Supporting Information

Ring-Opening Metathesis Polymerization of 1,2-Disubstituted Cyclopropenes

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1. Experimental

1.1 General Experimental Considerations

Materials. All chemicals were purchased from commercial sources and used as received. Compounds 1¹, 2-TMS², 2³, 2-methylcycloprop-2-ene-1-carboxylic acid³, 4⁴, and (2-methyl-3-(trimethylsilyl)cycloprop-2-en-1-yl)methanamine⁵ were synthesized following the literature procedures. All reactions were performed in flame-dried glassware under an atmosphere of N₂. Flash chromatography was performed using Aldrich silica gel (230-400 mesh) unless otherwise noted.

Characterization. ¹H and ¹³C NMR spectra were recorded in CDCl₃ using 400 MHz, 500 MHz, or 600 MHz Varian NMR spectrometers. Chemical shifts are reported in ppm relative to CDCl₃ ($\delta = 7.27$). MALDI-TOF mass spectrometry was performed on a Bruker Microflex LRF at the Stanford University Mass Spectrometry Facility, plating samples with dithranol and NaI. GPC was performed in THF on two PLgel 10 μ m mixed-B LS columns (Agilent Technologies) connected in series with a DAWN 8+ multiangle laser light scattering (MALLS) detector and an Optilab T-rEX differential refractometer (both from Wyatt Technology). No calibration standards were used, and dn/dc values were obtained by assuming 100% mass elution from the columns.

1.2 General Procedures

General Procedure for ROMP. The desired amounts of CP monomers were added in vials equipped with a stir bar under an N_2 atmosphere. Dry, degassed THF was added to the vials. A stock solution of catalyst was prepared in THF, and the required amount of catalyst was quickly injected to each vial to begin polymerization at room temperature. For most monomers, polymerization was allowed to proceed for 1 h. Upon completion of the polymerization, the reactions were terminated by the addition of a few drops of ethyl vinyl ether. The resulting polymers were isolated by precipitating into MeOH and drying under vacuum.

General Procedure for Kinetics Studies. 0.1 M solutions of the CP monomers in dry, degassed CDCl₃ were prepared under an atmosphere of N₂ and added to an NMR tube. 1 in CDCl₃ was injected at a ratio of [1]:[CP] = 1:100 at room temperature. At reported time intervals, ¹H NMR spectra were acquired with a delay time (d1) of 25 s and scan count (nt) of 2. The consumption of monomer was determined by comparing the integration of the CP olefin to that of a constant, such as the CHCl₃ signal.

1.3 Experimental Procedures and Compound Characterization



2-Methyl-*N***-propylcycloprop-2-ene-1-carboxamide (3)** To a solution of 2-methylcycloprop-2ene-1-carboxylic acid (494 mg, 5.04 mmol) in DCM (25 mL) was added oxalyl chloride (0.43 mL, 5.04 mmol, 1.0 eq) and a few drops of DMF. After 2 h, the crude acid chloride was concentrated and added to a solution of propylamine (0.41 mL, 5.04 mmol, 1.0 eq) and triethylamine (0.76 mL, 5.04 mmol, 1.0 eq) in DCM (20 mL). After 1 h of stirring at room temperature, the product was concentrated *in vacuo* and purified by column chromatography with neutral alumina (eluting with 5% MeOH in DCM) to yield the pure product (200 mg, 29%). ¹H NMR (400 MHz, CDCl₃): δ 6.40 (1H, s), 5.36 (1H, bs), 3.25 – 3.12 (2H, m), 2.14 (3H, d, *J* = 1.2 Hz), 1.96 (1H, d, *J* = 1.6 Hz), 1.53 – 1.40 (2H, m), 0.87 (3H, t, *J* = 7.4 Hz). ¹³C NMR (100 MHz, CDCl₃): δ 176.02, 114.31, 96.36, 41.25, 23.21, 22.61, 11.46, 10.79. MS (ESI) calcd. for C₈H₁₃NO [M+Na⁺]: 162.09; found: 162.10.



General Procedure for Derivatization of 4. To a 0.1 M solution of 4 in dry DCM was added 1.1 eq of either triethylamine or pyridine and 1.1 eq of the acid chloride or chloroformate dropwise at 0 °C. After 24 h, the solution was extracted with an aqueous 0.1 M NH₄Cl solution and brine, and the organic layer dried over MgSO₄. After filtration and concentration *in vacuo*, the crude product was purified by flash chromatography (eluting with 10% Et₂O in hexanes) to yield the TMS intermediate. The intermediates were deprotected by adding to a 0.25 mL solution of TMS-CP in THF 1.1 eq of 1 M TBAF in THF containing ~5% water at 0 °C. The solution was warmed to room temperature, and after 0.5 h the crude solution was passed through a plug of neutral alumina to furnish the pure product.

(2-Methylcycloprop-2-en-1-yl)methyl benzoate (5a) Following the general procedure above, a solution of 4 (360 mg, 2.3 mmol), Et₃N (356 uL, 2.5 mmol, 1.1 eq), and benzoyl chloride (295 uL, 2.5 mmol, 1.1 eq) in dry DCM (23 mL) afforded **5a-TMS** (465 mg, 78%) as a colorless oil. Then a solution of **5a-TMS** (450 mg, 1.7 mmol) and TBAF (2.1 mL, 2.1 mmol, 1.1 eq) in THF (6.9 mL) afforded **5a** (251 mg, 77%) as a colorless oil. ¹H NMR (500 MHz, CDCl₃): δ 8.10 – 7.99 (2H, m), 7.61 – 7.52 (1H, m), 7.48 – 7.39 (2H, m), 6.61 (1H, s), 4.32 – 4.10 (2H, m), 2.17 (3H, d, J = 1.1 Hz), 1.79 (1H, td, J = 5.1, 1.6 Hz). ¹³C NMR (125 MHz, CDCl₃): δ 167.15, 133.06, 131.18, 129.92, 128.67, 120.98, 102.48, 72.73, 17.41, 12.09. MS (ESI) calcd. for C₁₂H₁₂O₂ [M+Na⁺]: 211.07; found: 211.10.

(2-Methylcycloprop-2-en-1-yl)methyl hexanoate (5b) Following the general procedure above, a solution of 4 (500 mg, 3.2 mmol), Et₃N (495 uL, 3.5 mmol, 1.1 eq), and hexanoyl chloride (493 uL, 3.5 mmol, 1.1 eq) in dry DCM (30 mL) afforded **5b-TMS** (615 mg, 76%) as a colorless oil. Then a solution of **5b-TMS** (325 mg, 1.3 mmol) and TBAF (1.4 mL, 1.4 mmol, 1.1 eq) in THF (5.0 mL) afforded **5b** (155 mg, 67%) as a colorless oil. ¹H NMR (500 MHz, CDCl₃): δ 6.55 (1H, s), 4.02 – 3.88 (2H, m), 2.34 – 2.26 (2H, m), 2.12 (3H, d, *J* = 1.1 Hz), 1.67 – 1.57 (3H, m), 1.36 – 1.34 (4H, m), 0.95 – 0.85 (3H, m). ¹³C NMR (125 MHz, CDCl₃): δ 174.20, 120.79, 102.23, 71.74, 34.61, 31.48, 24.93, 22.50, 17.10, 14.09, 11.77.

(2-Methylcycloprop-2-en-1-yl)methyl phenyl carbonate (7a) Following the general procedure above, a solution of 4 (300 mg, 1.9 mmol), Et₃N (300 uL, 2.1 mmol, 1.1 eq), and phenyl chloroformate (260 uL, 2.1 mmol, 1.1 eq) in dry DCM (20 mL) afforded 7a-TMS (337 mg, 63%) as a colorless oil. Then a solution of 7a-TMS (335 mg, 1.2 mmol) and TBAF (1.33 mL, 1.3 mmol, 1.1 eq) in THF (4.8 mL) afforded 7a (55 mg, 22%) as a colorless oil. ¹H NMR (400 MHz, CDCl₃): δ 7.41 – 7.36 (2H, m), 7.25 – 7.23 (1H, m), 7.21 – 7.16 (2H, m), 6.61 (1H, s), 4.25 – 4.00 (2H, m), 2.17 (3H, d, *J* = 1.2 Hz), 1.77 (1H, td, *J* = 5.3, 1.6 Hz). ¹³C NMR (100 MHz, CDCl₃): δ 154.29, 151.62, 129.82, 126.27, 121.51, 120.71, 102.18, 76.95, 54.34, 29.62. MS (ESI) calcd. for C₁₂H₁₂O₃ [M+Na⁺]: 227.07; found: 227.1.

Ethyl ((2-methylcycloprop-2-en-1-yl)methyl) carbonate (7b) Following the general procedure above, a solution of **4** (300 mg, 1.9 mmol), pyridine (170 uL, 2.1 mmol, 1.1 eq), and ethyl chloroformate (200 uL, 2.1 mmol, 1.1 eq) in dry DCM (20 mL) afforded **7b-TMS** (256 mg, 58%) as a colorless oil. Then a solution of **7b-TMS** (256 mg, 1.1 mmol) and TBAF (1.23 mL, 1.2 mmol, 1.1 eq) in THF (2.5 mL) afforded **7b** (82.5 mg, 47%) as a colorless oil. ¹H NMR (400 MHz, CDCl₃): δ 6.57 (1H, s), 4.18 (2H, q, J = 7.1 Hz), 4.08 – 3.86 (2H, m), 2.14 (3H, d, J = 1.2 Hz), 1.69 (1H, td, J = 5.3, 1.5 Hz), 1.31 (3H, t, J = 7.1 Hz). ¹³C NMR (100 MHz, CDCl₃): δ 155.89, 120.97, 102.36, 75.96, 64.14, 17.31, 14.79, 12.11.



N-((2-methylcycloprop-2-en-1-yl)methyl)benzamide (6a) To a solution of (2-methyl-3-(trimethylsilyl)cycloprop-2-en-1-yl)methanamine (264 mg, 1.7 mmol) in dry DCM (17 mL) was added Et₃N (260 uL, 1.9 mmol, 1.1 eq) and benzoyl chloride (220 uL, 1.9 mmol, 1.1 eq) at 0 °C. After stirring overnight, the crude **6a-TMS** was concentrated *in vacuo* and subjected to flash chromatography (eluting with 40% Et₂O in hexanes) to yield **6a-TMS** (209 mg, 47%) as a white solid. **6a-TMS** was then dissolved in THF, and to this solution was added 1 M TBAF in THF containing ~5% water (0.5 mL, 0.5 mmol, 1.1 eq) at 0 °C. The solution was warmed to room temperature, and after 0.5 h the crude solution was passed through a plug of neutral alumina to furnish **6a** (80 mg, 98%) as a white solid. ¹H NMR (500 MHz, CDCl₃): δ 7.81 – 7.75 (2H, m), 7.55 – 7.48 (1H, m), 7.49 – 7.42 (2H, m), 6.66 (1H, s), 6.07 (1H, bs), 3.68 – 3.17 (2H, m), 2.18 (3H, d, *J* = 1.1 Hz), 1.70 (2H, td, *J* = 4.2, 1.7 Hz). ¹³C NMR (125 MHz, CDCl₃): δ 167.81, 135.47, 131.60, 128.92, 127.18, 122.01, 103.13, 45.90, 18.32, 12.07. MS (ESI) calcd. for C₁₂H₁₃NO [M+Na⁺]: 210.09; found: 210.12.

Tert-butyl ((2-methylcycloprop-2-en-1-yl)methyl)carbamate (6b) To a solution of (2-methyl-3-(trimethylsilyl)cycloprop-2-en-1-yl)methanamine (180 mg, 1.2 mmol) in dry DCM (12 mL) was added Et₃N (163 uL, 1.2 mmol, 1.0 eq) and Boc anhydride (252 mg, 1.2 mmol, 1.0 eq) at 0 °C. After stirring overnight, the crude **6b-TMS** was concentrated *in vacuo* and subjected to flash chromatography (eluting with 10% Et₂O in hexanes) to yield **6b-TMS** (240 mg, 81%) as a white solid. **6b-TMS** was then dissolved in THF, and to this solution was added 1 M TBAF in THF containing ~5% water (0.81 mL, 0.81 mmol, 1.1 eq) at 0 °C. The solution was warmed to room temperature, and after 0.5 h the crude solution was passed through a plug of neutral alumina to furnish **6b** (124 mg, 92%) as a white solid. ¹H NMR (500 MHz, CDCl₃): δ 6.59 (1H, s), 4.45 (1H, bs), 3.09 (2H, t, *J* = 5.1 Hz), 2.14 (3H, d, *J* = 1.1 Hz), 1.56 (1H, td, *J* = 4.2, 1.6 Hz), 1.46 (9H, s). ¹³C NMR (125 MHz, CDCl₃): δ 156.35, 122.01, 103.17, 79.23, 46.53, 28.82, 18.63, 12.03. MS (ESI) calcd. for C₁₀H₁₇NO₂ [M+Na⁺]: 206.12; found: 206.11.

2. Supporting Figures



Figure S1. ¹H NMR spectra of catalyst **1** (top), **1** + 1 eq **2** (middle), **1** + 11 eq **2** (bottom), showing the decomposition of metathesis-active species after addition of monomer **2**.



Figure S2. MALDI-TOF MS spectrum of poly(5a).



Figure S3. GPC traces of (a) poly(**5a**) and (b) poly(**5b**) demonstrating MW control by varying [CP]₀:[**1**]₀ from 50 to 200 (entries 3, 4, and 5 for poly(**5a**) and entries 6, 7, and 8 for poly(**5b**) in Table 1).



Figure S4. GPC traces of various poly(1,2-CP)s where $[CP]_0 = 0.5$ M and $[CP]_0:[1]_0 = 50$.



Figure S5. GPC traces of poly(5a)s where $[5a]_0 = 0.5$ M or 0.01 M and $[5a]_0$: $[1]_0 = 50$.



Figure S6. GPC traces of poly(**5a**) before and after addition of ~100 eq of *cis*-3-hexene as chain transfer agent and 10 eq Grubbs 2^{nd} generation catalyst. Complete overlapping of GPC traces indicates no secondary metathesis occurs on polymer backbone.



Figure S7. Potential ring-opened products of the reaction of 5a with equimolar 1.



Figure S8. ¹H NMR spectrum of the metathesis products of **5a** reacting with equimolar **1** followed by quenching with ethyl vinyl ether. Assignments are based on the COSY spectrum of the complex organic mixtures isolated from the metathesis reaction. Remaining minor peaks cannot be assigned due to low intensity of signals in COSY spectrum and lack of through-bond couplings.



Figure S9. GPC traces of poly(**5b**) and poly(**5b**-*b*-**5a**) where monomer **5a** was added after (a) 20 min and (b) 2 h. $[5b]_0 = 0.5$ M, $[5b]_0:[1]_0 = [5a]_0:[1]_0 = 50$.

3. NMR Spectra







¹³C NMR spectrum of **3**.



¹³C NMR spectrum of **5a**.



¹H NMR spectrum of **5b**.



¹³C NMR spectrum of **5b**.



¹H NMR spectrum of **6a**.



¹³C NMR spectrum of **6a**.



¹H NMR spectrum of **6b**.



¹³C NMR spectrum of **6b**.



¹H NMR spectrum of **7a**.



¹³C NMR spectrum of **7a**.



¹H NMR spectrum of **7b**.



¹³C NMR spectrum of **7b**.



¹H NMR spectrum of poly(**5***a*).



¹³C NMR spectrum of poly(**5***a*).

4. References

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