR spectrum of compound N-ethoxy-exo-5-norbornene-2,3-dicarboximide (M2).

Poly(propylene oxide) Macromonomer (PPO MM)

To a 20 mL vial, either **M1** (0.129 mmol) or **M2** (0.129 mmol) was measured out before THF (3.70 mL, [PO]₀ = 2 M) and TEB (1 M in hexanes, 0.0516 mmol) were added. A stir bar was then added, and the vial was placed on the stir plate before PO (9.66 mmol) was added to the stirring solution. Lastly, tBuP4 (0.8 M in hexanes, 0.00645 mmol) was added to start the polymerization. The vial was sealed, and the reaction was left to run for 18 hours overnight. The next morning, the reaction was “quenched” by adding boric acid solution (1 mL, 10 mg/mL in THF) and then a sample was prepared for SEC by taking 100 μL of the reaction and injecting it into 1 mL of THF.

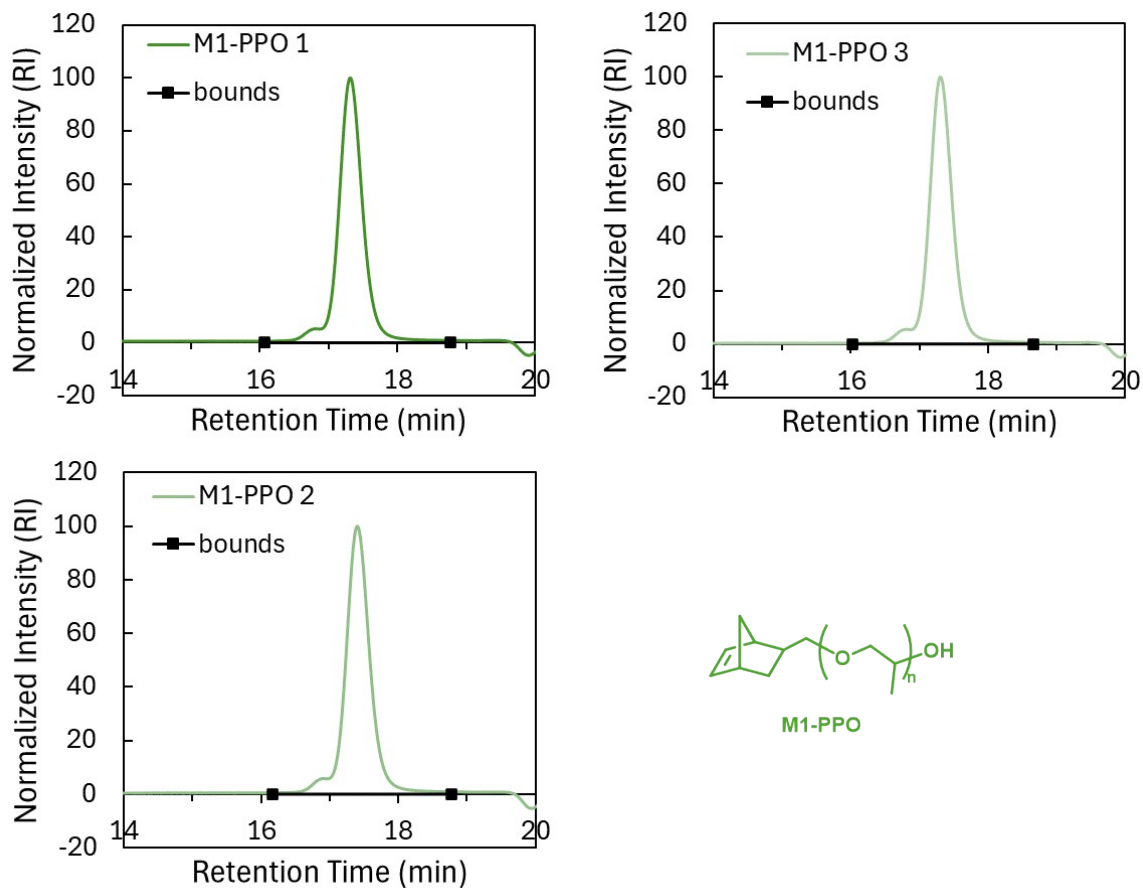


Figure S5. RI SEC traces of **M1-PPO** MM1s used for ROMP kinetic studies with bounds used for peak integration. The shoulder observed at the lower retention time are from a side reaction that we observed in the ROP of PO. The shoulder does not contain norbornene terminated chains as no change in the peak is observed during ROMP (**Figure S13**).

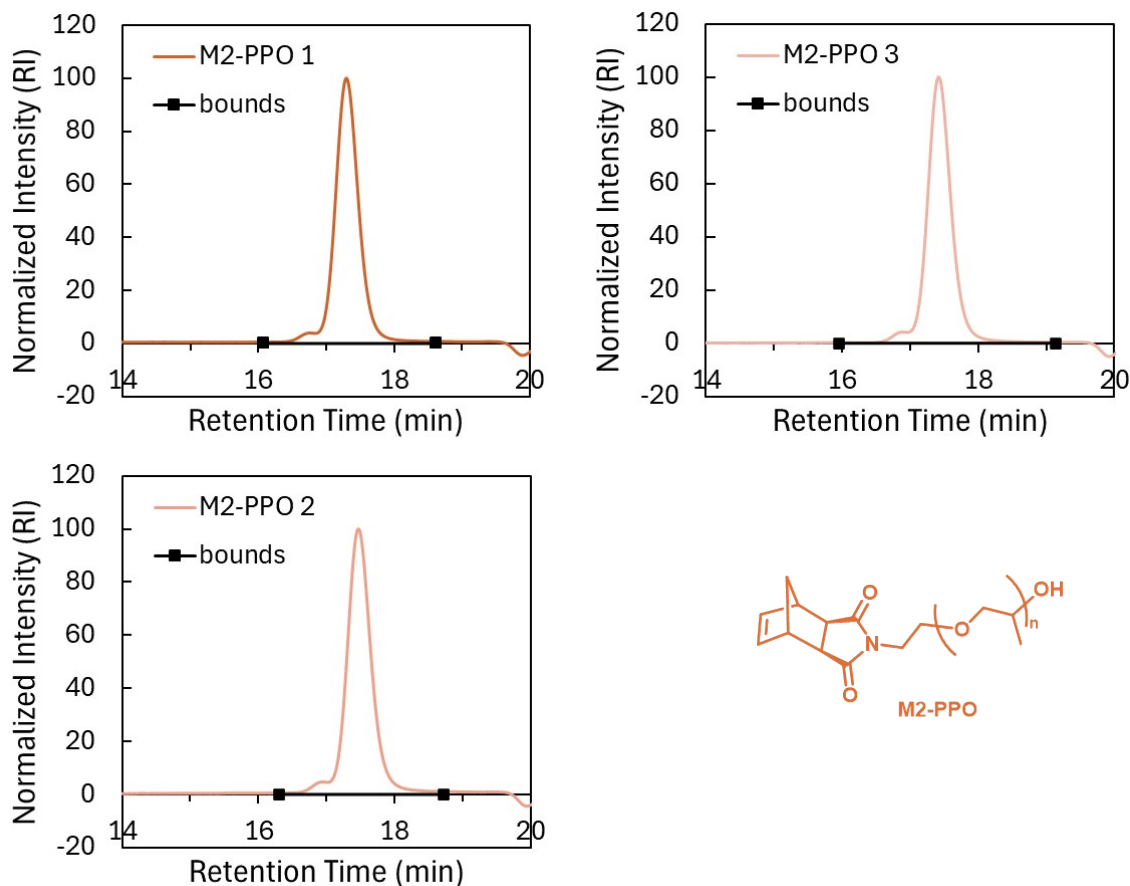


Figure S6. RI SEC traces of **M2-PPO** MMs used for ROMP kinetic studies with bounds used for peak integration. The shoulder observed at the lower retention time are from a side reaction that we observed in the ROP of PO. The shoulder does not contain norbornene terminated chains as no change in the peak is observed during ROMP (**Figure S14**).

Poly(lactic acid) Macromonomer (PLA MM)

To a 20 mL vial, either **M1** (0.129 mmol) or **M2** (0.129 mmol) was measured out before D,L lactide (5.16 mmol) was added, followed by THF (4.97 mL, $[LA]_0 = 1$ M). A stir bar was then added before the vial was placed on the stir plate. The solution was allowed to stir until the lactide completely dissolved. Lastly, DBU (0.0258 mmol) was added to start the polymerization. The reaction was allowed to run for 60 minutes before being quenched by adding boric acid solution (1 mL, 10 mg/mL in THF). A sample for SEC was next prepared by taking 100 μ L of the reaction and injecting it into 1 mL of THF.

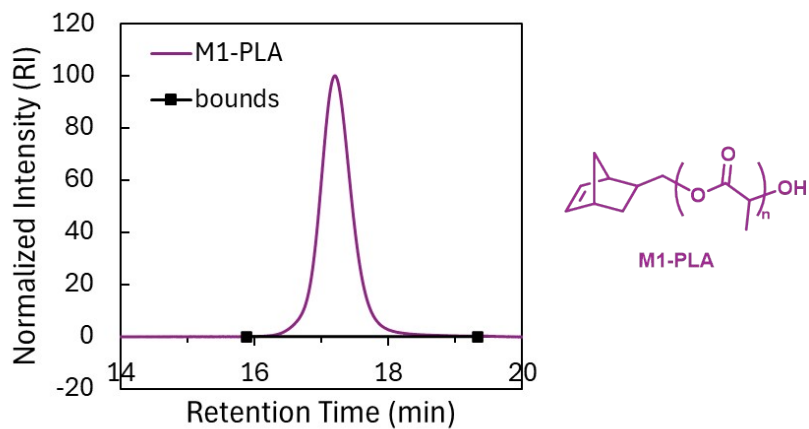


Figure S7. RI SEC trace of the **M1-PLA** MM used for ROMP kinetic studies with bounds used for peak integration.

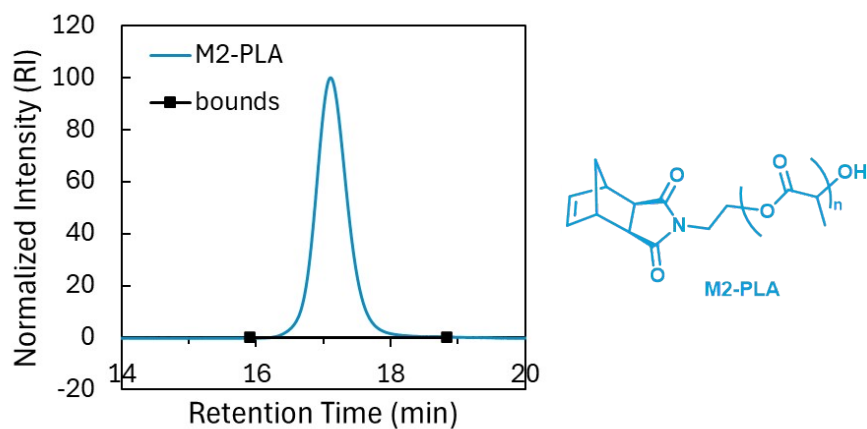
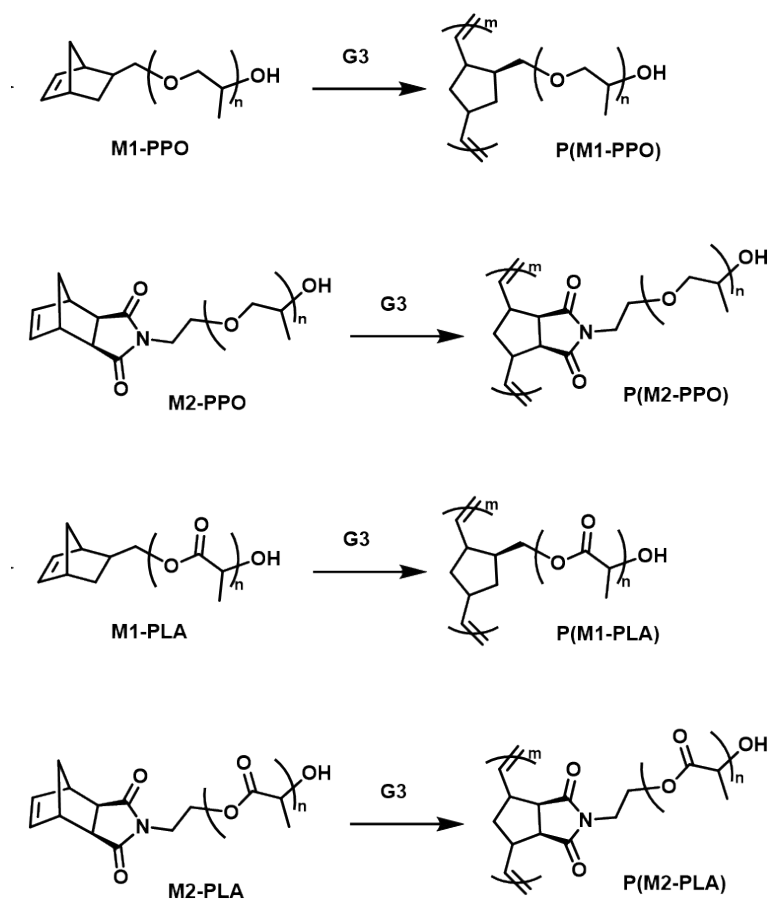


Figure S8. RI SEC trace of the **M2-PLA** MM used for ROMP kinetic studies with bounds used for peak integration.

III. Procedure for Ring Opening Metathesis Polymerization (ROMP) and Kinetic Studies



Grubbs 3rd generation initiator/catalyst precursor $[\text{H}_2\text{IMes})(3\text{-Br-py})_2(\text{Cl})_2\text{Ru}=\text{CHPh}]$ (G3)

G3 was synthesized according to literature.³

Poly(M1-PPO) and Poly(M2-PPO)

Immediately after quenching the PPO MM and taking a sample for SEC, THF ($[\text{PPO MM}]_0 = 0.020 \text{ M}$) was added before the addition of G3 ($0.645 \mu\text{mol}$) to start the polymerization. After 6 minutes, the ROMP reaction was quenched by adding $120 \mu\text{L}$ of ethyl vinyl ether.

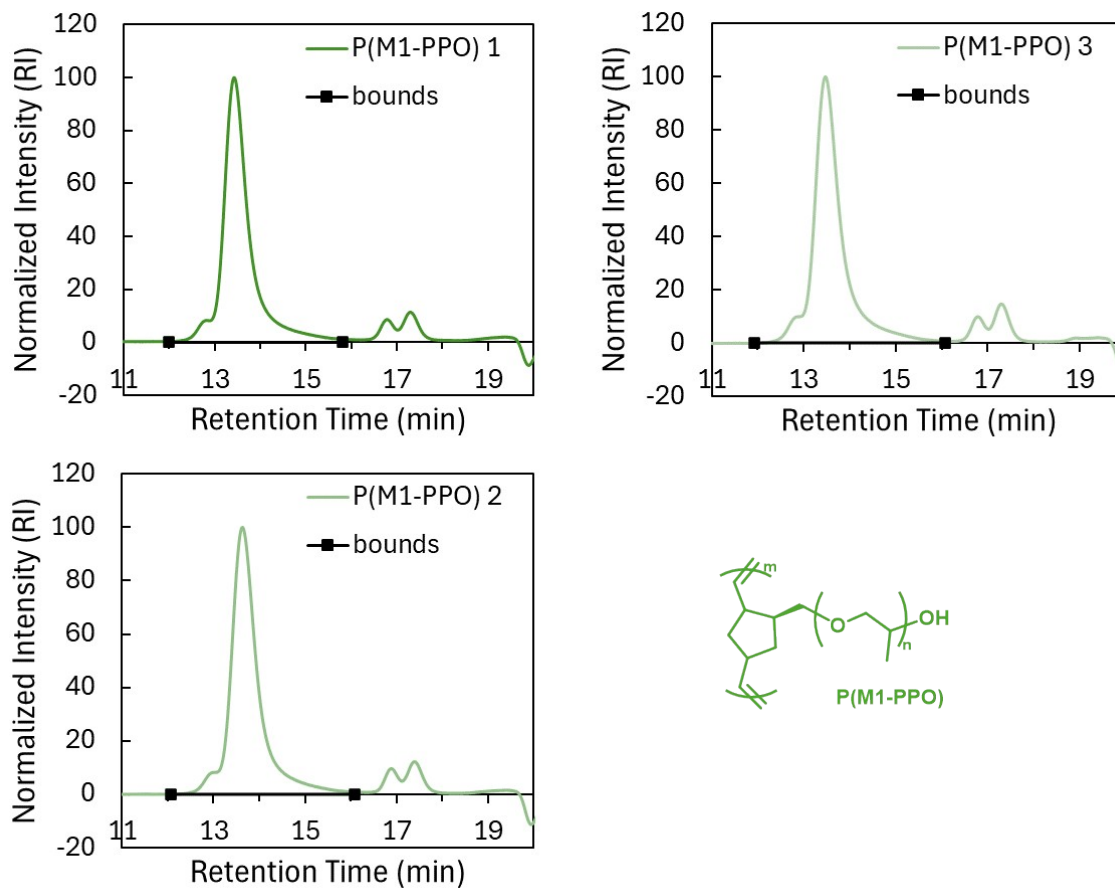


Figure S9. RI SEC traces of **P(M1-PPO)** BB with bounds used for peak integration. Remaining PPO chains observed at higher retention times are unfunctionalized with norbornene which is confirmed by the ROMP reaching a maximum conversion (**Figure S13**).

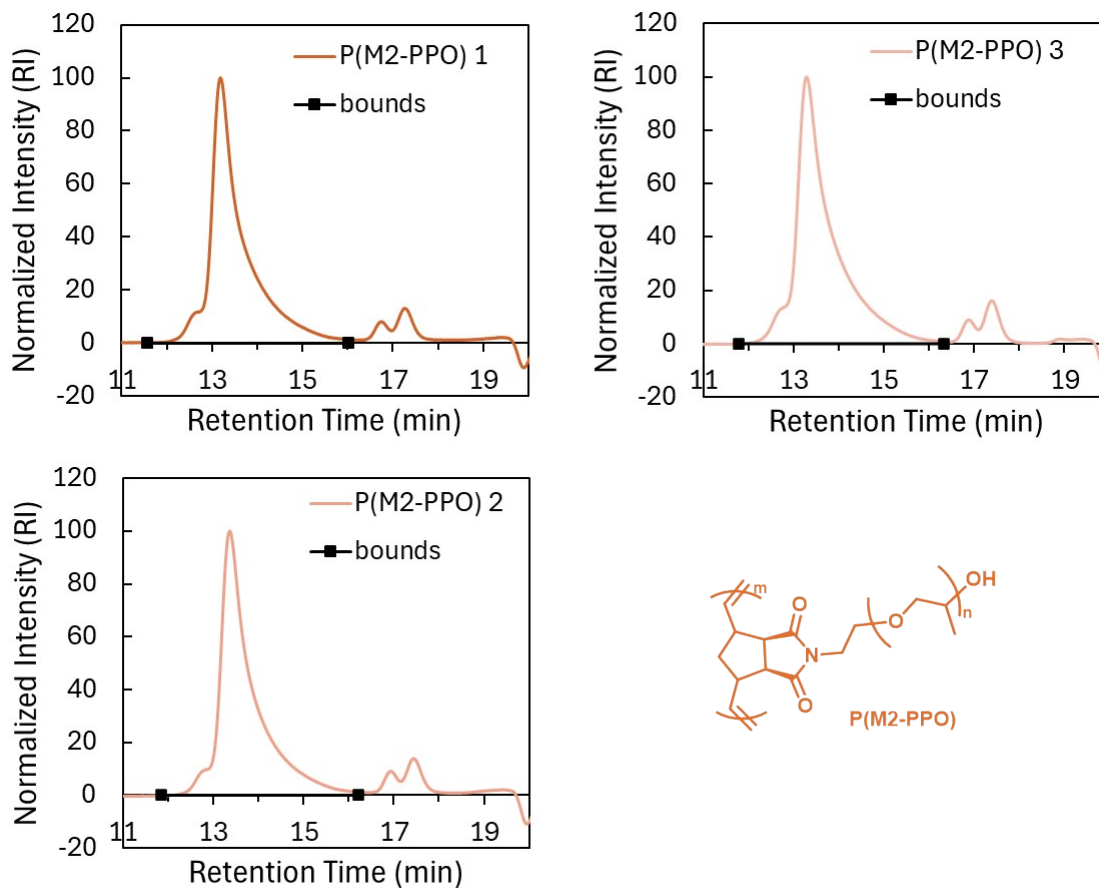


Figure S10. RI SEC traces of **P(M2-PPO)** BB with bounds used for peak integration. Remaining PPO chains observed at higher retention times are unfunctionalized with norbornene which is confirmed by the ROMP reaching a maximum conversion (**Figure S14**).

Poly(M1-PLA) and Poly(M2-PLA)

Immediately after quenching the PLA MM and taking a sample for SEC, the reaction solution was divided evenly into 3 vials. THF ($[PLA\ MM]_0 = 0.020\ M$) was added before the addition of G3 ($0.215\ \mu\text{mol}$) to start the polymerization. After 6 minutes, the ROMP reaction was quenched by adding $120\ \mu\text{L}$ of ethyl vinyl ether.

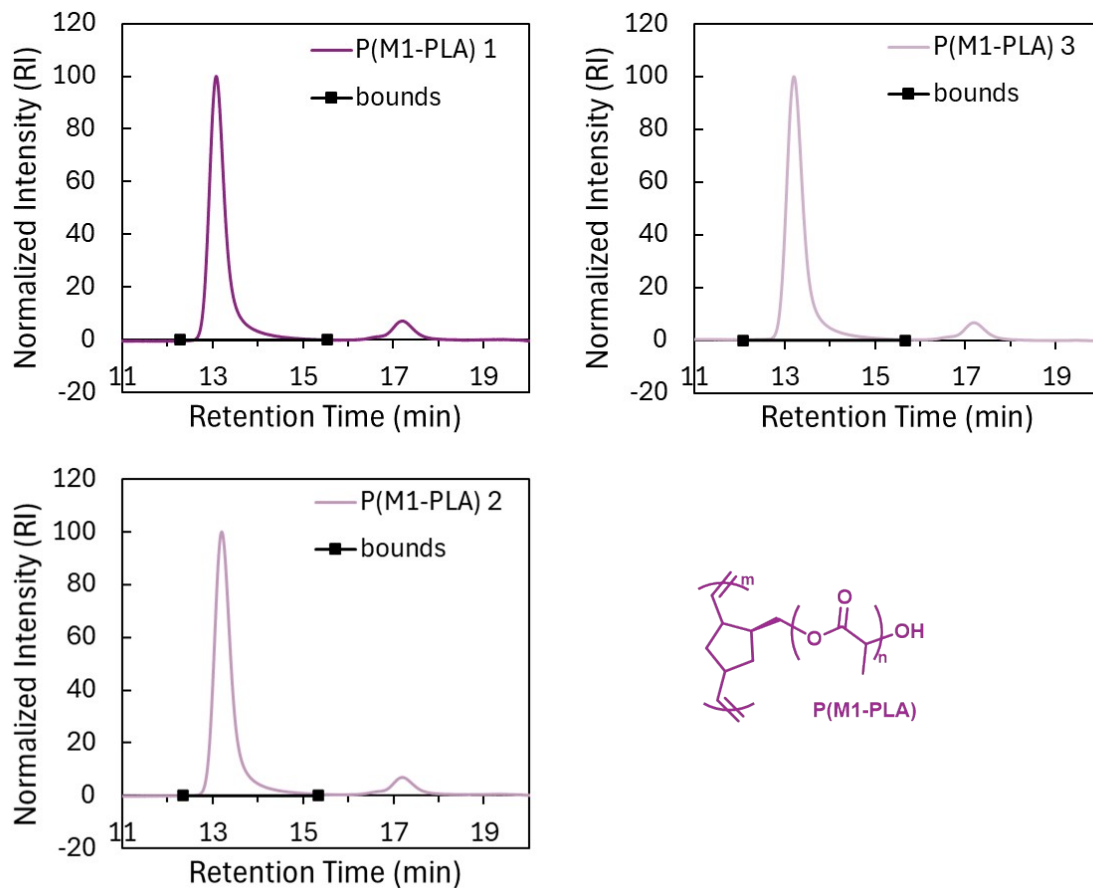


Figure S11. RI SEC traces of P(M1-PLA) BB with bounds used for peak integration. Remaining PLA chains observed at higher retention times are unfunctionalized with norbornene which is confirmed by the ROMP reaching a maximum conversion (**Figure S15**).

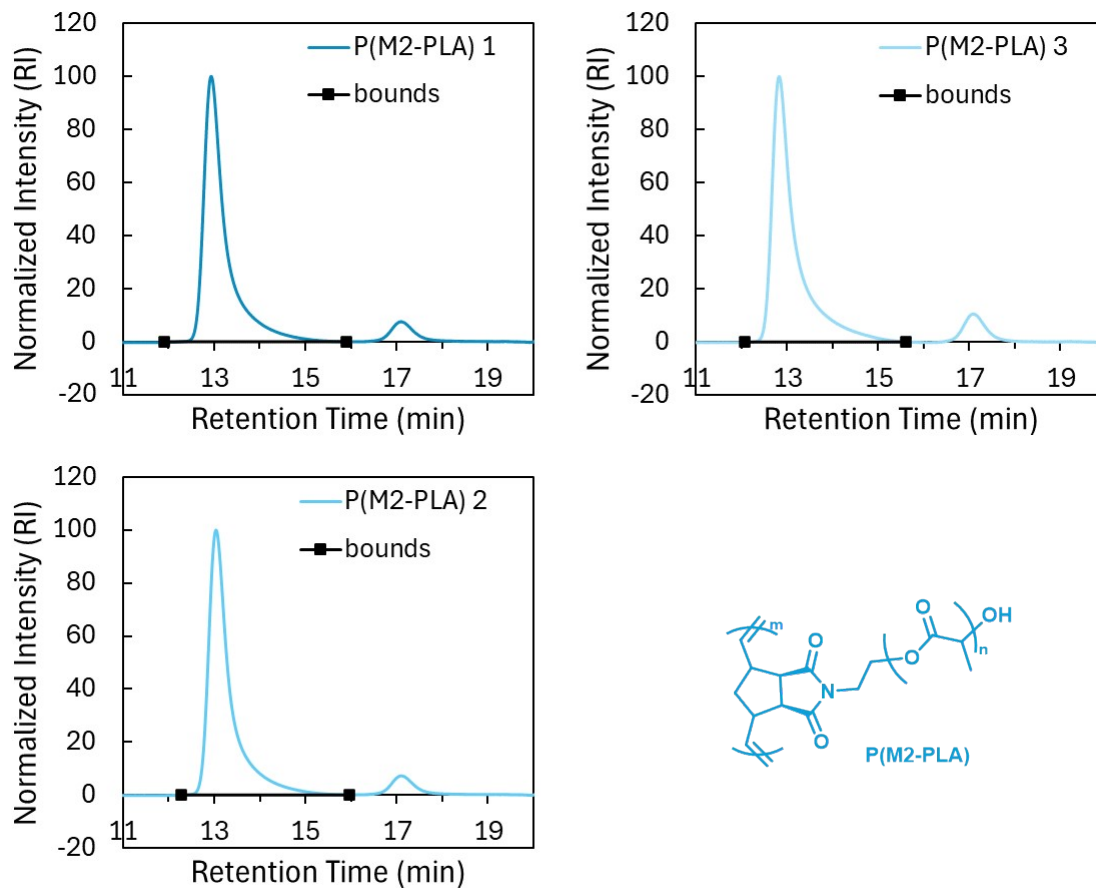


Figure S12. RI SEC traces of **P(M2-PLA)** BB with bounds used for peak integration. Remaining PLA chains observed at higher retention times are unfunctionalized with norbornene which is confirmed by the ROMP reaching a maximum conversion (**Figure S16**).

Kinetic Studies

During ROMP, kinetic samples were taken at 0.25, 0.5, 0.75, 1, 1.5, 3 and 5 minutes by taking 100 μL of the reaction and injecting it into an ethyl vinyl ether solution (1 mL, 70 $\mu\text{L}/\text{mL}$ in THF). Samples were then used directly for SEC. Conversion was calculated by comparing the area of the bottlebrush (BB) peak to the combined area of the BB peak and the MM peak.

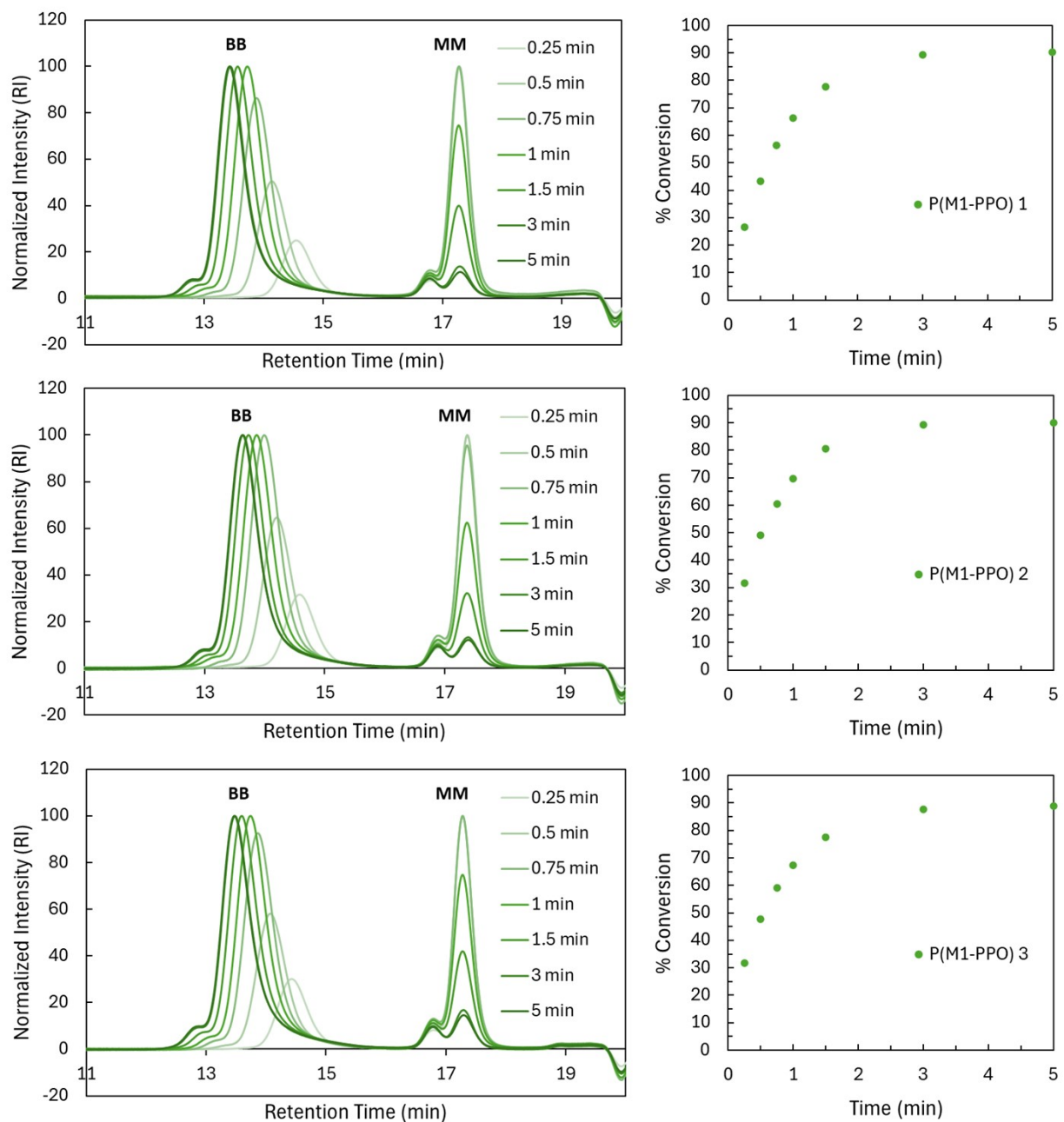


Figure S13. RI SEC traces from the ROMP of M1-PPO MM. The shoulder at low retention times for the BB peak are due to a coupling reaction that we have occasionally observed while quenching ROMP (left). Calculated conversion of M1-PPO MM found using the ratio of BB peak area to the total combined area of MM and BB (right).

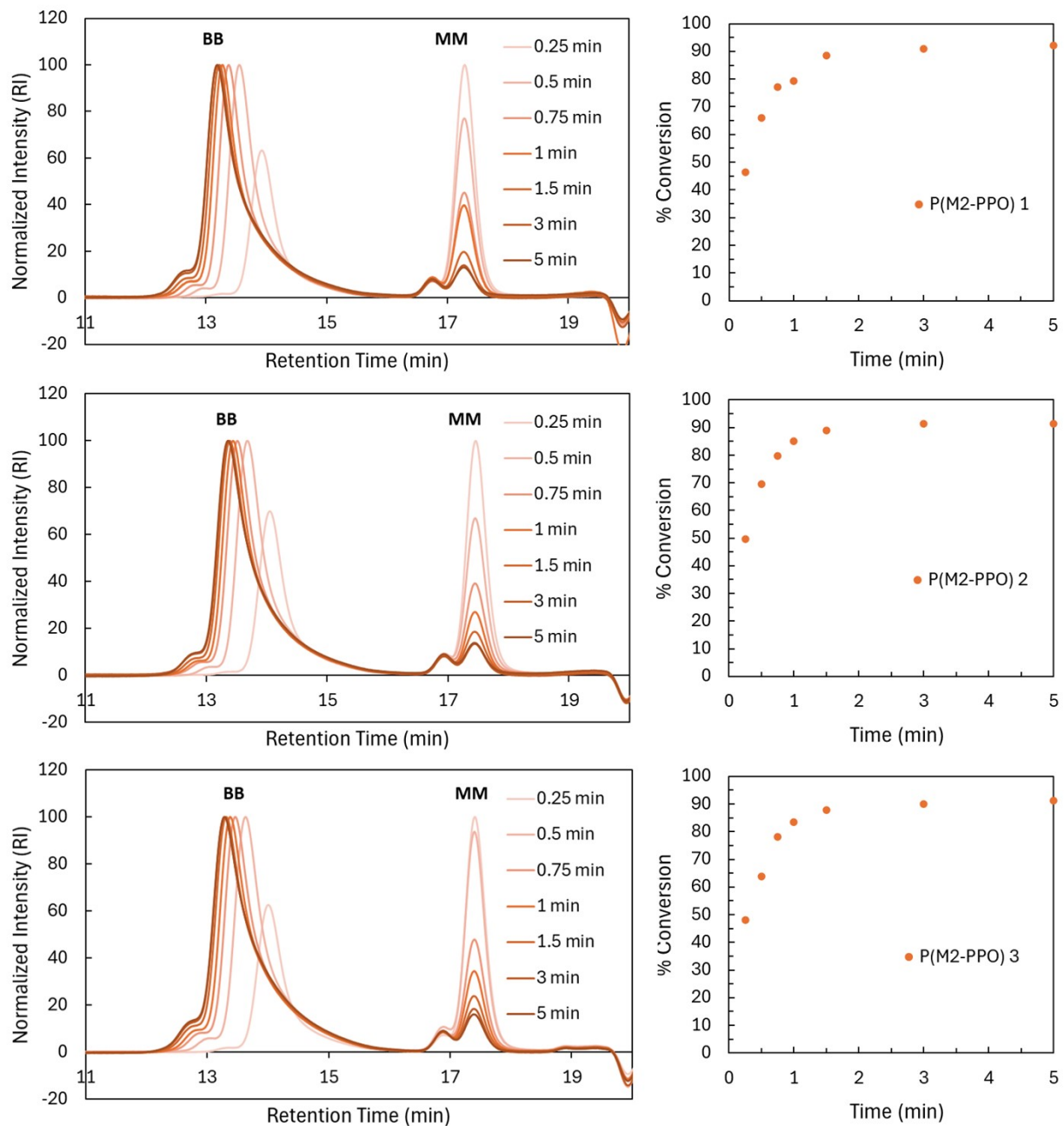


Figure S14. RI SEC traces from the ROMP of M2-PPO MM. The shoulder at low retention times for the BB peak are due to a coupling reaction that we have occasionally observed while quenching ROMP (left). Calculated conversion of M2-PPO MM found using the ratio of BB peak area to the total combined area of MM and BB (right).

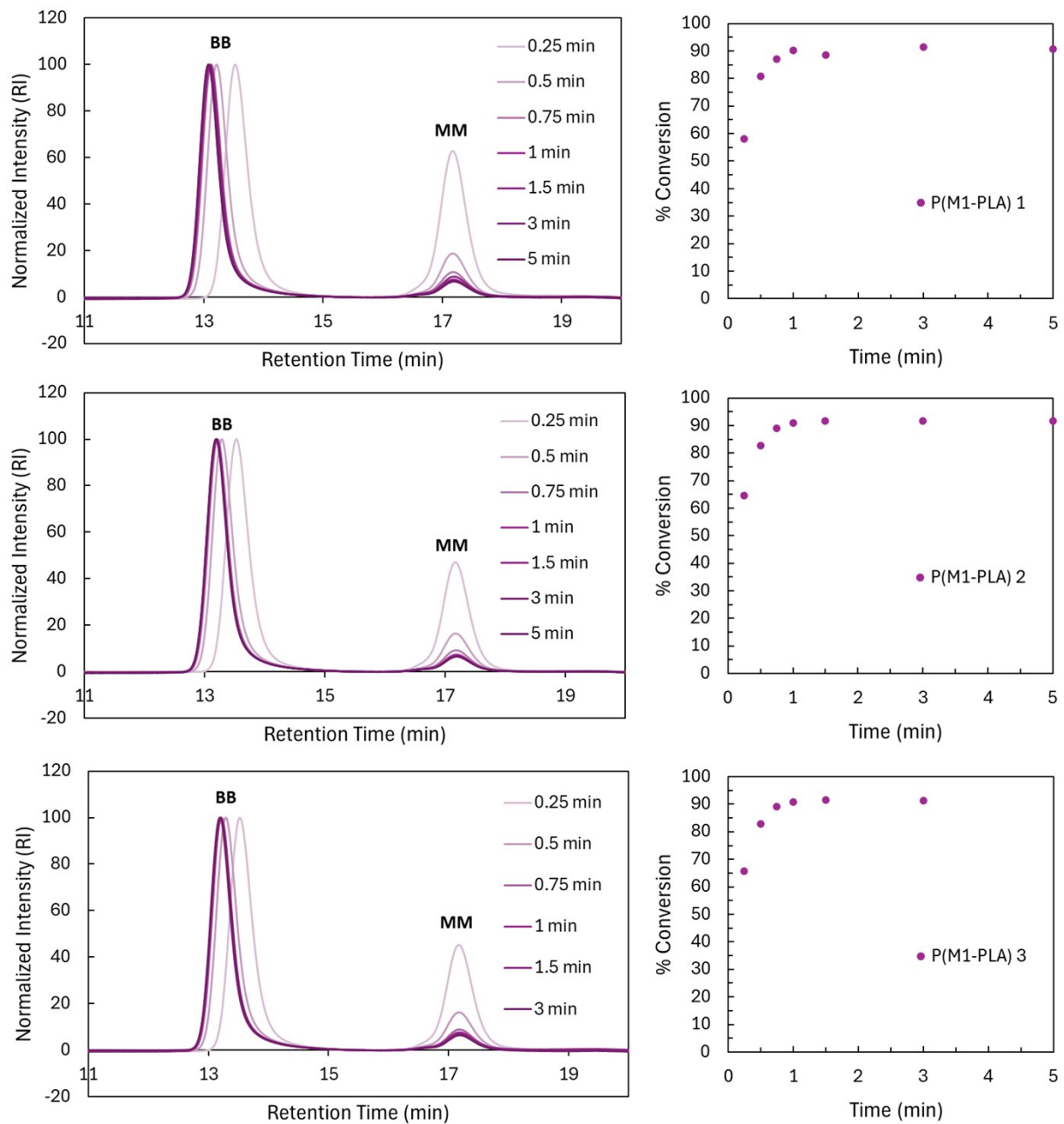


Figure S15. RI SEC traces from the ROMP of M1-PLA MM (left). Calculated conversion of M1-PLA MM found using the ratio of BB peak area to the total combined area of MM and BB (right).

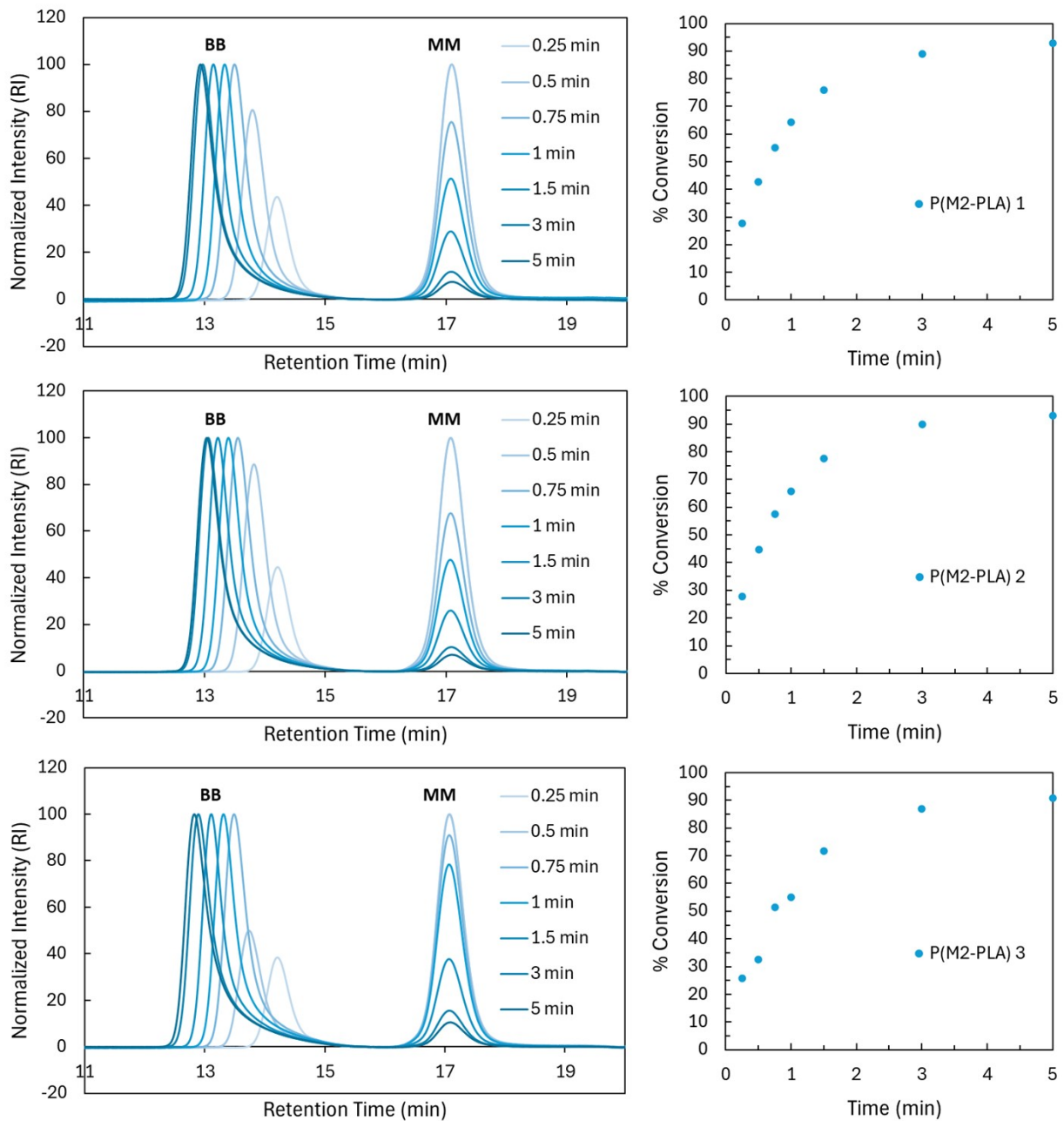


Figure S16. RI SEC traces from the ROMP of **M2-PLA** MM (left). Calculated conversion of **M2-PLA** MM found using the ratio of BB peak area to the total combined area of MM and BB (right).

IV. Control Experiments

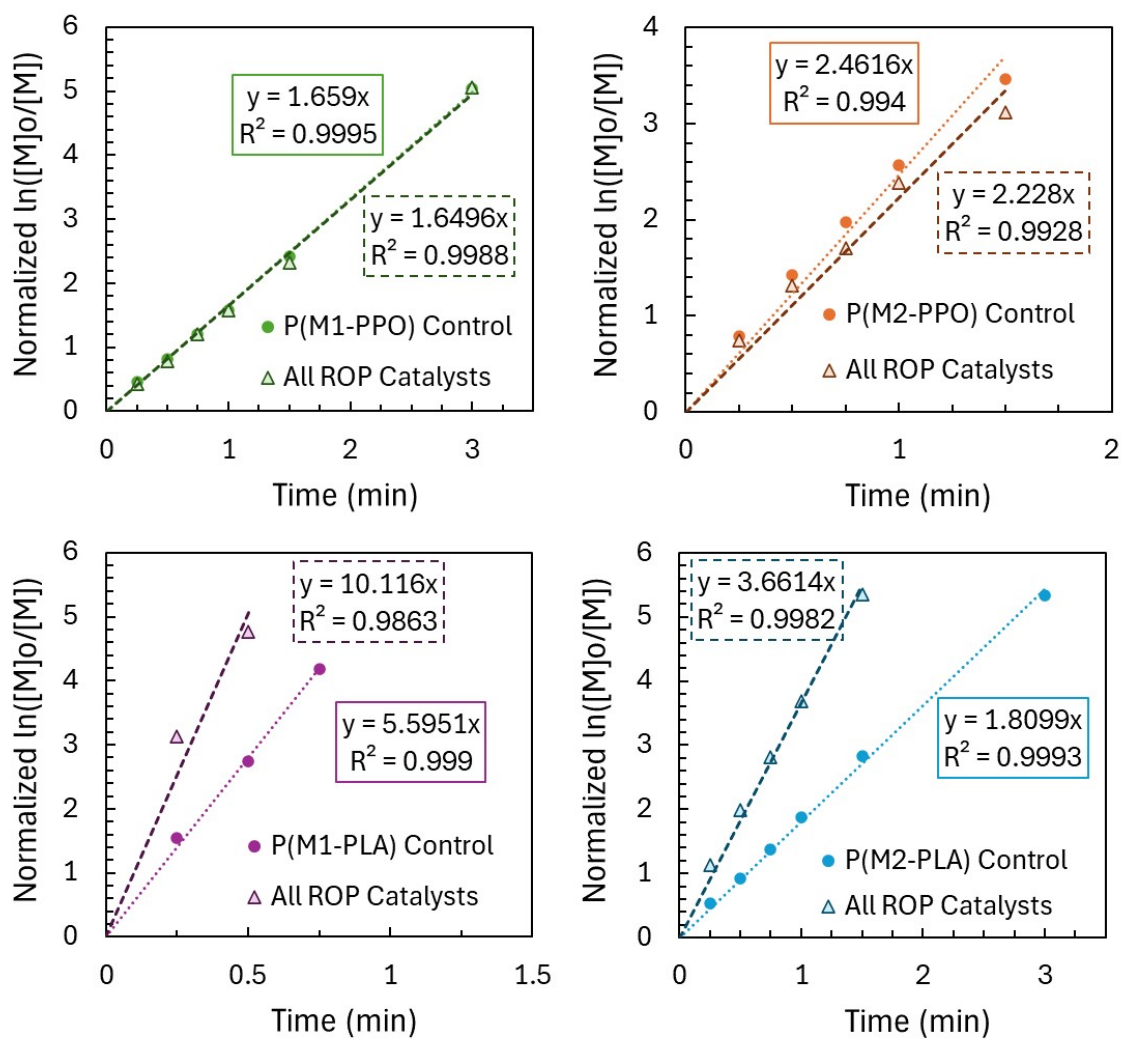


Figure S17. Natural log plots from control experiments calculated using normalized conversion. “Control” indicates that the ROMP only had ROP catalysts that were used for the synthesis of the MMs; tBuP4 and TEB for the PPO MMs; DBU for the PLA MMs. “All ROP Catalysts” indicates that all of the catalysts used for ROP are present during ROMP (tBuP4, TEB and DBU).

Poly(M1-PPO) and Poly(M2-PPO) Control Experiments

Two batches of **M1-PPO** and two batches of **M2-PPO** MMs were synthesized as described previously. The first batch of **M1-PPO** and **M2-PPO** were used directly for ROMP as described previously (control experiment). The second batch of **M1-PPO** and **M2-PPO** each had DBU (0.0258 mmol) added before proceeding with ROMP as described previously (all ROP catalysts present for ROMP). Kinetics for ROMP were performed as previously described.

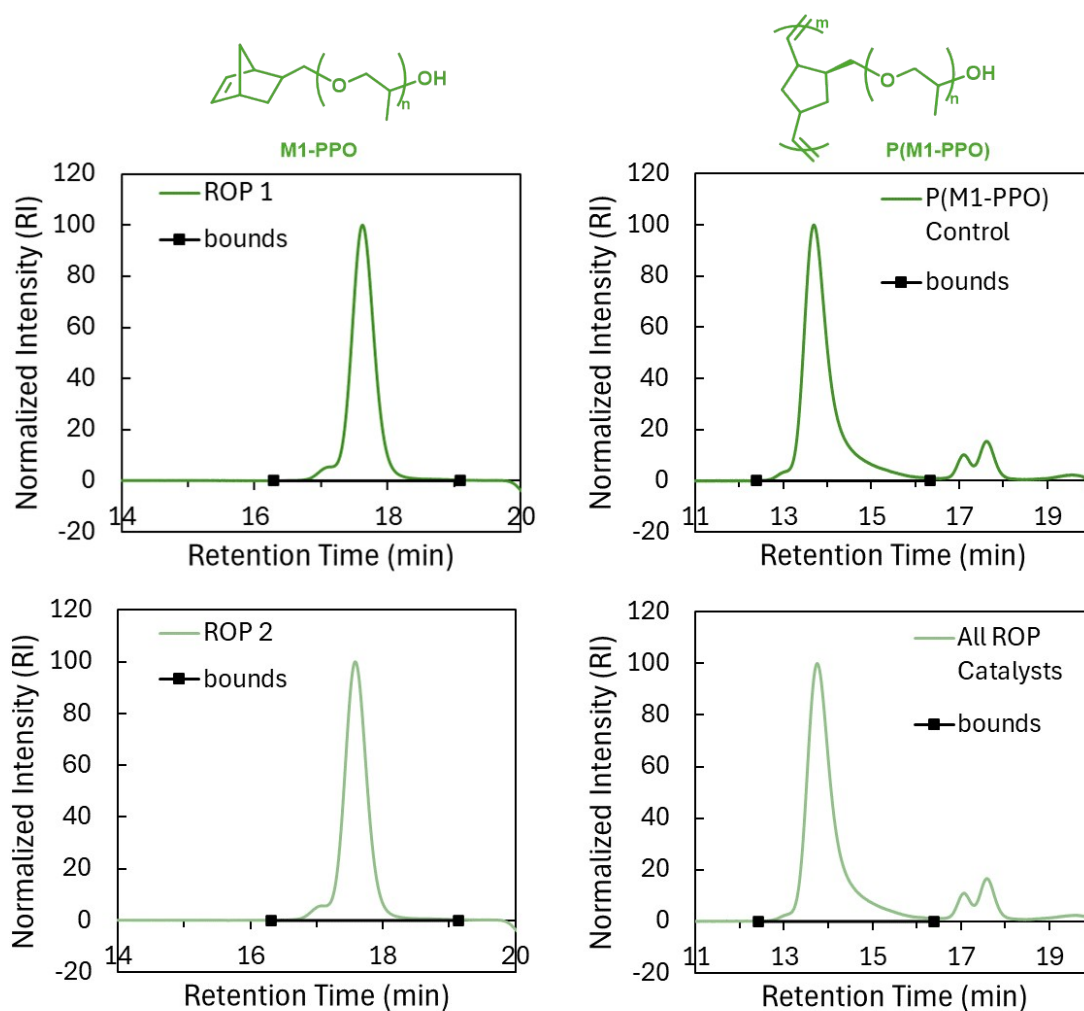


Figure S18. RI SEC traces of **M1-PPO** MMs (left) and **P(M1-PPO)** BBs (right) from control experiments with bounds used for peak integration. “Control” indicates that the ROMP only had ROP catalysts that were used for the synthesis of the PPO MMs (tBuP4 and TEB). “All ROP Catalysts” indicated that all of the catalysts used for ROP are present during ROMP (tBuP4, TEB and DBU).

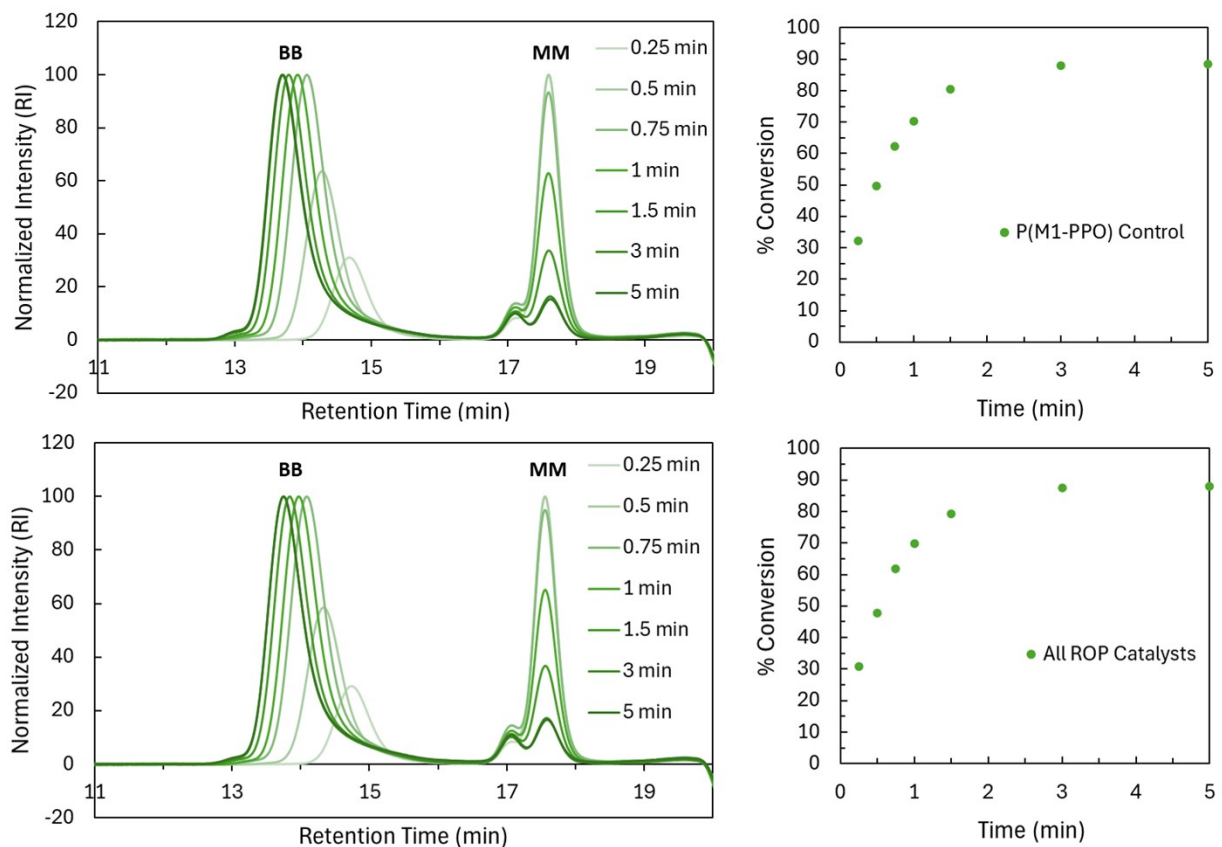


Figure S19. RI SEC traces from the ROMP of **M1-PPO** MM from the control experiments (left). Calculated conversion of **M1-PPO** MM from the control experiments found using the ratio of BB peak area to the total combined area of MM and BB (right).

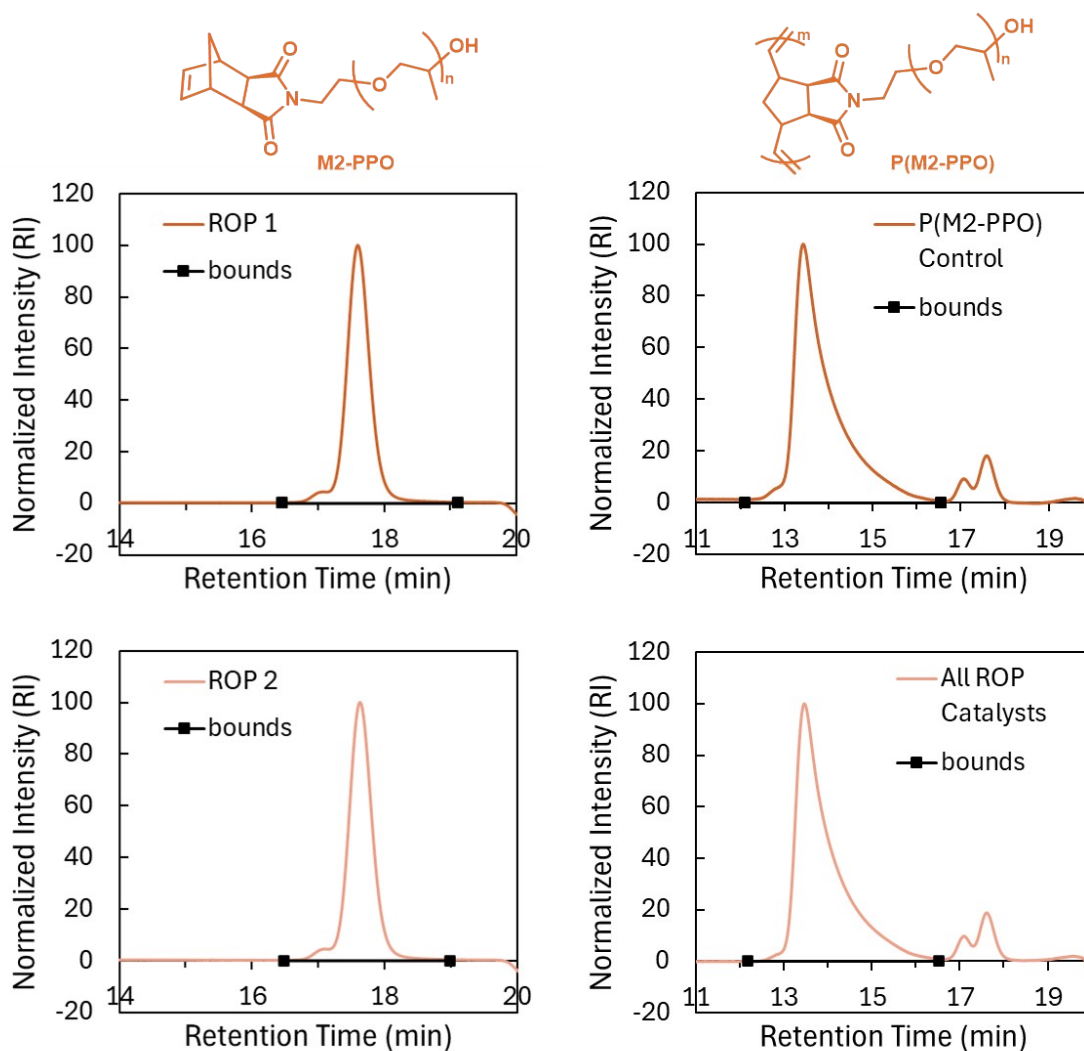


Figure S20. RI SEC traces of **M2-PPO** MMs (left) and **P(M2-PPO)** BBs (right) from control experiments with bounds used for peak integration. “Control” indicates that the ROMP only had ROP catalysts that were used for the synthesis of the PPO MMs (tBuP4 and TEB). “All ROP Catalysts” indicated that all of the catalysts used for ROP are present during ROMP (tBuP4, TEB and DBU).

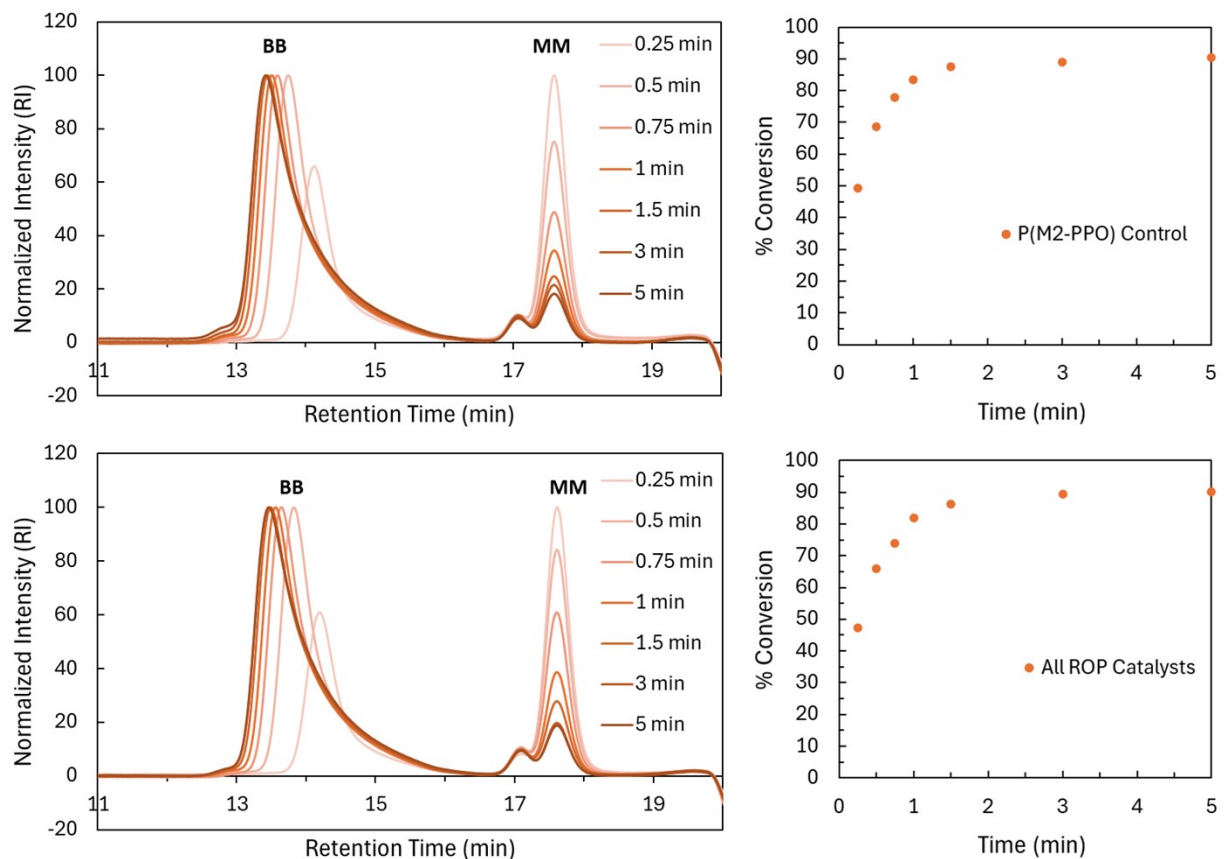


Figure S21. RI SEC traces from the ROMP of **M2-PPO** MM from the control experiments (left). Calculated conversion of **M2-PPO** MM from the control experiments found using the ratio of BB peak area to the total combined area of MM and BB (right).

Poly(M1-PLA) and Poly(M2-PLA) Control Experiments

Two batches of **M1-PLA** and two batches of **M2-PLA** MMs were synthesized as described previously. The first batch of **M1-PLA** and **M2-PLA** were used directly for ROMP as described previously (control experiment). The second batch of **M1-PLA** and **M2-PLA** each had TEB (1 M in hexanes, 0.0516 mmol) and tBuP4 (0.8 M in hexanes, 0.00645 mmol) added before proceeding with ROMP as described previously (all ROP catalysts present for ROMP). Kinetics for ROMP were performed as previously described.

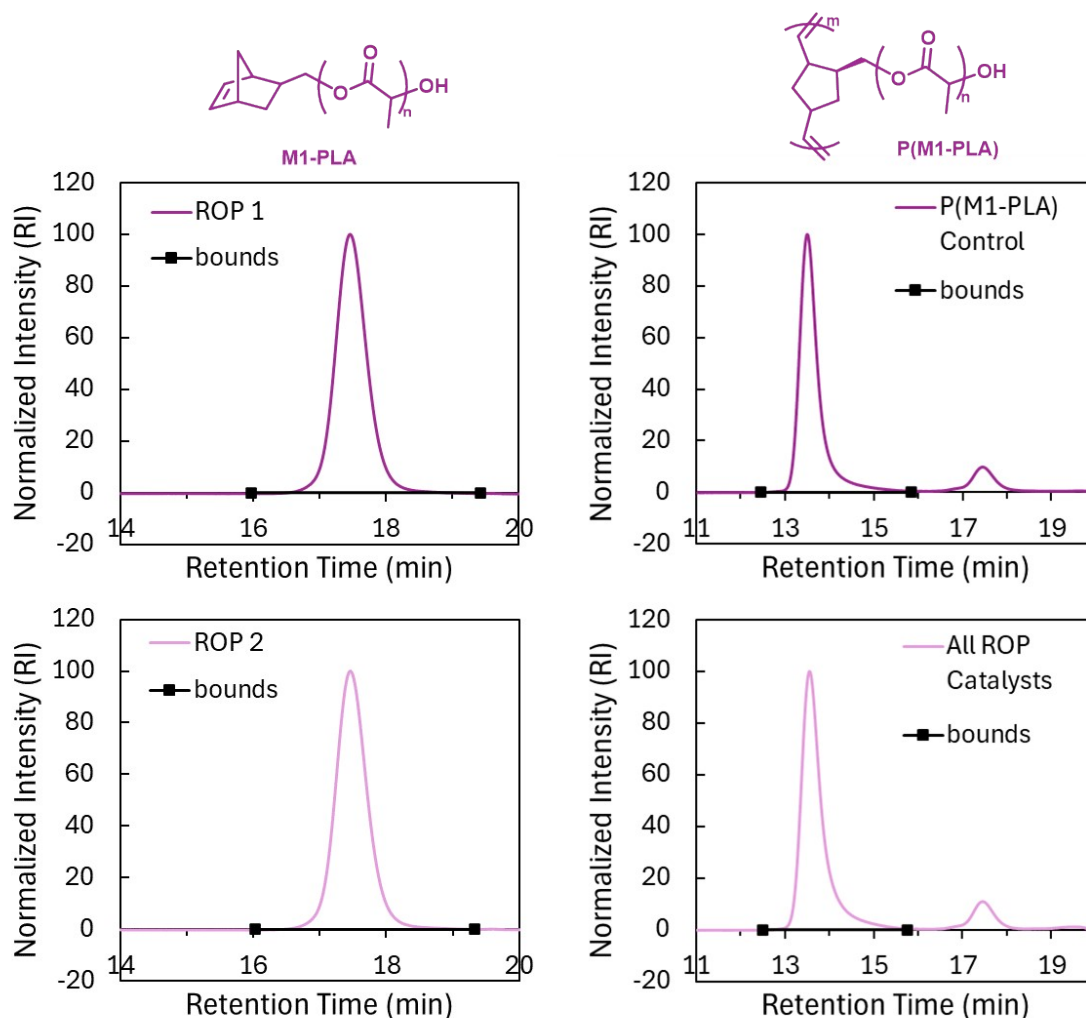


Figure S22. RI SEC traces of **M1-PLA** MMs (left) and **P(M1-PLA)** BBs (right) from control experiments with bounds used for peak integration. “Control” indicates that the ROMP only had ROP catalysts that were used for the synthesis of the PLA MMs (DBU). “All ROP Catalysts” indicated that all of the catalysts used for ROP are present during ROMP (DBU, tBuP4 and TEB).

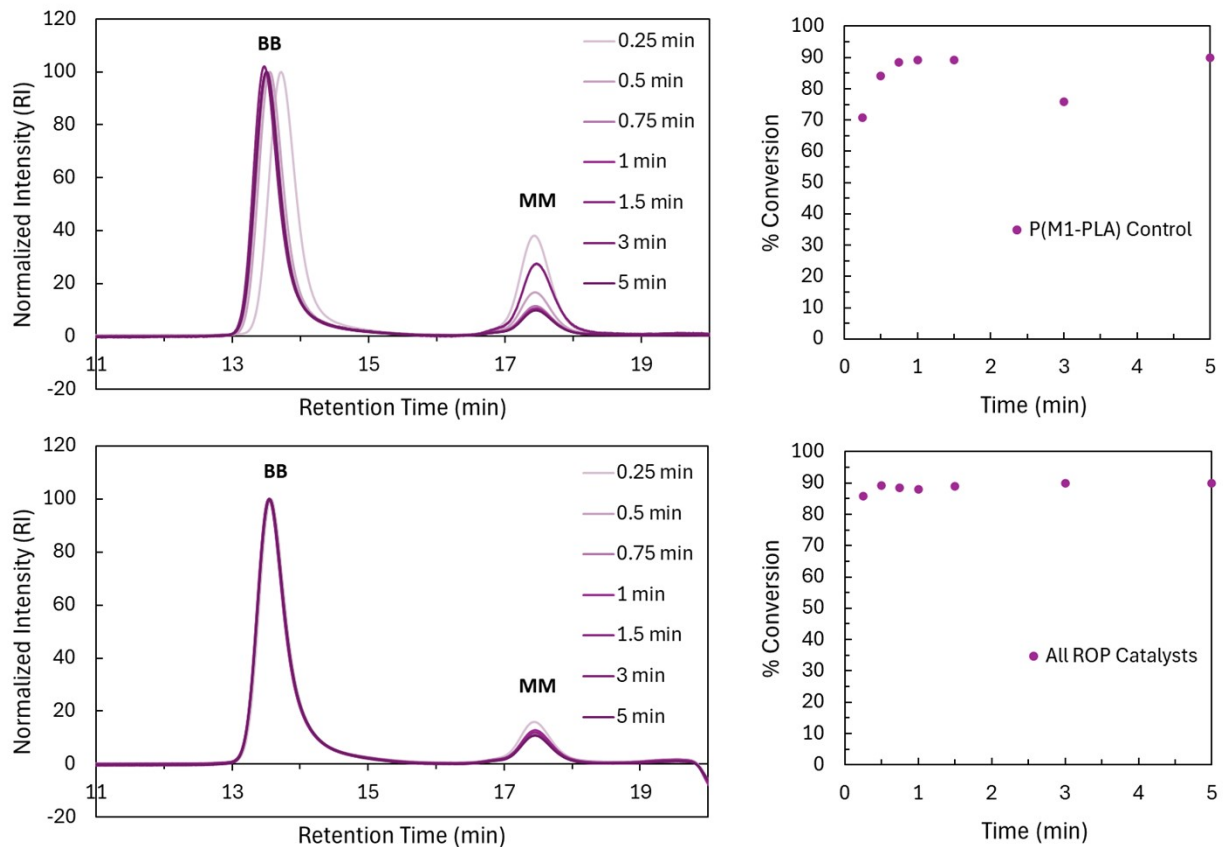


Figure S23. RI SEC traces from the ROMP of **M1-PLA** MM from the control experiments (left). Calculated conversion of **M1-PLA** MM from the control experiments found using the ratio of BB peak area to the total combined area of MM and BB (right).

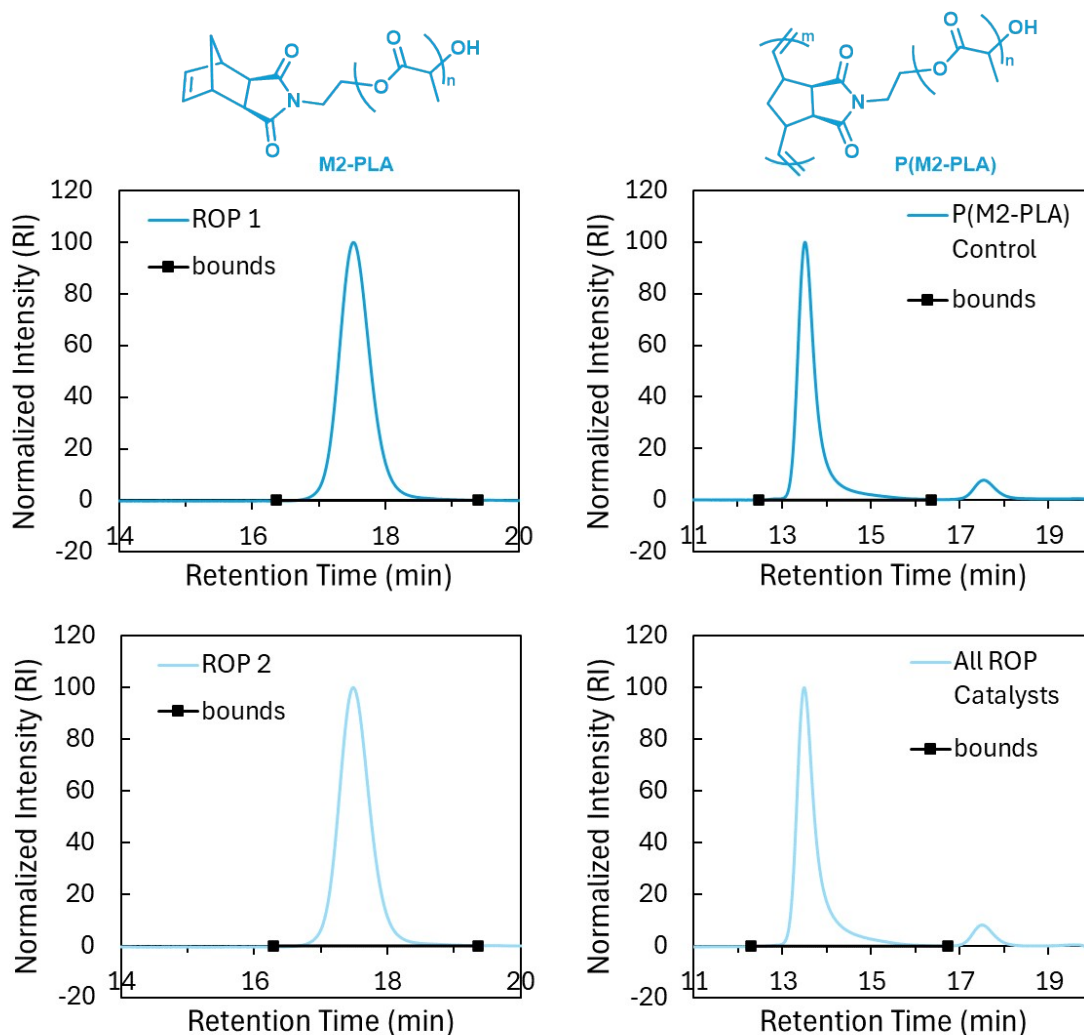


Figure S24. RI SEC traces of **M2-PLA** MMs (left) and **P(M2-PLA)** BBs (right) from control experiments with bounds used for peak integration. “Control” indicates that the ROMP only had ROP catalysts that were used for the synthesis of the PLA MMs (DBU). “All ROP Catalysts” indicated that all of the catalysts used for ROP are present during ROMP (DBU, tBuP4 and TEB).

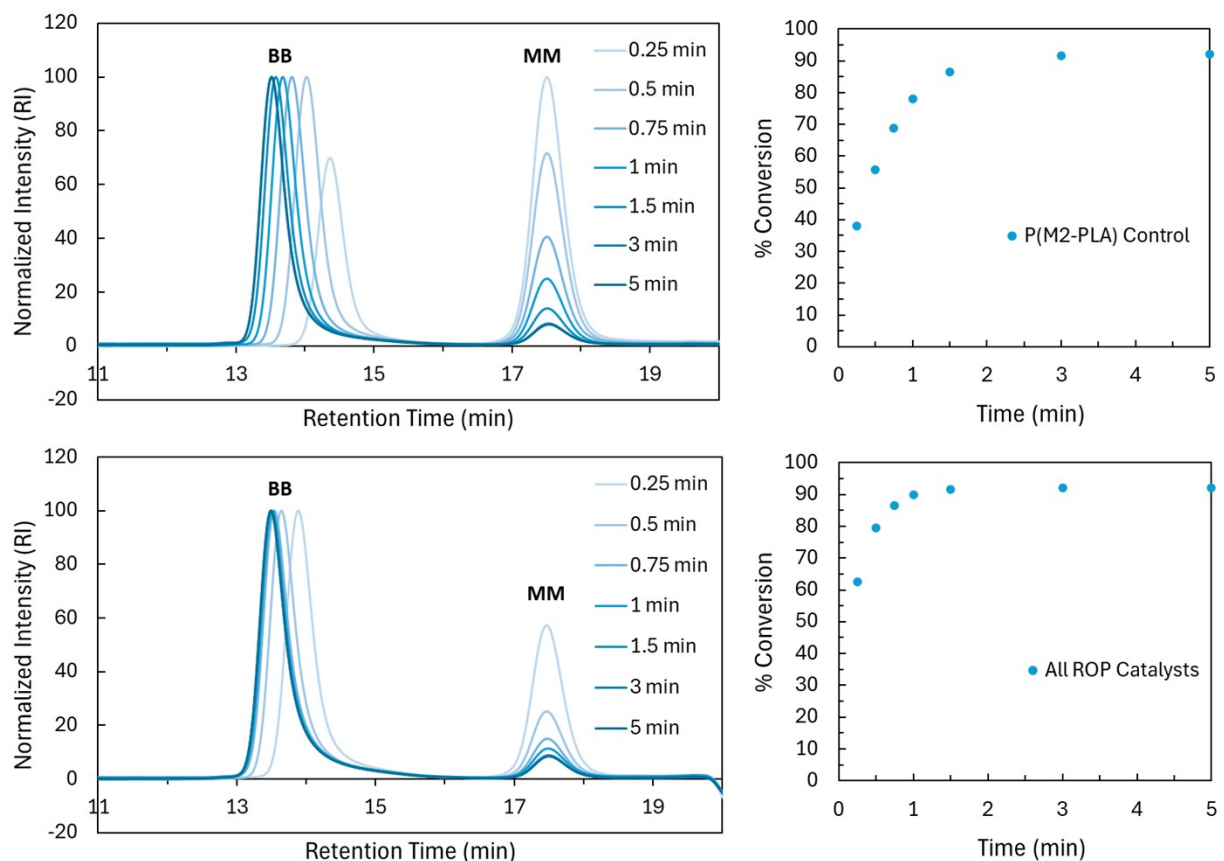


Figure S25. RI SEC traces from the ROMP of **M2-PLA** MM from the control experiments (left). Calculated conversion of **M2-PLA** MM from the control experiments found using the ratio of BB peak area to the total combined area of MM and BB (right).

V. Isolating PLA MMs Before ROMP

One batch of **M1-PLA** MM and one batch of **M2-PLA** MM were synthesized in 20 mL vials as described previously. After the polymerizations were quenched with boric acid, they were removed from the glovebox and crude samples were taken for SEC (**Figure S24**) and ^1H NMR (**Figure S25**) analysis. The polymer solutions were then fully dried before the 20 mL vials were filled with 18 mL methanol. The dried polymer was then gently scraped off of the walls and bottom of the vial using a spatula and the methanol solution with solid polymer chunks was whisked and stirred until the polymer became fluffy and powdery in solution. The polymer was then gravity filtered and washed with fresh methanol before being transferred into a clean vial and dried under vacuum. Samples of the isolated **M1-PLA** and **M2-PLA** MMs were taken for SEC (**Figure S24**) and ^1H NMR (**Figure S25**) analysis to compare to the crude samples. The ^1H NMR spectra shows

that we successfully isolated the PLA MMs using our precipitation method once, however, from both the SEC and ^1H NMR characterizations, we observed an increase in the PLA MMs molecular weight after isolation due to removal of low molecular weight polymer chains.

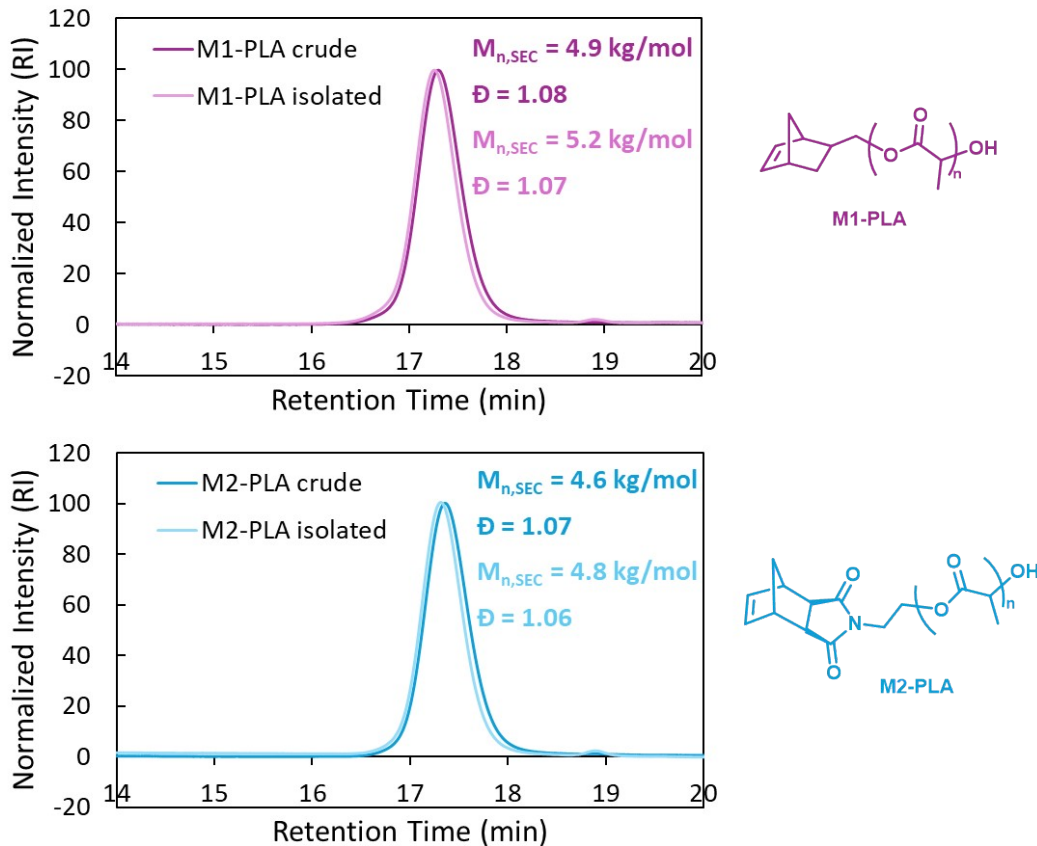


Figure S26. RI SEC traces of the crude and isolated **M1-PLA** and **M2-PLA** MMs. The isolated MMs are slightly shifted to lower retention times due to removal of low molecular weight polymer chains during the precipitation process.

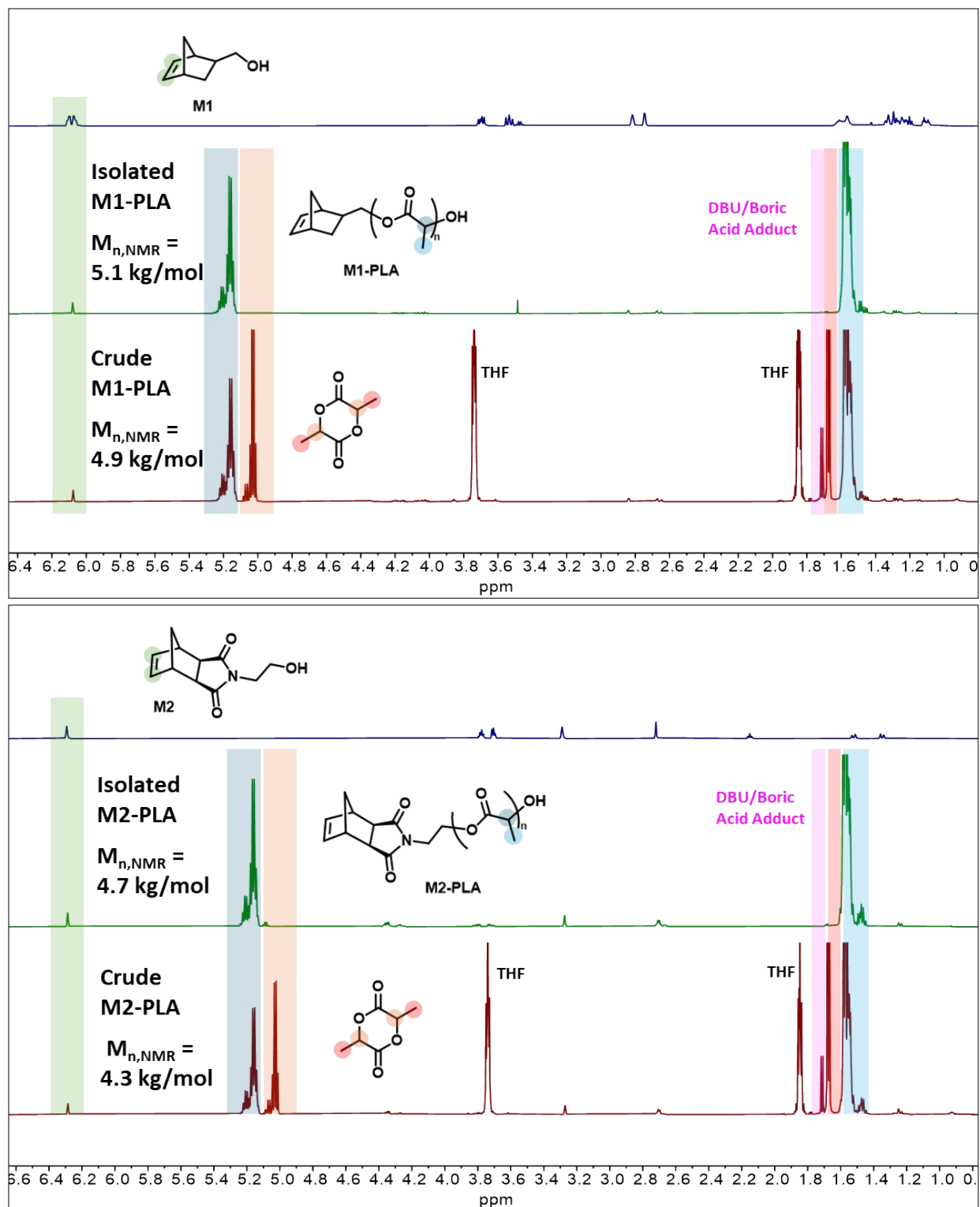


Figure S27. Crude and isolated ^1H NMR spectra of **M1-PLA** (top) and **M2-PLA** (bottom) MMs measured in CDCl_3 . Polymer isolation method was successful in removing unreacted lactide and the DBU/boric acid adduct. Molecular weight calculated using the polymer peak integration normalized to the norbornene olefin showed a slight increase in molecular weight for both MMs after isolation due to removal of low molecular weight polymer chains.

ROMP of Isolated PLA MMs

ROMP of the isolated PLA MMs was set up identical to previous ROMP reactions. Briefly, the isolated PLA MMs (30 μmol) were measured out into a 20 mL glass vial and a stir bar was added. THF ($[\text{PLA MM}]_0 = 0.020 \text{ M}$) was then added before the addition of G3 (0.15 μmol) to start the polymerization. Kinetics for ROMP were performed as previously described (**Figure S26** and **S27**, **Table S1**). After 6 minutes, the ROMP reaction was quenched by adding 120 μL of ethyl vinyl ether.

While the rates of the isolated PLA MMs differ from the non-isolated PLA MMs (**Table S1**), the trend observed for the non-isolated PLA MMs, where **M1-PLA** is faster than **M2-PLA**, is maintained.

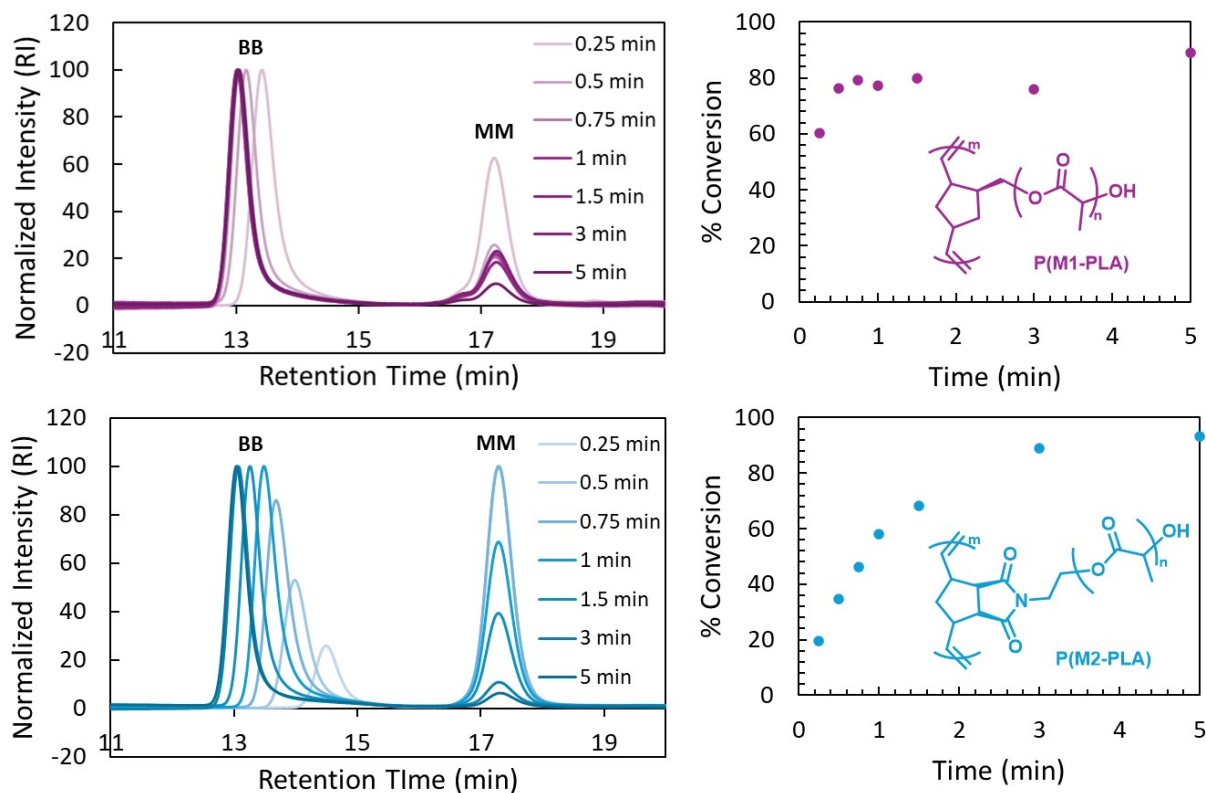


Figure S28. RI SEC traces from the ROMP of isolated **M1-PLA** MM (top left) and isolated **M2-PLA** MM (bottom left). Calculated conversion of isolated **M1-PLA** MM (top right) and isolated **M2-PLA** MM (bottom right) found using the ratio of BB peak area to the total combined area of MM and BB.

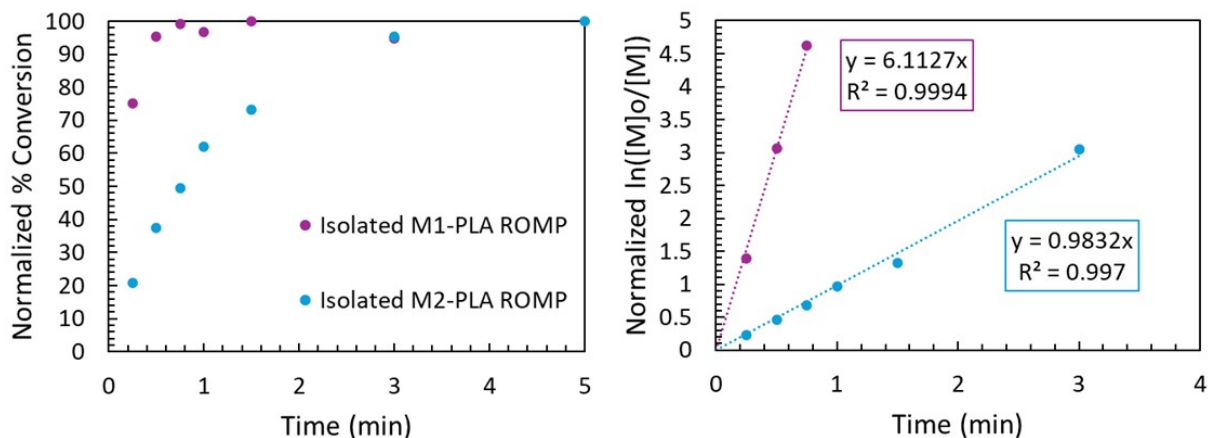


Figure S29. Normalized % conversions for the ROMP of isolated **M1-PLA** MM and isolated **M2-PLA** MM (left). Natural log plots calculated using normalized conversion, showcasing the ROMP rates observed for the isolated **M1-PLA** MM and isolated **M2-PLA** MM (right).

MM	Isolated?	MM $M_{n,SEC}^a$ (kg/mol)	ROMP k_{obs}^b (min^{-1})
M1-PLA	No	4.8	4.6(3) ^c
	Yes	5.2	6.1
M2-PLA	No	5.3	1.10(7) ^c
	Yes	4.8	0.98

^aDetermined from RI SEC traces, measured in THF, using PS calibration standards. ^bApparent rate constants calculated from polymerization conversion determined from reaction aliquots measured by SEC. ^cAveraged from three separate ROMP reactions performed using the same starting PLA MM.

VI. References

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- (3) Mukherjee, S.; Dinda, H.; Shashank, L.; Chakraborty, I.; Bhattacharyya, R.; Das Sarma, J.; Shunmugam, R. Site-Specific Amphiphilic Magnetic Copolymer Nanoaggregates for Dual Imaging. *Macromolecules* **2015**, *48* (19), 6791–6800.