Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information for

Photoinduced SET to Access Olefin-Acrylate Copolymers

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Supporting Information:

Materials and Instrumentation

Materials:

All chemicals were used as received unless otherwise noted. Azobisisobutyronitrile (AIBN, Millipore Sigma, 98%) was recrystallized from methanol and dried *in vacuo* prior to use. Methyl acrylate (MA, Millipore Sigma, 99%) was passed through a plug of basic alumina to remove inhibitor immediately prior to use. Tris[2-(dimethylamino)ethyl]amine was synthesized according to literature procedure.[1] 4-Cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic acid (CDP) was synthesized according to literature procedure.[2] Acetone (ACS grade), copper wire, diisopropylethylamine (DIPEA, 99%), Eosin Y (EY, 90%), *N*-hydroxyphthalimide (98%), triethylamine (TEA, 99%) were purchased from Fisher. Acryloyl chloride (97%), bromoisobutyryl bromide (98%), cyclohexanecarbonyl chloride (98%), methacryloyl chloride (97%) were purchased from Millipore Sigma. Dichloromethane (DCM, ACS grade) and dimethylformamide (DMF, ACS grade) were dried using the mBraun solvent purification system prior to use.

Instrumentation

NMR Spectroscopy. ^{1}H NMR spectroscopy, ^{13}C NMR spectroscopy, heteronuclear single quantum coherence (HSQC) spectroscopy and correlation spectroscopy (COSY) spectra were recorded using an Inova 500 MHz 2 RF channel spectrometer. ^{1}H NMR chemical shifts in $CDCl_3$ were referenced to $CHCl_3$ (7.26 ppm). ^{13}C NMR chemical shifts in $CDCl_3$ were referenced to $CHCl_3$ (77.1 ppm).

Gel permeation chromatography (GPC). GPC was performed in DMAc with 50 mM LiCl at 50 °C and a flow rate of 1.0 mL/min (Agilent isocratic pump, degasser, and autosampler; columns: Viscogel I-series 5 μm guard + two ViscoGel I-series G3078 mixed bed columns, molecular weight range $0-20 \times 10^3$ and $0-100 \times 10^4$ g/mol). Detection consisted of a Wyatt Optilab T-rEX refractive index detector operating at 658 nm. Molecular weights and dispersities were calculated using the Wyatt ASTRA software and polystyrene standards.

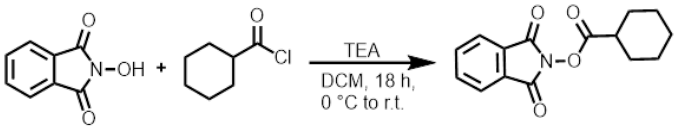
Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS). MALDI-TOF-MS was performed on Phth-PMA-Br both before and after decarboxylation on a Bruker Autoflex LRF operated in reflectron, positive ion mode with the pulsed smartbeam-II UV laser. The instrument can resolve molecules up to 20,000 Da in reflectron mode and was calibrated with the Peptide Calibration Standard II set purchased from Bruker Daltonics. This mixture covers a mass range of ~700 Da – 3200 Da with peptides Angiotensin II, Angiotensin I, Substance P, Bombesin, ACTH clip 1-17, ACTH clip 18-39, Somatostatin 28, Bradykinin Fragment 1-7, and Renin Substrate Tetradecapeptide porcine. Samples were obtained using a laser power intensity of 21%. Both polymer samples were prepared by mixing solutions of trans-2-[3-(4-t-butylphenyl)-2-methyl2-propenylidene]malononitrile (DCTB, Santa Cruz Biotechnology, 99%) matrix (20 mg/mL in THF), polymer (2 mg/mL in THF), and NaTFA (1 mg/mL in THF) at volume ratio of 5:1:1 matrix:polymer:salt. Samples were spotted in 1.00 μL aliquots and left to air dry on a polished stainless steel Bruker plate.

Green light set-up. Decarboxylation reactions were stirred while being irradiated with green light from a RGBW color-changing 12 W light bulb set to green with an intensity of 0.04 mW/cm^2 at a distance of 2 cm.

Small Molecule Synthesis and Characterization

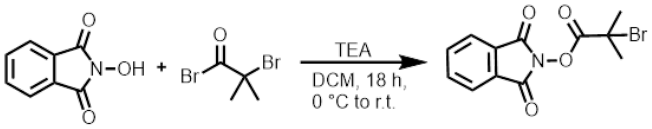
Synthetic Procedures

Phthalimidyl cyclohexanoate **(PhthCy)**



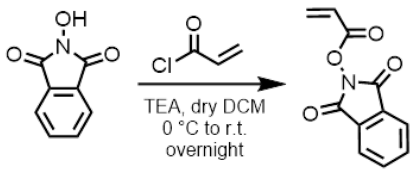
N-Hydroxyphthalimide (1.00 equiv, 10.0 g, 61.3 mmol) and triethylamine (1.10 equiv, 9.40 mL, 67.5 mmol) were combined in dry DCM (200 mL) and stirred at 0 °C for 10 min. Cyclohexane carbonyl chloride (1.20 equiv, 9.85 mL, 73.6 mmol) was added slowly to the stirred solution. The mixture was allowed to warm to room temperature while stirring overnight. The DCM mixture was washed with acidic brine (x3) prior to drying of the DCM layer with sodium sulfate. Removal of solvent under reduced pressure yielded crude product which was recrystallized from methanol to provide pure product (11.1 g, 66%) which was characterized via ^{1}H NMR spectroscopy.

Phthalimidyl bromoisobutyrate **(PhthBr)**



N-Hydroxyphthalimide (1.00 equiv, 2.00 g, 12.3 mmol) and triethylamine (1.10 equiv, 1.88 mL, 13.5 mmol) were combined in dry DCM (20 mL) and stirred at 0 °C for 10 min. Bromoisobutyryl bromide (1.65 equiv, 2.50 mL, 20.2 mmol) was added slowly to the stirred solution. The mixture was allowed to warm to room temperature while stirring overnight. Then the DCM mixture was washed with acidic brine (x3) prior to drying of the DCM layer with sodium sulfate. Removal of solvent under reduced pressure yielded crude product which was recrystallized from methanol to provide pure product (2.3 g, 60%) which was characterized via ^{1}H NMR spectroscopy.

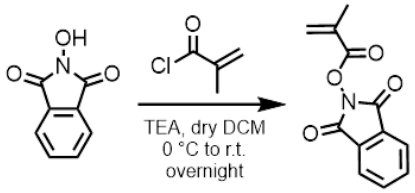
N-(acryloxy)phthalimide **(PhthA)**



N-Hydroxyphthalimide (1.00 equiv, 10.0 g, 61.3 mmol) was suspended in dry DCM (100 mL). Triethylamine (2.00 equiv, 17.1 mL, 123 mmol) was added and the resulting mixture was stirred at 0 °C for 15 min. Acryloyl chloride (2.00 equiv, 9.91 mL, 123 mmol) was added dropwise to the stirring solution via addition funnel over 30 min. The reaction was stirred overnight and allowed to warm to room temperature. Precipitated triethylammonium chloride was removed by filtration

prior to washing the organic DCM phase with acidic brine (x3), saturated sodium bicarbonate (x2), and brine (x1). The organic phase was dried with anhydrous sodium sulfate, and the solvent was removed under reduced pressure yielding the crude solid. Purification of the product via column chromatography (silica) using 80:20 DCM:hexanes as eluent yielded pure product (6.1 g, 46%) which was characterized via ^{1}H NMR spectroscopy.

N-(methacryloxy)phthalimide **(PhthMA)**



N-Hydroxyphthalimide (1.00 equiv, 20.0 g, 123 mmol) was suspended in dry DCM (200 mL). Triethylamine (2.00 equiv, 34.2 mL, 245 mmol) was added, and the resulting mixture was stirred at 0 °C for 25 minutes. Methacryloyl chloride (2.00 equiv, 24.0 mL, 245 mmol) was added dropwise to the stirring solution via addition funnel over 30 minutes. The reaction was stirred overnight and allowed to warm to room temperature. Precipitated triethylammonium chloride was removed by filtration prior to washing the organic DCM phase with acidic brine (x3), saturated sodium bicarbonate (x2), and brine (x1). The organic phase was dried with anhydrous sodium sulfate, and the solvent was removed under reduced pressure yielding the crude solid. Recrystallization of the crude product from methanol yielded pure product (14.8 g, 52%) which was characterized via ^{1}H NMR spectroscopy.

^{1}H NMR Spectroscopy

PhthCy

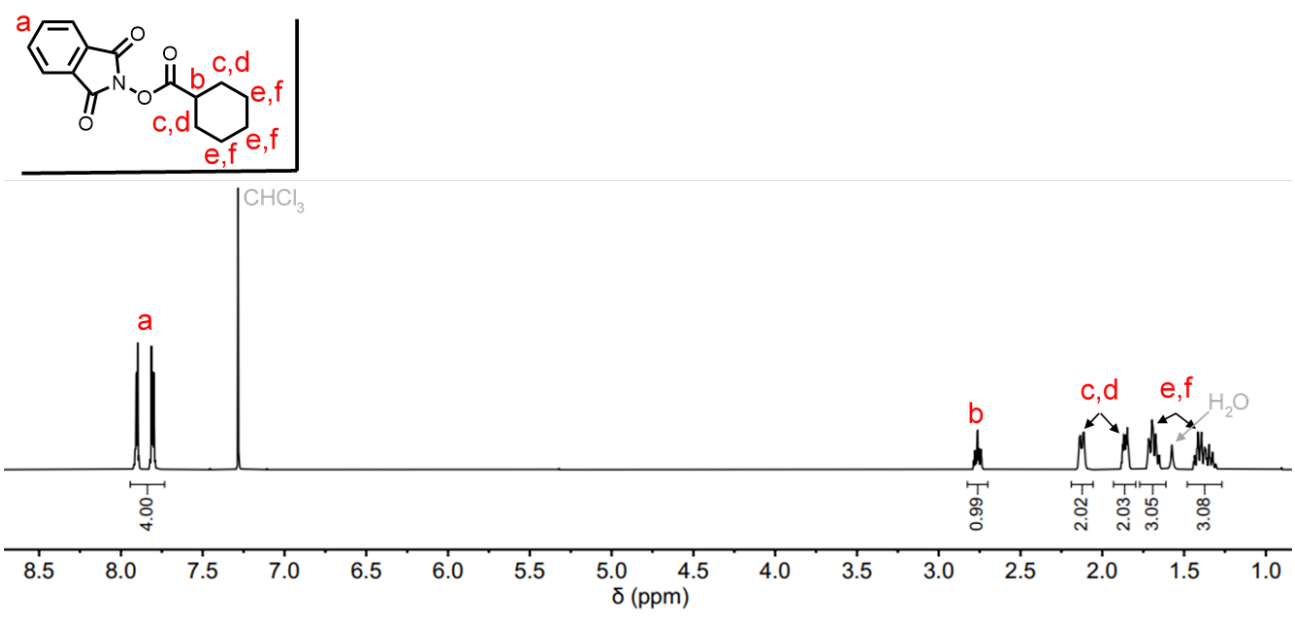


Figure S1. ^{1}H NMR spectrum of PhthCy.

PhthBr

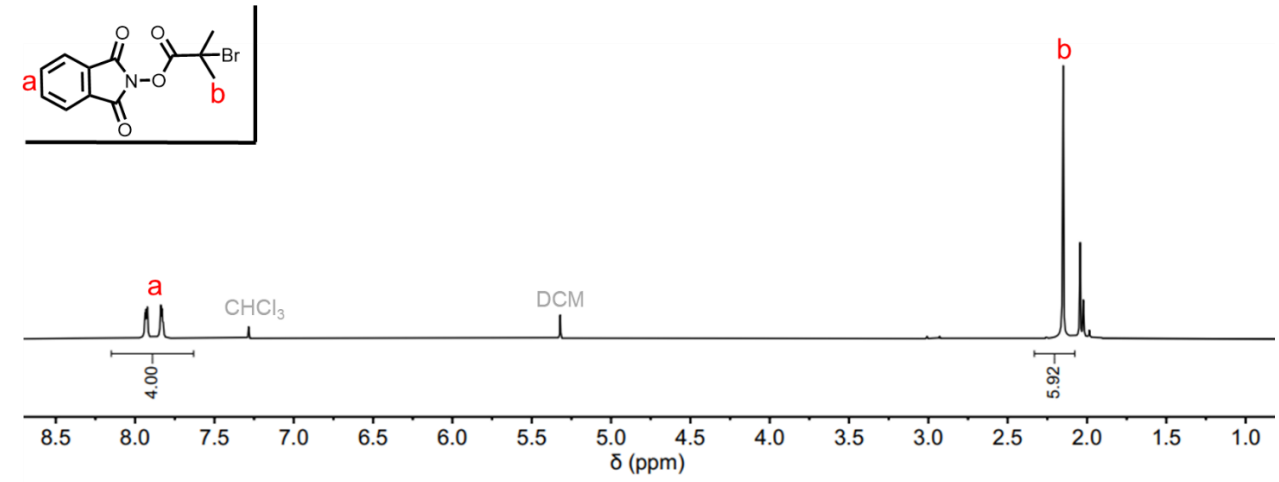


Figure S2. ^{1}H NMR spectrum of PhthBr.

PhthA

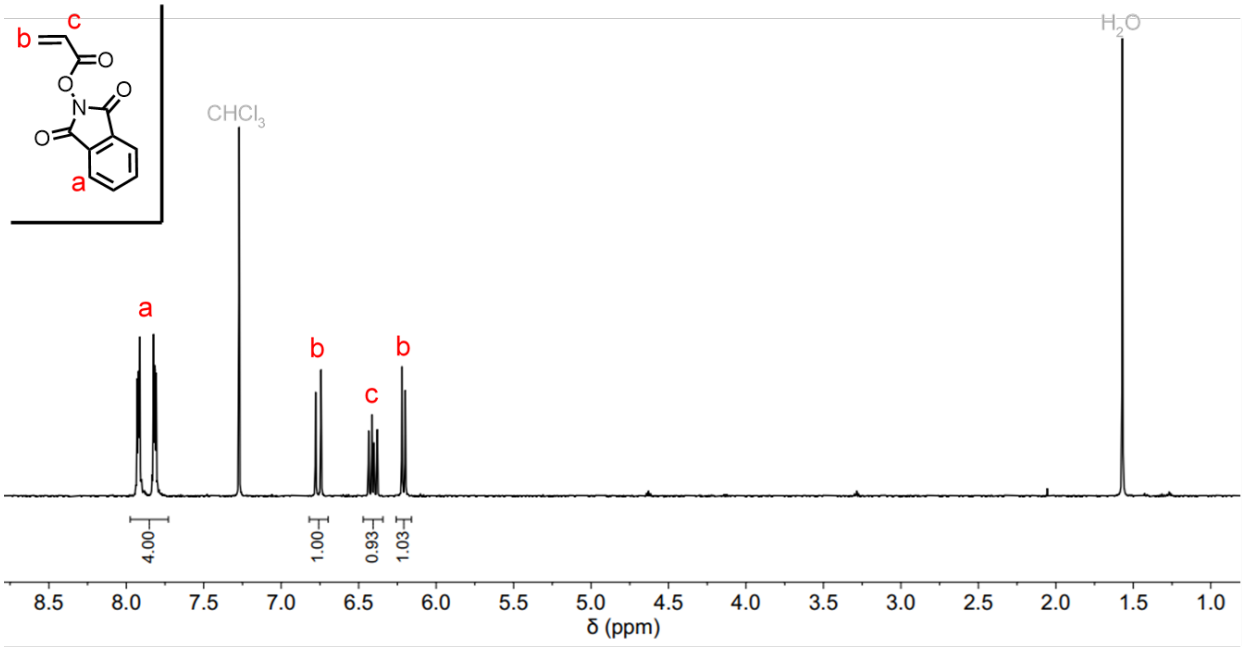


Figure S3. ^{1}H NMR spectrum of PhthA.

PhthMA

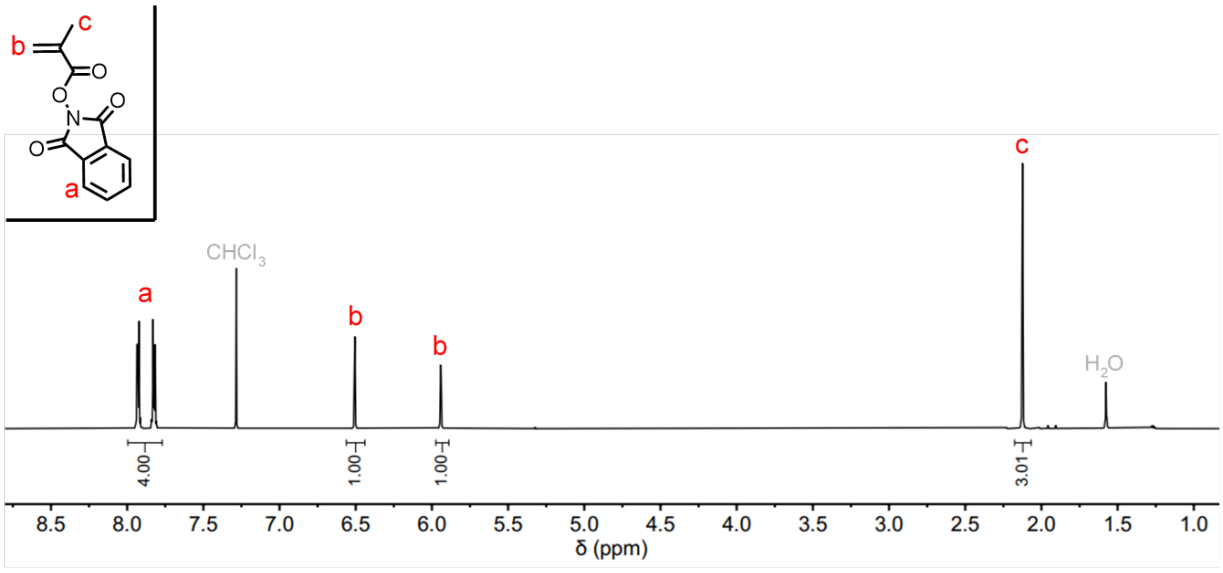
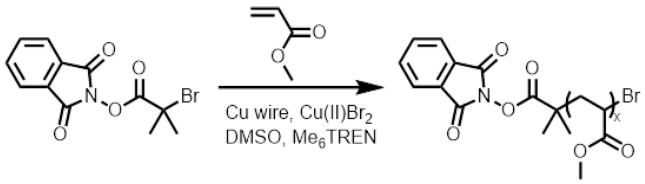


Figure S4. ^{1}H NMR spectrum of PhthMA.

Polymer Synthesis and Characterization

Synthetic Procedures

Phth-PMA



Methyl acrylate (MA, 100 equiv, 2.77 g, 32.2 mmol) was combined with PhthBr (1.00 equiv, 100 mg, 0.32 mmol), Me_6TREN (0.20 equiv, 14.8 mg, 0.06 mmol), and Cu(II)Br_2 (0.10 equiv, 7.2 mg, 0.03 mmol) in DMSO (3 mL) with copper wire (1.7 cm) suspended above the solution. The solution was sparged with argon for 20 minutes at room temperature prior to introduction of the copper wire which started the polymerization. The final polymer was dialyzed against acetone before removing the solvent under reduced pressure to yield pure Phth-PMA which was characterized via ^{1}H NMR spectroscopy and GPC.

CA P(PhthA-*co*-MA) via conventional radical polymerization

Methyl acrylate (MA, 150 equiv, 393 mg, 4.57 mmol) was combined with PhthA (50.0 equiv, 330 mg, 1.52 mmol) and AIBN (1.0 equiv, 5.0 mg, 0.03 mmol) in DMSO (5 mL) in a 10 mL Schlenk flask. The solution was sparged with argon for 15 minutes at room temperature before the flask was submerged in a preheated oil bath set to 70 °C. The final polymer was dialyzed against acetone before removing the solvent under reduced pressure to yield pure P(PhthA-*co*-MA) which was characterized via ^{1}H NMR spectroscopy and GPC.

CM P(PhthMA-*co*-MA) via conventional radical polymerization

Methyl acrylate (MA, 170 equiv, 891 mg, 10.4 mmol) was combined with PhthMA (30.0 equiv, 422 mg, 1.83 mmol) and AIBN (1.00 equiv, 10.0 mg, 0.06 mmol) in DMSO (10 mL) in a 10 mL Schlenk flask. The solution was sparged with argon for 15 minutes at room temperature before the flask was submerged in a preheated oil bath set to 70 °C. The final polymer was dialyzed against acetone before removing the solvent under reduced pressure to yield pure P(PhthMA-*co*-MA) which was characterized via ^{1}H NMR spectroscopy and GPC.

RA P(PhthA-*co*-MA) via RAFT polymerization

Methyl acrylate (MA, 180 equiv, 3.45 g, 40.1 mmol) was combined with PhthA (20.0 equiv, 968 mg, 4.46 mmol), AIBN (0.10 equiv, 3.60 mg, 0.02 mmol), and CDP (1.0 equiv, 90 mg, 0.2 mmol) in DMSO (24 mL) in a 50 mL Schlenk flask. The solution was sparged with argon for 25 minutes at room temperature before the flask was submerged in a preheated oil bath set to 70 °C. The

final polymer was dialyzed against acetone before removing the solvent under reduced pressure to yield pure P(PhthA-*co*-MA) which was characterized via ^{1}H NMR spectroscopy and GPC.

RM P(PhthMA-*co*-MA) via RAFT polymerization

Methyl acrylate (MA, 190 equiv, 1.62 g, 18.8 mmol) was combined with PhthMA (15 equiv, 343 mg, 1.5 mmol), AIBN (0.10 equiv, 1.60 mg, 0.01 mmol), and CDP (1.0 equiv, 40 mg, 0.1 mmol) in DMSO (8 mL) in a 10 mL Schlenk flask. The solution was sparged with argon for 15 minutes at room temperature before the flask was submerged in a preheated oil bath set to 70 °C. The final polymer was dialyzed against acetone before removing the solvent under reduced pressure to yield pure P(PhthMA-*co*-MA) which was characterized via ^{1}H NMR spectroscopy and GPC.

Table S1. Phthalimide ester-containing copolymers.

Polymer ID[a]	X_{Phth}[b]	X_{MA}[c]	$M_{n,0}$[d]	$M_{n,theo}$[e]	$M_{n,f}$[f]	*% Decarboxylation*[g]
CA	0.23	0.77	30.3	19.0	7.6	>95%
CM	0.26	0.74	22.3	12.2	5.5	>95%
RA	0.14	0.86	17.2	12.6	9.4	>95%
RM	0.11	0.89	10.1	7.4	8.0	>95%

[a] Code in the form of *AB* where *A* = C for conventional radical polymerization or *A* = R for RAFT polymerization and *B* = A for PhthA or *B* = M for PhthMA. [b] Mole fraction of phthalimide monomer. [c] Mole fraction of methyl acrylate. [d] M_n before decarboxylation. [e] Theoretical polymer molecular weight after decarboxylation. [f] M_n after decarboxylation. [g] According to ^{1}H NMR spectroscopy.

Discussion: Complete decarboxylation was observed using ^{1}H NMR spectroscopy. Molecular weight decrease was observed using GPC. Discrepancies between theoretical and observed molecular weight after decarboxylation can potentially be attributed to the use of polystyrene standards for molecular weight determination. The poor solubility of the polyolefin units that result from this approach likely leads to poorer polymer solvation, particularly for polymers with higher degrees of polymerization. A less solvated polymer would appear to be lower in apparent molecular weight in GPC as the hydrodynamic diameter will be more similar to lower molecular weight polystyrene standards.

Nuclear Magnetic Resonance (^{1}H NMR) Spectroscopy

Phth-PMA

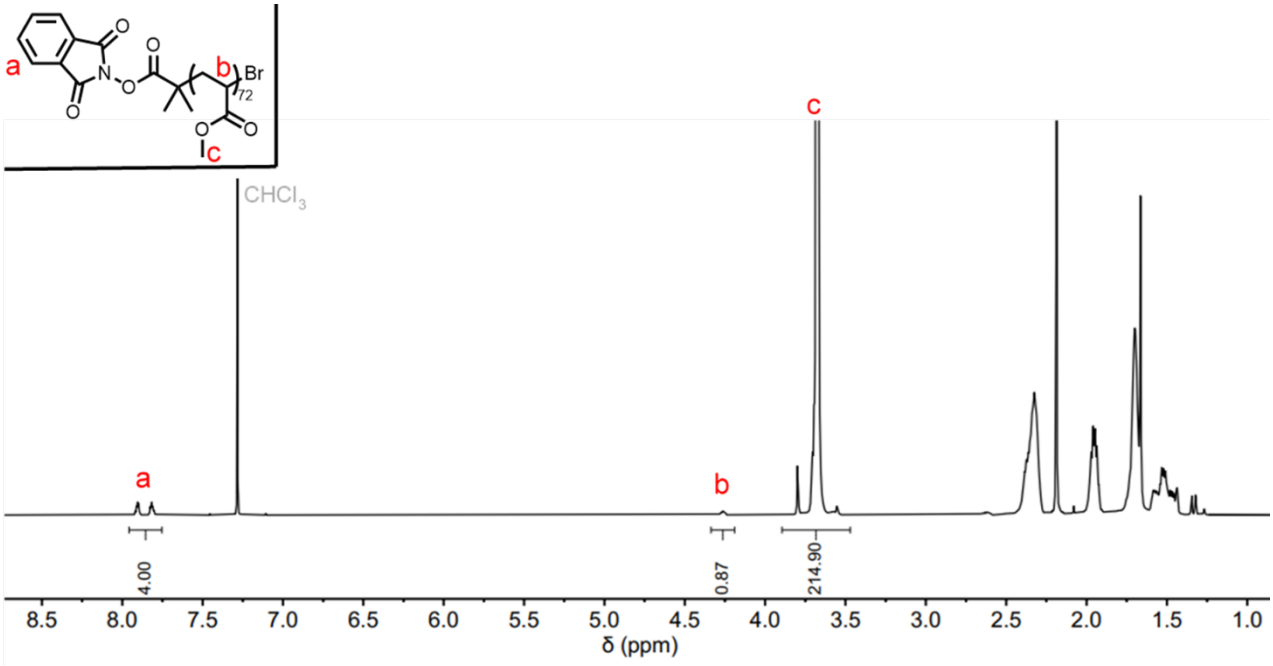


Figure S5. ^{1}H NMR spectrum of Phth-PMA.

P(PhthA-*co*-MA) **CA**

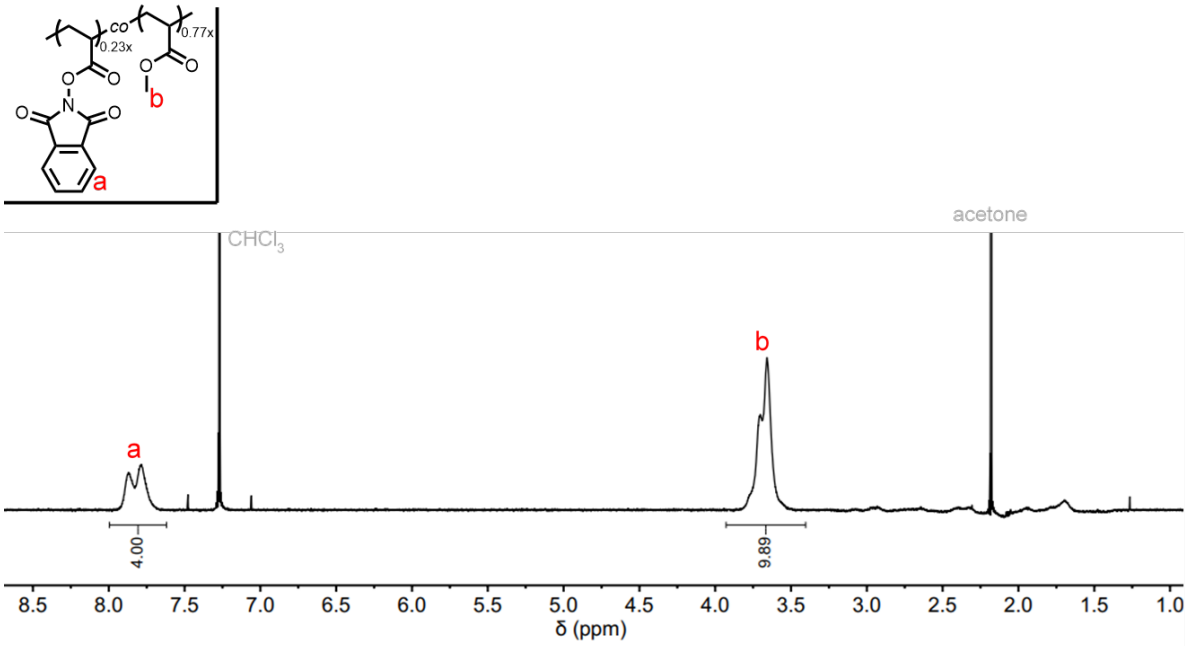


Figure S6. ^{1}H NMR spectrum of P(PhthA-*co*-MA) (**CA**) prepared via conventional radical polymerization.

P(PhthMA-*co*-MA) **CM**

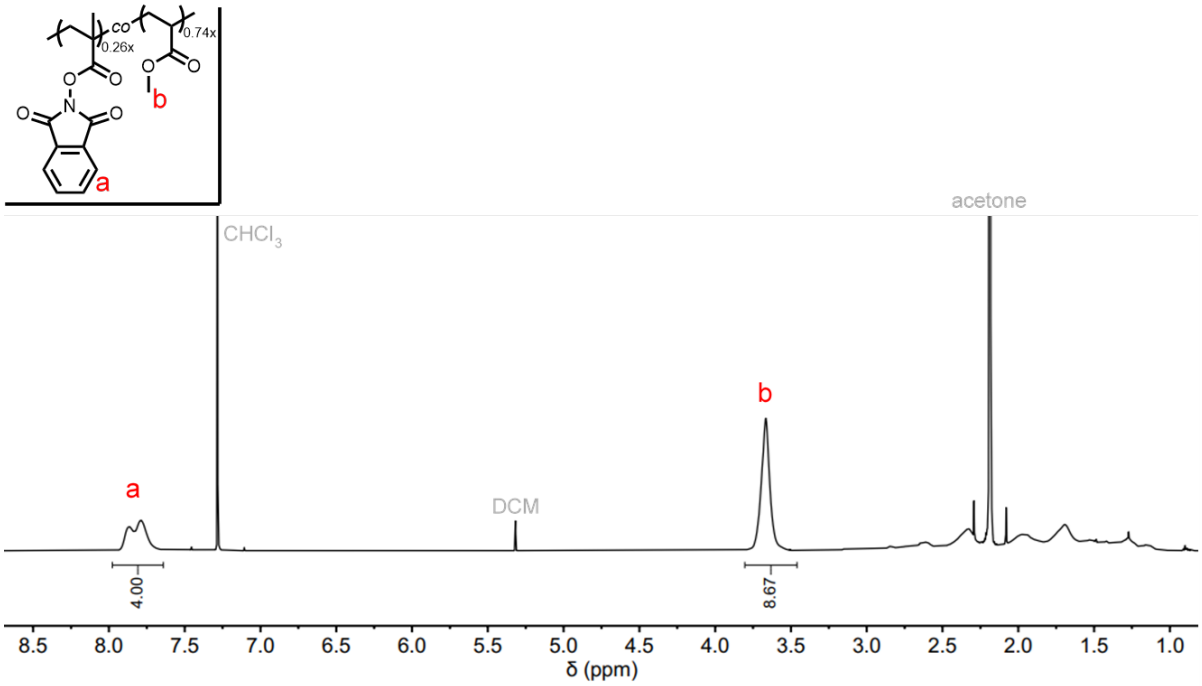


Figure S7. ^{1}H NMR spectrum of P(PhthA-*co*-MA) (**CM**) prepared via conventional radical polymerization.

P(PhthA-*co*-MA) **RA**

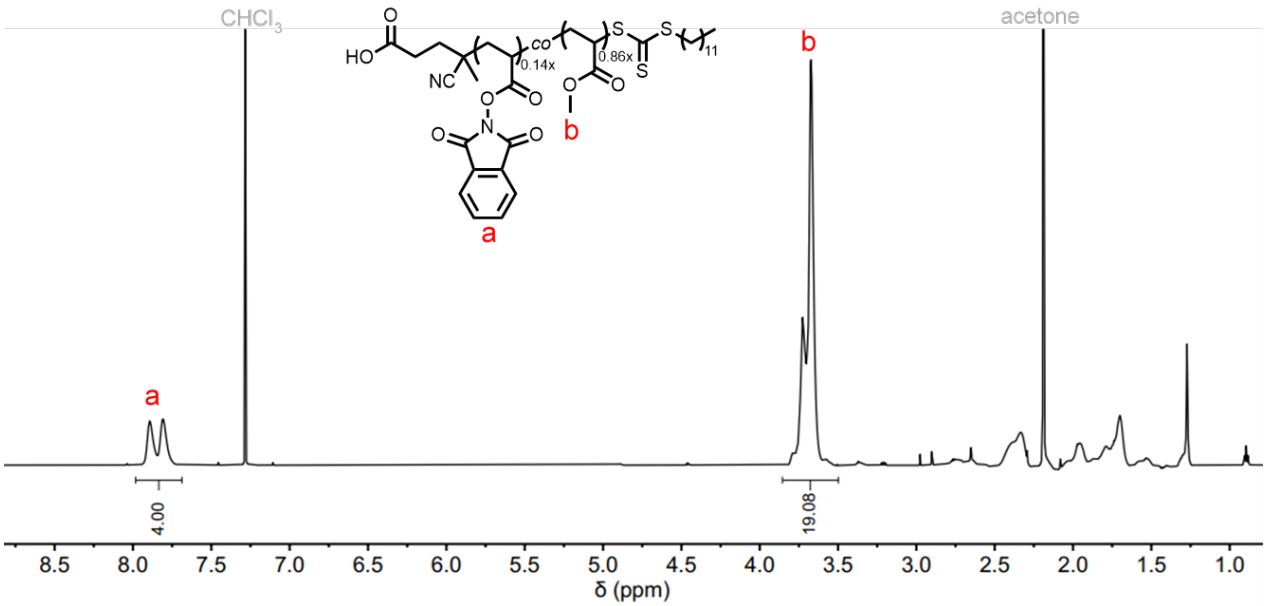


Figure S8. ^{1}H NMR spectrum of P(PhthA-*co*-MA) (**RA**) prepared via RAFT polymerization.

P(PhthMA-*co*-MA) **RM**

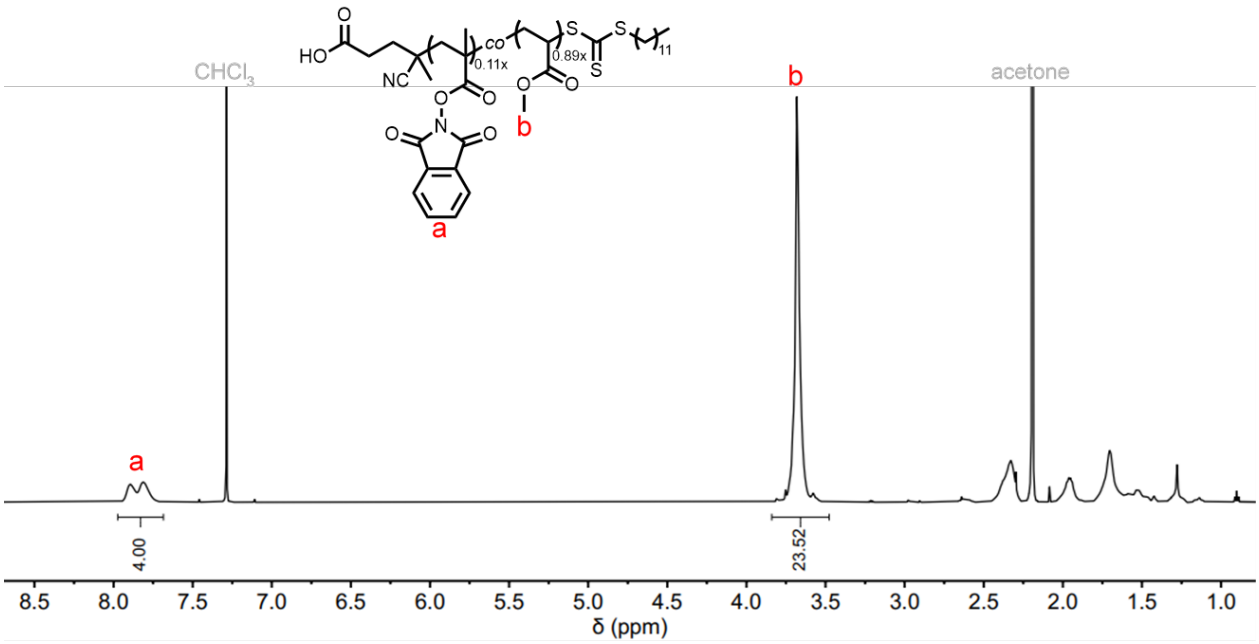


Figure S9. ^{1}H NMR spectrum of P(PhthMA-*co*-MA) (**RM**) prepared via RAFT polymerization.

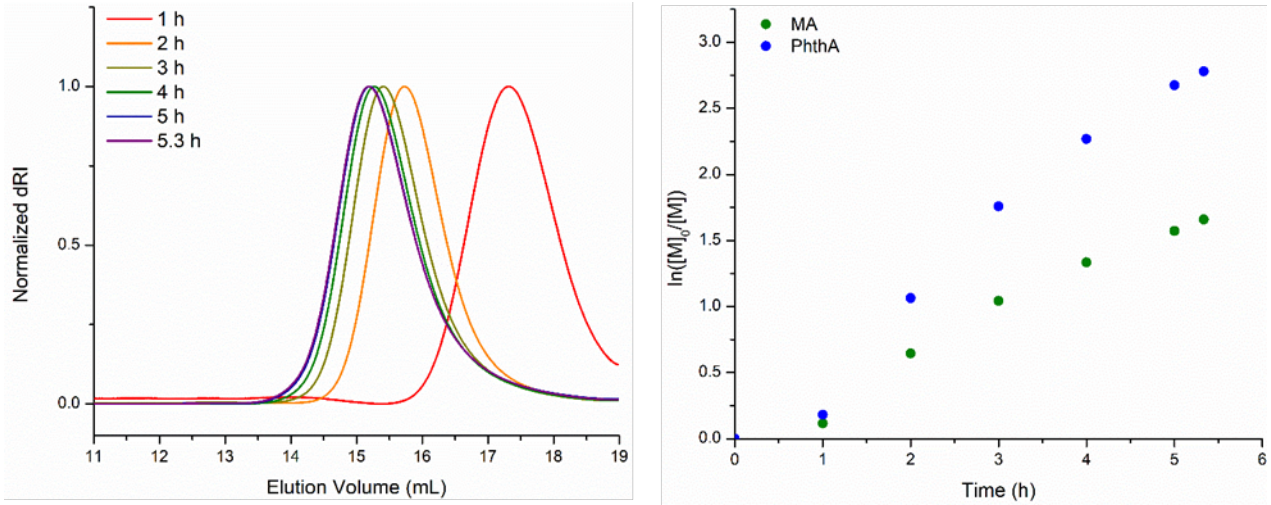


Figure S10. GPC traces for polymerization of **RA** showing consistent evolution of molecular weight throughout the polymerization (left) and linear pseudo-first-order kinetics for each monomer (right).

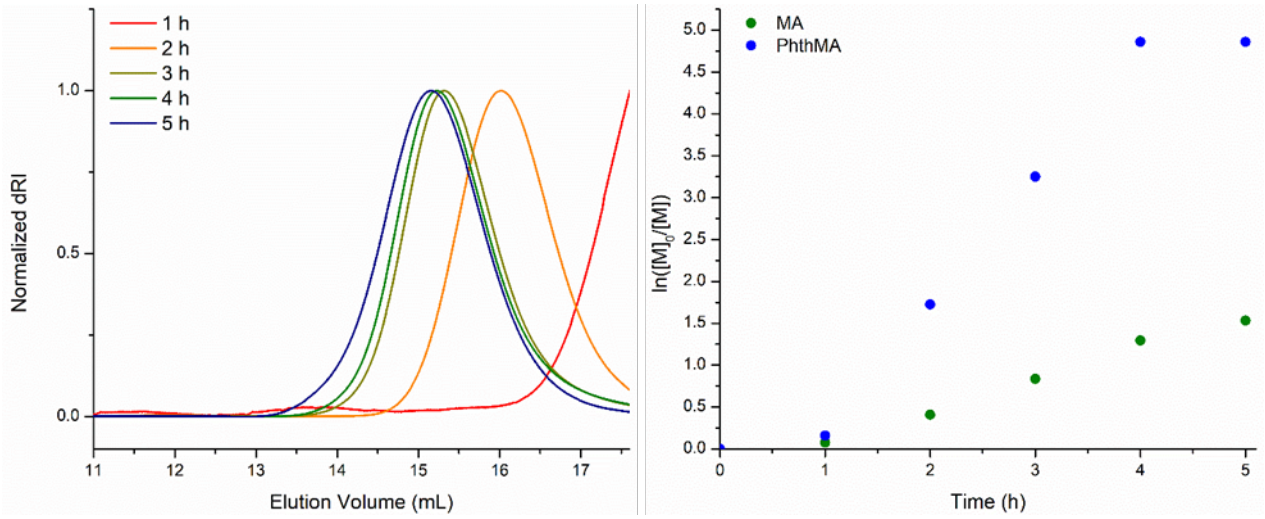


Figure S11. GPC traces for polymerization of **RM** showing consistent evolution of molecular weight throughout the polymerization (left) and linear pseudo-first-order kinetics for each monomer (right).

Gel Permeation Chromatography (GPC)

P(PhthA-*co*-MA) **CA**

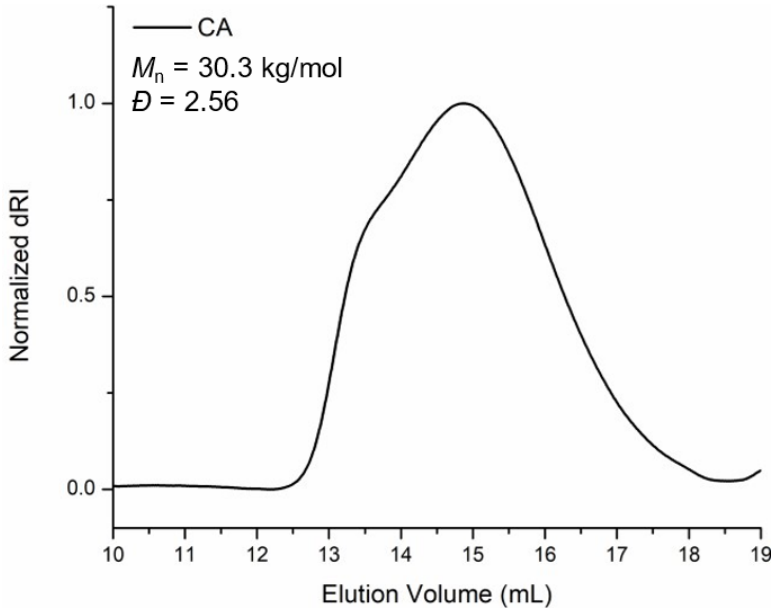


Figure S12. GPC elugram of P(PhthA-*co*-MA) (**CA**) prepared via conventional radical polymerization.

P(PhthMA-*co*-MA) **CM**

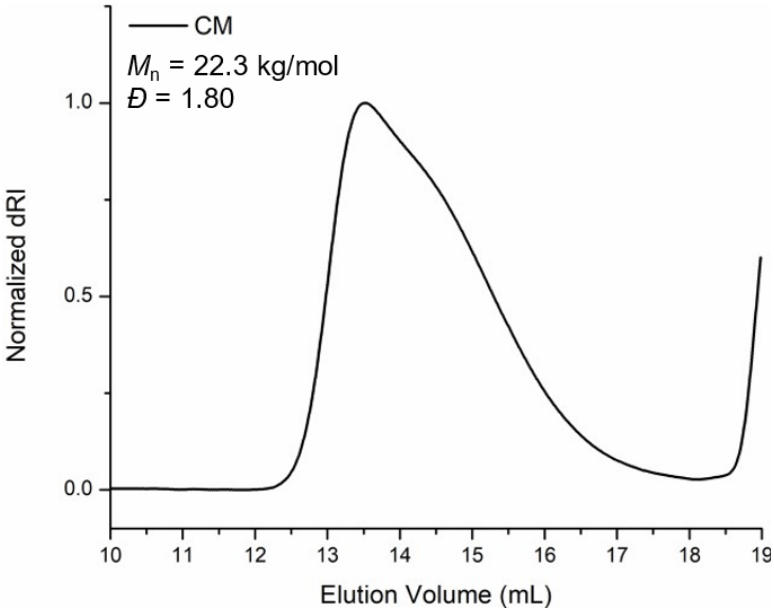


Figure S13. GPC elugram of P(PhthMA-*co*-MA) (**CM**) prepared via conventional radical polymerization.

P(PhthA-*co*-MA) **RA**

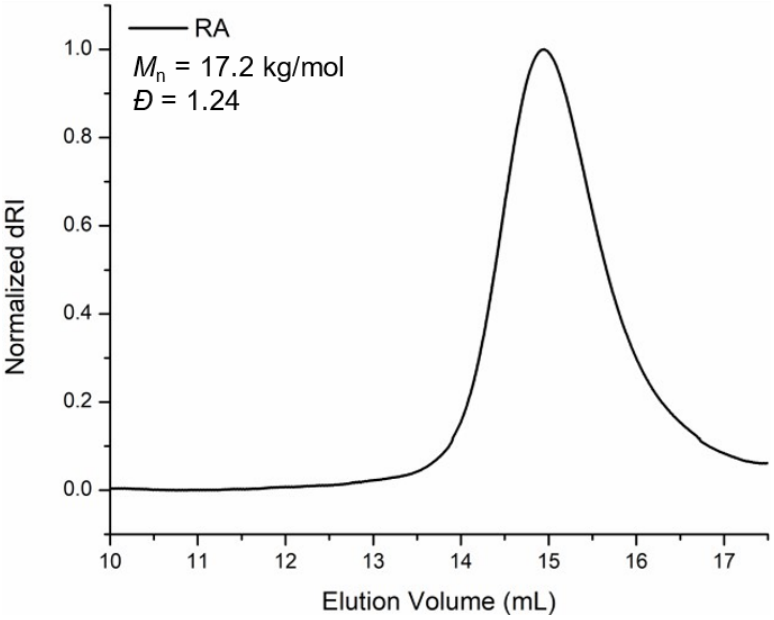


Figure S14. GPC elugram of P(PhthA-*co*-MA) (**RA**) prepared via RAFT polymerization.

P(PhthMA-*co*-MA) **RM**

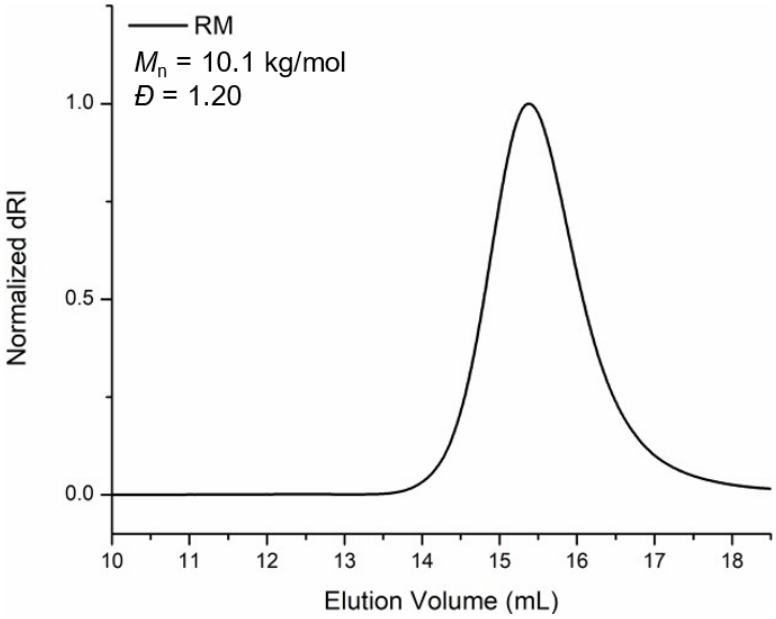


Figure S15. GPC elugram of P(PhthMA-*co*-MA) (**RM**) prepared via RAFT polymerization.

Decarboxylation Characterization

General decarboxylation procedure:

EY (0.1 equiv), DIPEA (2 equiv), and Bu_3SnH (5 equiv) were combined with a phthalimide ester derivative (1 equiv phthalimide ester). Phthalimide ester weight percent of each polymer was calculated using ^1H NMR to determine the necessary amount of polymer.

Polymer Example: **RA** (355 mg polymer, 31 w% PhthA, 110 mg PhthA, 1.00 equiv PhthA), was combined with eosin Y (35.1 mg, 0.10 equiv), DIPEA (131 mg, 2.00 equiv), and Bu_3SnH (738 mg, 5.00 equiv) in dry DCM (5 mL). The mixture was sparged with argon for 5 minutes prior to green light irradiation at a distance of 2 cm. Following decarboxylation, the resulting polymer was precipitated multiples times into hexanes and characterized by ^1H NMR spectroscopy and GPC.

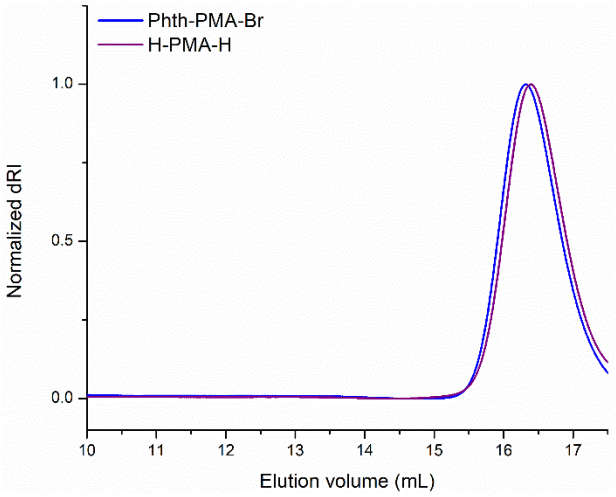


Figure S16. Decarboxylation of **Phth-PMA-Br.** GPC of the polymer before and after decarboxylation showing slight mass loss due to loss of phthalimide ester and bromine and absence of chain-end coupling.

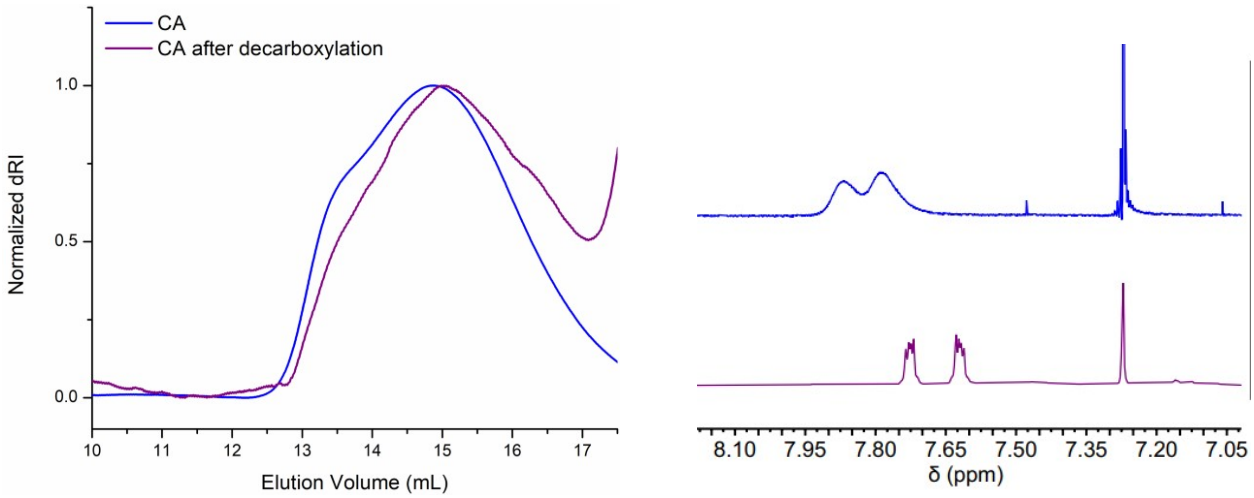


Figure S17. Decarboxylation of **CA**. GPC (left) of the polymer before and after decarboxylation showing mass loss and absence of cross-linking. ^{1}H NMR spectra (right) showing quantitative shift for phthalimide protons, evidence of complete decarboxylation.

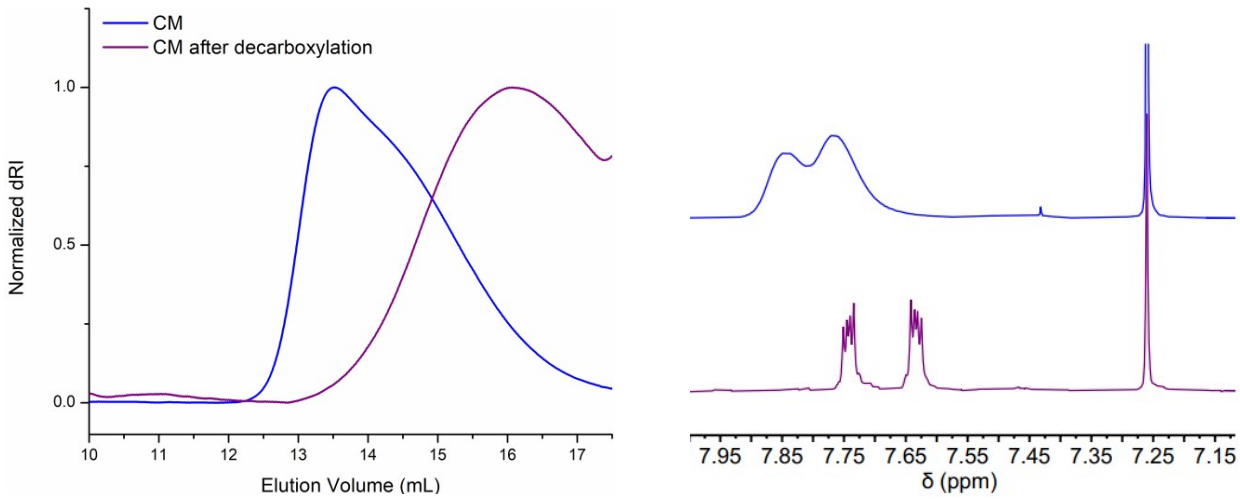


Figure S18. Decarboxylation of **CM**. GPC (left) of the polymer before and after decarboxylation showing mass loss and absence of cross-linking. ^{1}H NMR spectra(right) showing quantitative shift for phthalimide protons, evidence of complete decarboxylation.

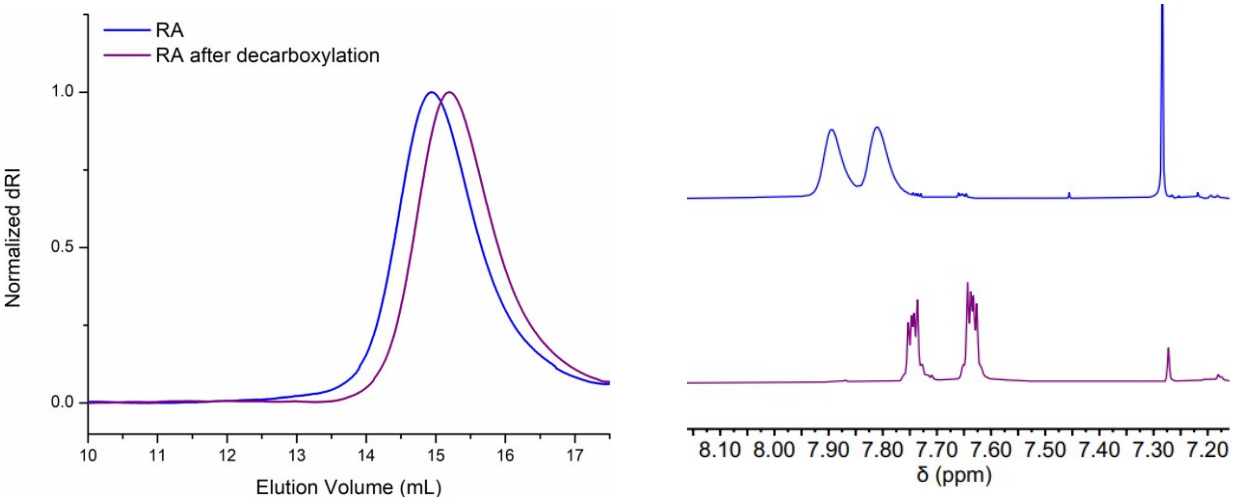


Figure S19. Decarboxylation of **RA**. GPC (left) of the polymer before and after decarboxylation showing mass loss and absence of cross-linking. ^{1}H NMR spectra (right) showing quantitative shift for phthalimide protons, evidence of complete decarboxylation.

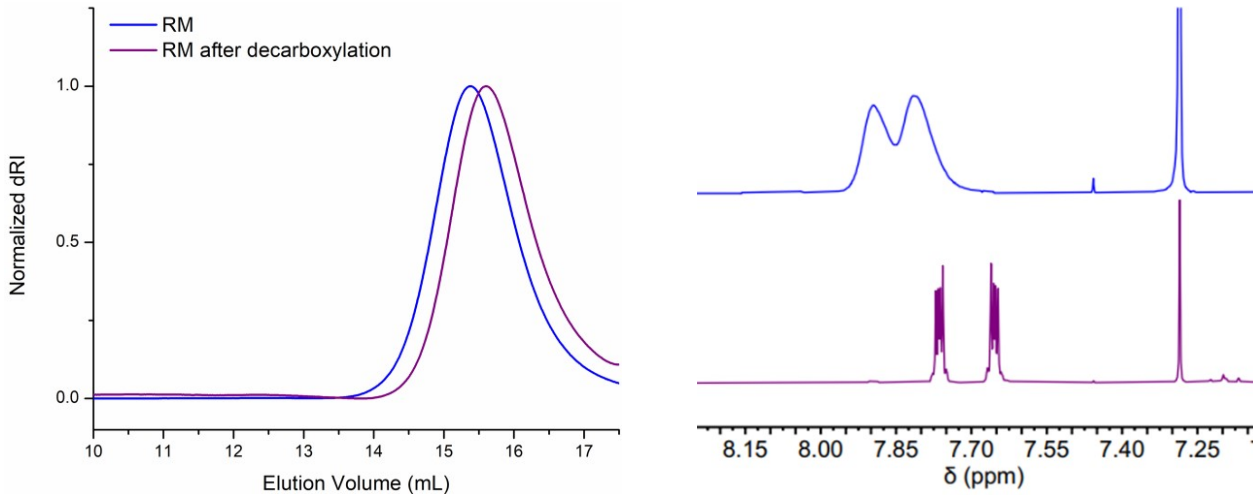


Figure S20. Decarboxylation of **RM**. GPC (left) of the polymer before and after decarboxylation showing mass loss and absence of cross-linking. ^{1}H NMR spectra (right) showing quantitative shift for phthalimide protons, evidence of complete decarboxylation.

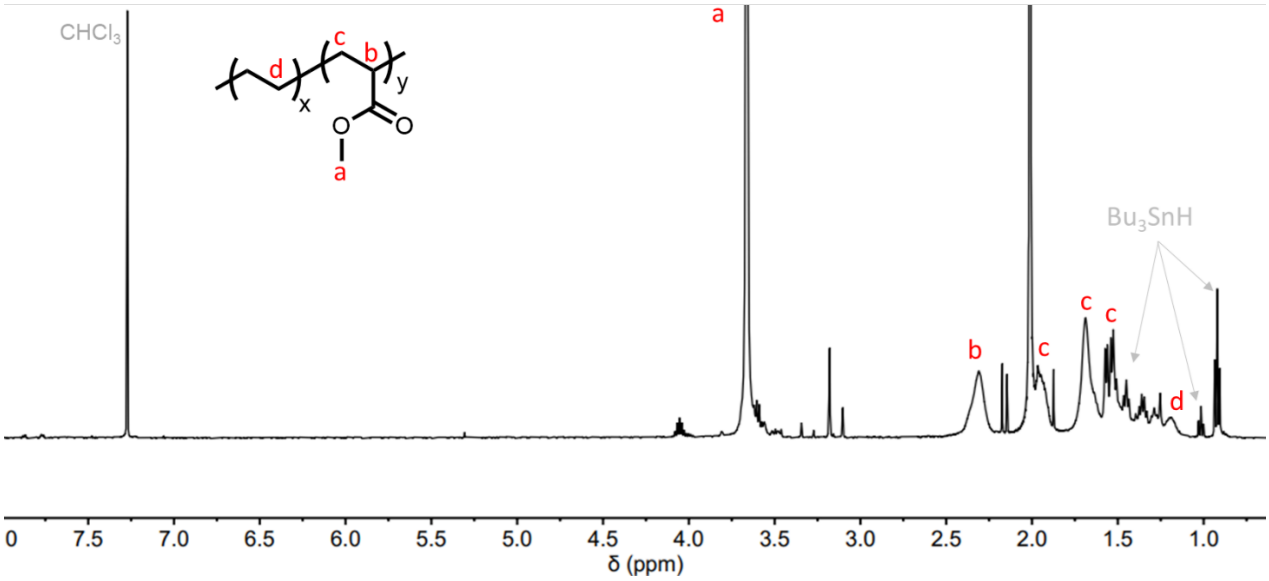


Figure S21. ^{1}H NMR spectrum **RA** after purification. Peak d is not present in PMA homopolymer (refer to Figure S5 for PMA homopolymer made by ATRP).

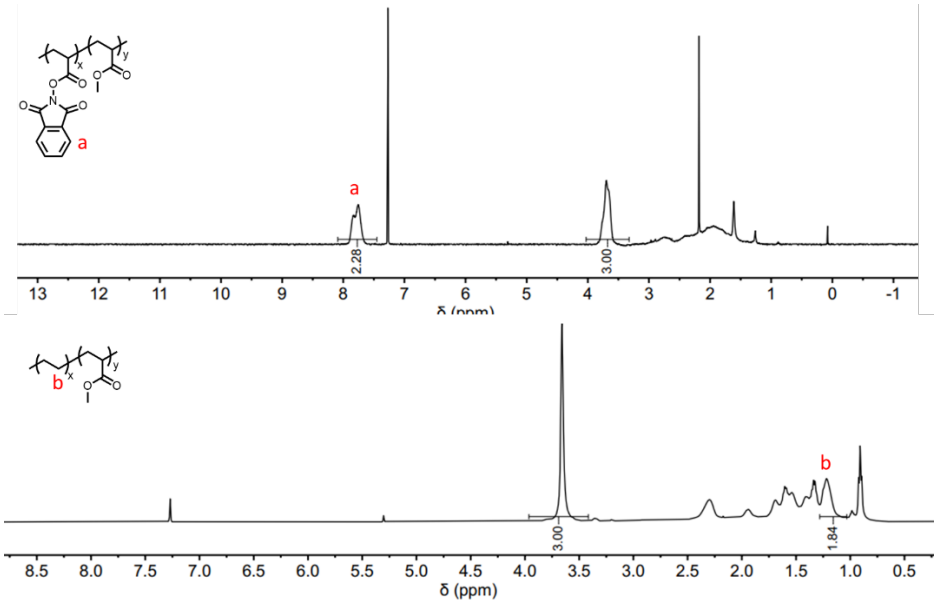


Figure S22. [1]HNMR spectroscopy of **RA2** before (top) and after (bottom) decarboxylation. Integrals show the ratio of methyl acrylate to PhthA repeat units in the top spectrum and the ratio of methyl acrylate to ethylene repeat units in the bottom spectrum. 4*2.28/4 = 2.28 which would be the theoretical ethylene integration.

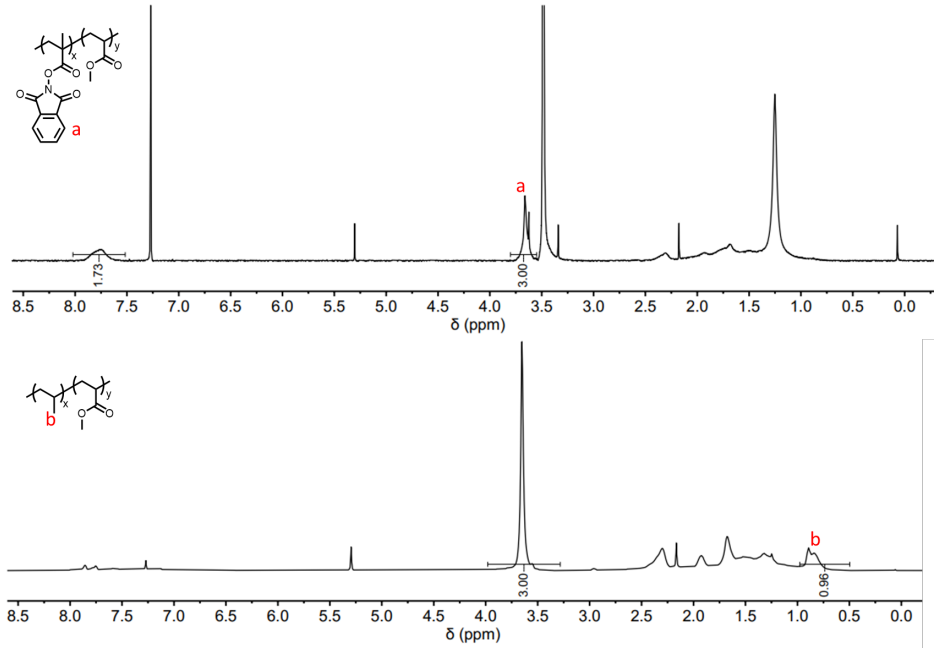


Figure S23. [1]HNMR spectroscopy of **RM2** before (top) and after (bottom) decarboxylation. Integrals show the ratio of methyl acrylate to PhthA repeat units in the top spectrum and the ratio of methyl acrylate to propylene repeat units in the bottom spectrum. 3*1.73/4 = 1.30 which would be the theoretical propylene integration.

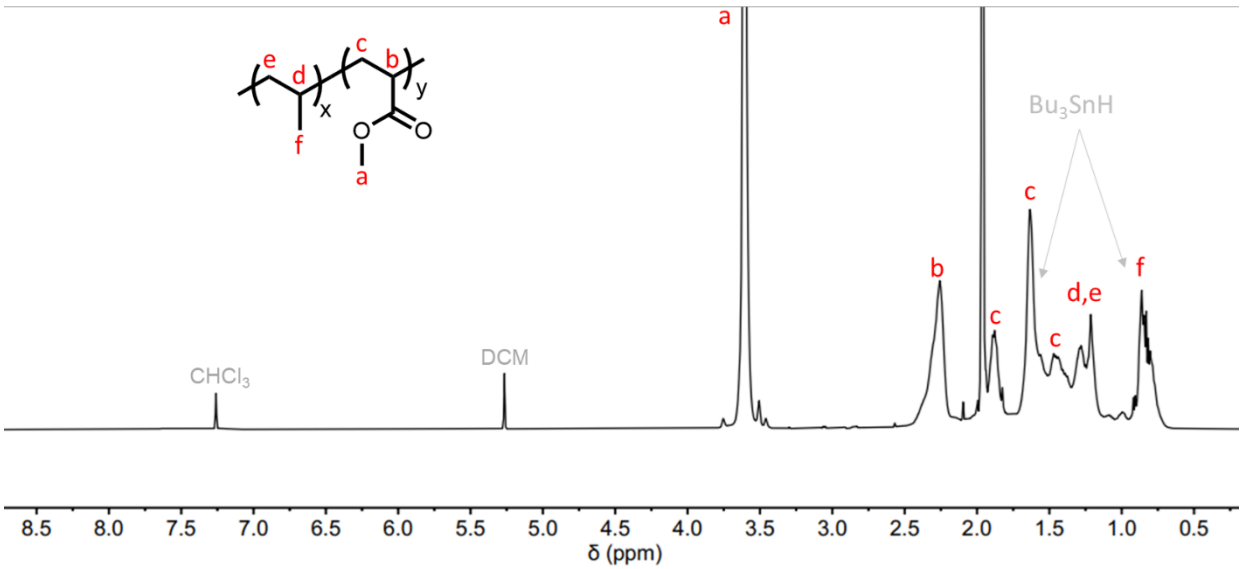


Figure S24. ^{1}H NMR spectrum **RM** after purification. Peaks d, e, and f are not present in PMA homopolymer (refer to Figure S5 for PMA homopolymer made by ATRP).

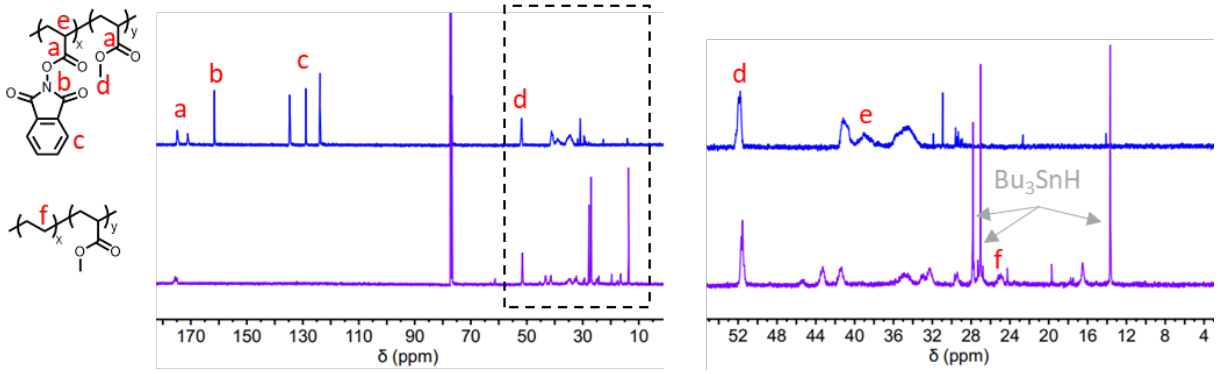


Figure S25. ^{13}C NMR spectrum **RA2** before (blue, top) and after (purple, bottom) decarboxylation. Peaks b and c are removed through decarboxylation and peak e appears as ethylene repeat unit peaks.

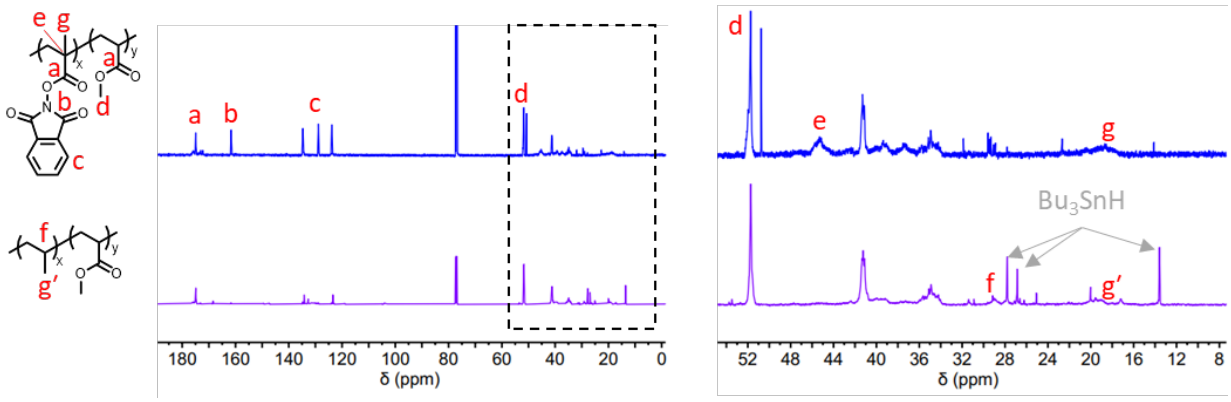


Figure S26. ^{13}C NMR spectrum **RM2** before (blue, top) and after (purple, bottom) decarboxylation. Peaks b and c are removed through decarboxylation and peak e and f' appear as propylene repeat unit peaks.

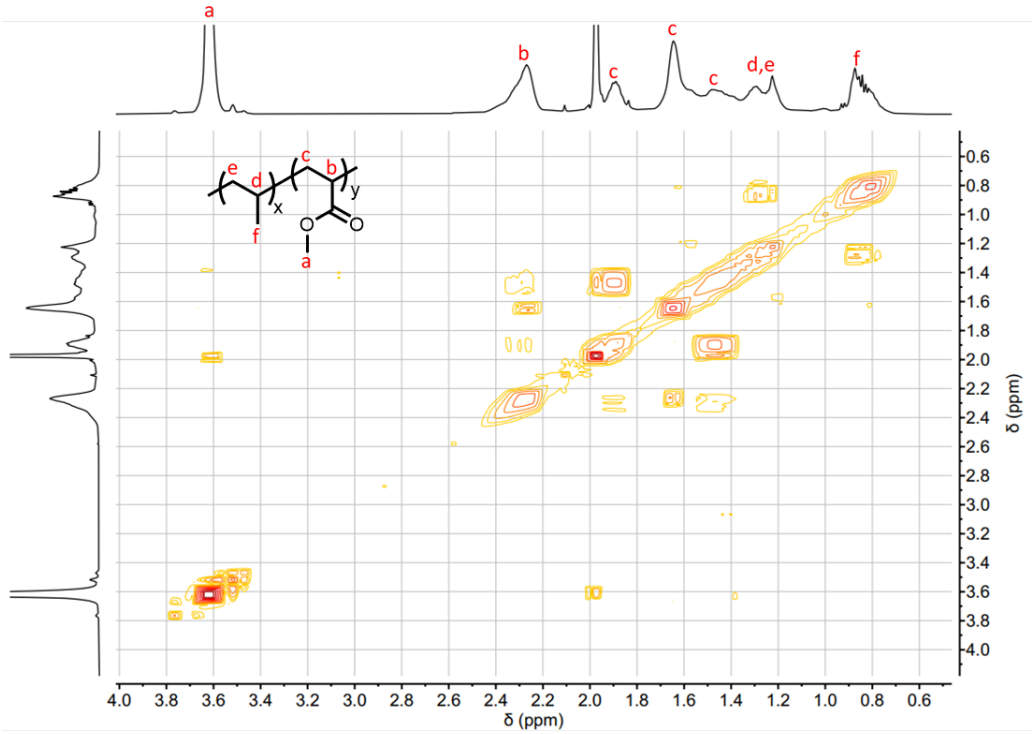


Figure S27. COSY of purified **RM**. Peaks d, e, and f appear that do not appear in PMA homopolymer (refer to Figure S5 for PMA homopolymer made by ATRP). Coupling between peaks d and f assisted in peak assignment.

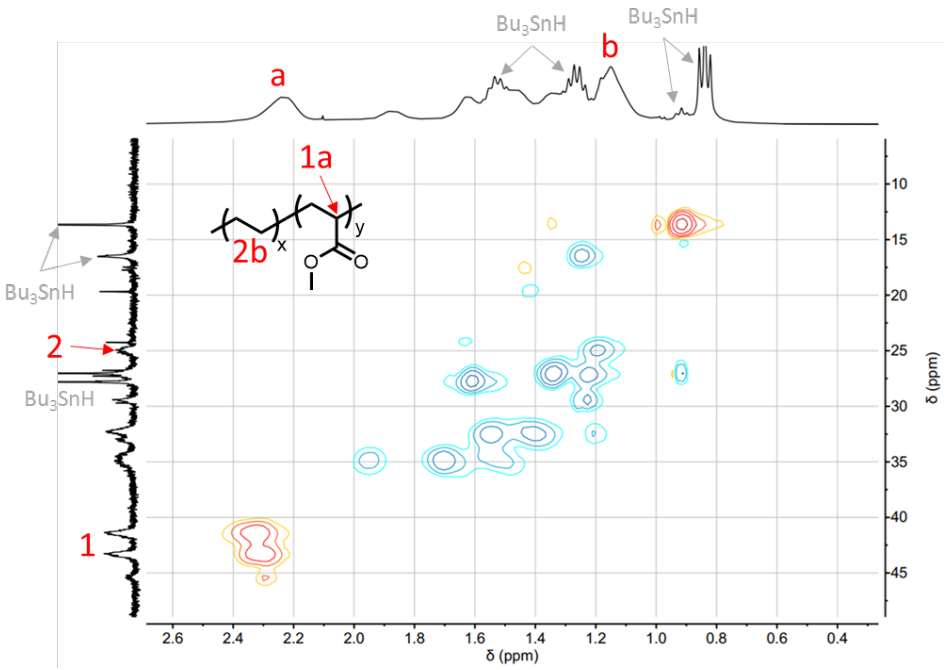


Figure S28. HSQC of purified **RA2**. Red peaks are -CH- or -CH_3 carbons and blue peaks are -CH_2- carbons. Crosspeak 2b reveals ethylene repeat units.

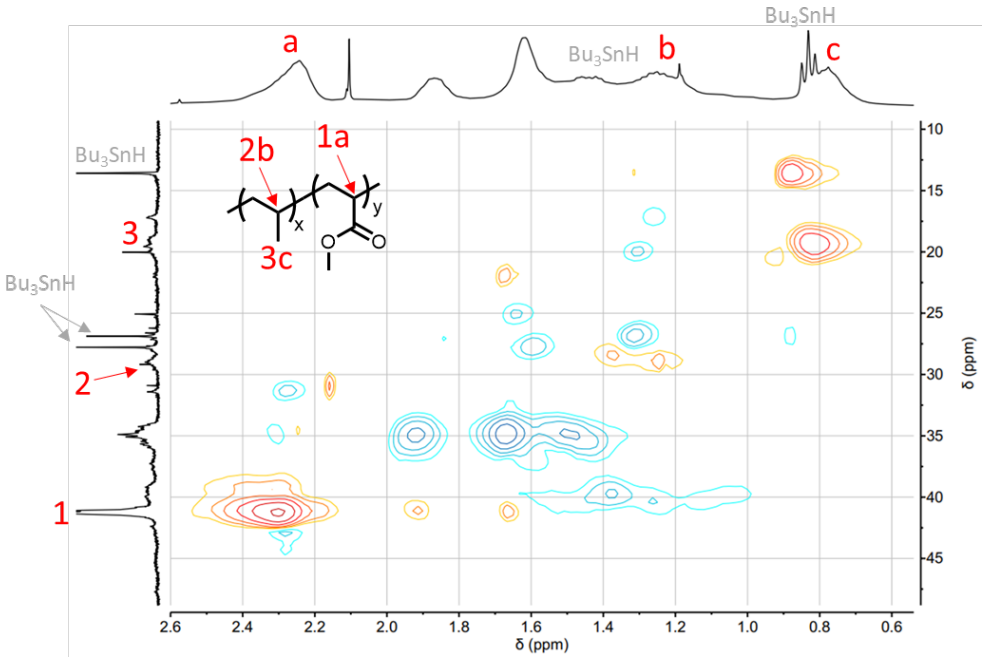


Figure S29. HSQC of purified **RM2**. Red peaks are -CH- or -CH_3 carbons and blue peaks are -CH_2- carbons. Crosspeak 2b reveals ethylene repeat units. Crosspeak 2b is the methine carbon of a propylene unit and crosspeak 3c is the methyl carbon of a propylene repeat unit.

References

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(2) Moad, G.; Chong, Y. K.; Postma, A.; Rizzardo, E.; Thang, S. H. Advances in RAFT Polymerization: The Synthesis of Polymers with Defined End-Groups. *Polymer.* **2005,** *46* (19 SPEC. ISS.), 8458–8468.