**Supporting Information**

# Synthesis of Norbornenyl Polymers With Bioactive Oligopeptides by Ring-Opening Metathesis Polymerization

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## Experimental

**Materials.** 5-Norbornene acid-*endo*-2-carboxylic acid (*endo* **18**) was purchased from Aldrich. 5-Norbornene acid-*exo*-2-carboxylic acid (*exo* **18**)[1] and acid chloride[2] as well as **5**[3] were synthesized according to literature procedures. Methylene chloride used in the polymerization reactions was dried over $CaH_2$, degassed, and vacuum transferred before use. 2-Aminoethanol and solvents were purchased from EM science. Glycine methyl ester hydrochloride and alanine methyl ester hydrochloride were purchased from Sigma. Penta(ethylene glycol) was purchased

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[1] Ver Nooy, C. D.; Rondestvedt, Jr., C. S. *J. Am. Chem. Soc.* **1955**, *77*, 3583-3586.

[2] Stille, J. R.; Santarsiero, B. D.; Grubbs, R. H. *J. Org. Chem.* **1990**, *55*, 843-862.

[3] Heated in 1,2-dichlorobenzene to 185 °C, see: Craig, D. *J. Am. Chem. Soc.* **1951**, *73*, 4889-4892.

from Aldrich and dried over 4 Å molecular sieves (Linde). All other chemicals were purchased from Aldrich and used as received.

**Techniques.** All operations were carried out under a dry nitrogen or argon atmosphere. Dry box operations were performed in a nitrogen-filled Vacuum Atmospheres dry box. Column chromatography was performed using silica gel 60 (230-400 mesh) from EM science. $^1$H NMR spectra were recorded on a General Electric QE-300 (300.1 MHz) spectrometer, a JEOL GX-400 (399.65 MHz) spectrometer, or a Varian UnityPlus 600 (600.203 MHz) spectrometer as indicated. $^{13}$C NMR (75.49 MHz) spectra were recorded on a General Electric QE-300 spectrometer. Chemical shifts are reported downfield from tetramethylsilane (TMS). Infrared spectroscopy was performed on a Perkin Elmer Paragon 1000 FT-IR spectrometer using a thin film of sample cast on a NaCl plate or a KBr pellet as indicated. Optical rotations were recorded on a Jasco P-1010 digital polorimeter at 589 nm. High-resolution mass spectra were provided by the Southern California Mass Spectrometry Facility (University of California, Riverside). Gel permeation chromatographs with $CH_2Cl_2$ as the eluent (flow rate of 1 mL/min) were obtained using an HPLC system equipped with an Altex model 110A pump, a Rheodyne model 7125 injector with a 100 μL injection loop, two American Polymer Standards 10 micron mixed bed columns, a Knauer differential refractometer, and poly(styrene) as the calibration standard. Aqueous GPC (0.1 M $Na_2HPO_4$ dibasic buffer) or DMF (both with a flow rate of 1 mL/min) were conducted using an HPLC system equipped with a Waters 515 HPLC pump, a Rheodyne model 7725 injector with a 200 μL injection loop, a Waters 2487 Dual λ absorbance detector, a Waters 2410 refractometer, two TSK columns (TASK 3000PW, TSK 5000PW) and poly(ethylene oxide) or poly(styrene) as the calibration standard as indicated. Differential scanning calorimetry was measured on a Perkin-Elmer DSC-7 for $T_g$'s above 25 °C and on a

Perkin-Elmer Pyris1 for $T_g$'s below 25 °C. The results are given for the second heating using a scan rate of 10 °C/min. The HPLC results were obtained on a Beckman 126 Solvent Module HPLC equipped with a 166 UV Detector and an Altech 18-LL column using a $H_2O/CH_3CN$ solvent system (7% $CH_3CN$ for 6 min, 7-90% $CH_3CN$ over 38 min, and 90% $CH_3CN$ for 8 min).

**Monomer Synthesis**

**4-Hydroxymethyl-10-oxa-4-aza-tricyclo[5.2.1.$0^{2,6}$]dec-8-ene-*exo*-3,5-dione (6).** Prepared as for the **7** (*vide infra*) with 6.10 g (36.80 mmol) **4** and 2.22 mL (36.80 mmol) of 2-aminoethanol in THF/MeOH (30 mL, 1/1) resulting in 2.78 g (36%) of **6** as a white crystalline solid. $^1$H NMR ($D_2O$, 500 MHz) δ 6.48 (2H, s), 5.17 (2H, s), 3.56 (2H, t, J = 4.5), 3.50 (2H, t, J = 4.5), 2.99 (2H, s). $^{13}$C NMR ($D_2O$, 300 MHz) δ 179.32, 136.28, 80.83, 58.12, 47.31, 40.87. IR (KBr pellet): 3475, 3001, 2969, 2931, 2894, 1766, 1688, 1438, 1407, 1386, 1335, 1316, 1268, 1219, 1169, 1155, 1099, 1054, 1014, 956, 938, 915, 878, 849, 810, 773, 723, 704, 653, 597 $cm^{-1}$. HRMS (DCI/$NH_3$) calcd for $(MH)^+$ 210.0766 found 210.0763.

**4-Hydroxymethyl-4-aza-tricyclo[5.2.1.$0^{2,6}$]dec-8-ene-*exo*-3,5-dione (7).** 2-Aminoethanol (0.74 mL, 12.20 mmol) was added to a solution of **5** (2.00 g, 12.20 mmol) in THF/MeOH (1/1, 30 mL) and the mixture was heated to 50 °C for 12 h. After cooling to room temperature, the solvent was removed *in vacuo* and the product was recrystallized from MeOH/hex (2/1) to afford 1.11 g (44%) of **7** as white crystals. $^1$H NMR ($CDCl_3$, 300 MHz) δ 6.26-6.32 (2H, m), 3.77-3.82 (2H, m), 3.69-3.74 (2H, m), 3.30 (2H, s), 2.73 (2H, s), 2.18 (1H, bs), 1.53 (1H, d, J = 8.7), 1.35 (1H, d, J = 8.7). $^{13}$C NMR ($CDCl_3$, 300 MHz) δ 178.65, 137.70, 60.02, 47.78, 45.14, 42.68, 41.15. IR (NaCl plate): 3506, 2984, 2954, 2885, 1758, 1689, 1423,

1403, 1341, 1329, 1166, 1152, 1063, 989, 935, 900, 881, 856, 767, 733, 649 $cm^{-1}$. HRMS ($DCI/NH_3$) calcd for $(MH)^+$ 208.0974, found 208.0969.

**4-(*Exo*-3,5-dioxo-10-oxa-4-aza-tricyclo[5.2.1.$0^{2,6}$]dec-8-en-4-yl)-butyric acid (8).** Same procedure as for the synthesis of the **7** was followed with 3.00 g (18.00 mmol) of **4** and 1.86 g (18.00 mmol) 4-aminobutyric acid in THF/MeOH (36 mL, 1:1). The crude product was subjected to column chromatography (EtOAc with 3% AcOH) to give 1.83 g (41%) of **8** as a white solid. $^1H$ NMR ($CDCl_3$, 300 MHz) δ 6.51 (2H, s), 5.26 (2H, s), 3.56 (2H, t, J = 6.9 Hz), 2.85 (2H, s), 2.34 (2H, t, J = 7.5 Hz), 1.90 (2H, t, J = 7.2 Hz). $^{13}C$ NMR ($CDCl_3$, 300 MHz) δ 176.01, 168.60, 136.51, 80.95, 47.40, 37.96, 30.81, 22.59. IR (NaCl plate): 3480.6, 2977.1, 2677.2, 2495.1, 2355.9, 1770.9, 1696.0, 1562.1, 1396.1, 1165.8, 1096.1, 1015.0, 914.1, 871.2, 849.8, 807.0, 721.3, 651.6, 603.4 $cm^{-1}$. HRMS ($DCI/NH_3$) calcd for $(MH)^+$ 252.0872 found 252.0878.

***Exo*-(3,5-dioxo-10-oxa-4-aza-tricyclo[5.2.1.$0^{2,6}$]dec-8-en-4-yl)-acetic acid methyl ester (9).** The same procedure as for **15** was followed (*vide infra*) with 1.42 g (8.53 mmol) of **4**, 1.07 g (8.53 mmol) glycine methyl ester hydrochloride, and 3.50 mL (25.16 mmol) of triethylamine in $CH_2Cl_2$ (43 mL) to yield 0.17 g (9%) of **9** as a white solid. $^1H$ NMR ($CDCl_3$, 300 MHz) δ 6.54 (2H, m), 5.31 (2H, s), 4.24 (2H, s), 3.76 (3H, s), 2.97 (2H, s). $^{13}C$ NMR ($CDCl_3$, 300 MHz) δ 175.85, 167.62, 137.09, 81.45, 53.02, 48.22, 39.92. IR (NaCl plate): 3100, 3029, 3011, 2992, 2958, 1747, 1707, 1423, 1373, 1326, 1267, 1221, 1180, 1154, 1102, 1081, 1014, 983, 951, 915, 874, 848, 806, 713, 656, 619, 593 $cm^{-1}$. HRMS ($DCI/NH_3$) calcd for $(MH)^+$ 238.0716, found 238.0704.

***Exo*-2-(3,5-dioxo-10-oxa-4-aza-tricyclo[5.2.1.0$^{2,6}$]dec-8-en-4-yl)-propionic acid methyl ester (10).** Compound **10** was synthesized according to literature procedure[4] in 25% yield. $^1$H NMR ($CDCl_3$, 500 MHz) δ 6.53 (2H, s), 5.29 (2H, s), 4.74 (1H, q, J = 7.4 Hz), 3.73 (3H, s), 2.84-2.92 (2H, m), 1.54 (3H, d, J = 7.5).

**2-*tert*-Butoxycarbonylamino-propionic acid *exo*-3,5-dioxo-10-oxa-4-aza-tricyclo[5.2.1.0$^{2,6}$]dec-8-en-4-ylmethyl ester (11).** The same procedure as for **17** (*vide infra*) was followed with 0.50 g (2.39 mmol) of **6**, 0.45 g (2.39 mmol) of N-tert-butoxycarbonyl-L-alanine, 0.49 g (2.39 mmol) of 1,3-dicyclohexylcarbodiimide (DCC), and 0.04 g (0.36 mmol) of 4-(dimethylamino)pyridine (DMAP) in 20 mL $CH_2Cl_2$. The product was purified by recrystallization from MeOH/hex (2/1) to yield 0.46 mg (50%) of **11** as white crystals. $^1$H NMR ($CDCl_3$, 500 MHz) δ 6.51 (2H, s), 5.27 (2H, s), 5.02 (1H, bs), 4.30 (2H, t, J = 5.3 Hz), 4.23-4.29 (1H, m), 3.73-3.81 (2H, m), 2.86-2.89 (2H, m), 1.42 (9H, s), 1.34 (3H, d, J = 7.2 Hz). $^{13}$C NMR ($CDCl_3$, 300 MHz) δ 175.91, 172.76, 154.97, 136.44, 80.79, 61.17, 49.06, 47.38, 47.36, 37.63, 28.23, 18.25. IR (NaCl plate): 3356.0, 2967.3, 2936.6, 1742.0, 1701.1, 1511.8, 1455.6, 1430.0, 1394.2, 1363.5, 1332.8, 1251.0, 1158.9, 1066.8, 1020.8, 886.0, 855.4, 713.9, 647.4. $[\alpha]_D^{25}$ = -10.6. HRMS ($DCI/NH_3$) calcd for $(MH)^+$ 381.1662 found 381.1645.

**(*Exo*-3,5-dioxo-10-oxa-4-aza-tricyclo[5.2.1.0$^{2,6}$]dec-8-en-4-ylmethoxy)-acetic acid methyl ester (12).** Methyl bromoacetate (1.81 mL, 19.12 mmol) was added to a solution of the **6** (1.00 g, 4.78 mmol), potassium carbonate (0.80 g, 5.76 mmol), and tetrabutylammonium bromide (0.02 g, 0.06 mmol) in anhydrous DMF (20 mL). The solution was stirred at room temperature for 12 h. $CHCl_3$ (100 mL) was added, and the organic layer was successively

[4] Biagini, S. C. G.; Bush, S. M.; Gibson, V. C.; Mazzariol, L.; North, M.; Teasdale, W. G.; Williams, C. W.; Zagotto, G.; Zamuner, D. *Tetrahedron* **1995**, *51*, 7247-7262.

washed with $H_2O$ (twice) and 5% $HBr_{aq}$. The aqueous layers were combined and washed with $CH_2Cl_2$ (three times). The organic layers were pooled, dried over $MgSO_4$, and the solvent was removed *in vacuo*. The crude product was recrystallized from a mixture of EtOAc and ether (4:1) to give 0.66 g (49%) of **12** as a white solid. $^1$H NMR ($CDCl_3$, 300 MHz) δ 6.51 (2H, s), 5.27 (2H, s), 4.62 (2H, s), 4.34 (2H, t, J = 5.4 Hz), 3.81 (2H, t, J = 4.5 Hz), 3.78 (3H, s), 2.89 (2H, s). $^{13}$C NMR ($CDCl_3$, 300 MHz) δ 175.87, 167.66, 154.36, 136.44, 80.81, 63.35, 52.27, 47.39, 37.46. IR (NaCl plate): 3009.3, 2966.4, 2355.9, 1754.9, 1701.3, 1428.2, 1396.1, 1337.1, 1288.9, 1214.0, 1149.7, 1122.9, 1021.2, 919.4, 876.6, 849.8, 785.5, 721.3, 646.3, 592.7 cm$^{-1}$.

**[4-(*Exo*-3,5-dioxo-10-oxa-4-aza-tricyclo[5.2.1.0$^{2,6}$]dec-8-en-4-yl)-butyrylamino]-acetic acid methyl ester (13).** Same procedure as for **19** was followed (*vide infra*) with 2.21 mL (15.89 mmol) triethylamine, 0.65 g (4.77 mmol) 1-hydroxybenzotriazole (HOBT), 0.61 g (3.18 mmol) 1-[3-(dimethylamine)propyl]-3-ethylcarbodiimide hydrochloride (EDC), 0.40 g (3.19 mmol) glycine methyl ester hydrochloride, and 0.80 g (3.18 mmol) of **8** in 64 mL $CH_2Cl_2$. The crude product was subjected to column chromatography (EtOAc) to give 0.58 g (57%) of **13** as a white solid. $^1$H NMR ($CDCl_3$, 300 MHz) δ 6.53 (2H, s), 5.28 (2H, s), 4.05 (2H, d, J = 5.1 Hz), 3.76 (3H, s), 3.62 (2H, t, J = 6.3 Hz), 2.86 (2H, s), 2.19 (2H, t, J = 6.9 Hz), 1.97 (2H, t, J = 6.3 Hz). $^{13}$C NMR ($CD_2Cl_2$, 300 MHz) 177.09, 172.47, 136.98, 81.56, 54.68, 52.64, 47.99, 41.66, 38.42, 33.39, 24.22. IR (NaCl plate): 3563.8, 3292.9, 3084.6, 2949.2, 2355.5, 1750.7, 1698.6,1547.6, 1433.0, 1401.8, 1370.5, 1282.0, 1214.3, 1162.2, 1021.6, 917.4, 875.0, 849.7, 802.9, 719.5, 651.8, 589.3, 500.8 cm$^{-1}$. HRMS (EI) calcd for $(MH)^+$ 323.1243 found 323.1241.

***Exo*-(3,5-dioxo-4-aza-tricyclo[5.2.1.0$^{2,6}$]dec-8-en-4-yl)-acetic acid methyl ester (15).** A literature procedure[4] was followed except that $CH_2Cl_2$ was used as the solvent to give **15** in 59% yield as a white solid. $^1$H NMR ($CDCl_3$, 300 MHz) δ 6.29-6.30 (2H, m), 4.22 (2H, s), 3.73

(3H, s), 3.30-3.32 (2H, m), 2.75 (2H, d, J = 1.5 Hz), 1.70 (1H, d, J = 9.9 Hz), 1.52 (1H, d, J = 9.9 Hz).

***Exo*-2-(3,5-dioxo-4-aza-tricyclo[5.2.1.0$^{2,6}$]dec-8-en-4-yl)-propionic acid methyl ester (16).** Compound **16** was synthesized according to literature procedure[4] in 51% yield. $^1$H NMR ($CDCl_3$, 300 MHz) δ 6.27-6.28 (2H, m), 4.75 (1H, q, J = 7.5 Hz), 3.70 (3H, s), 3.27-3.28 (2H, m), 2.69-2.70 (2H, m), 1.53 (3H, d, J = 7.2 Hz), 1.50-1.54 (2H, m).

**2-*tert*-Butoxycarbonylamino-propionic acid *exo*-3,5-dioxo-4-aza-tricyclo[5.2.1.0$^{2,6}$]dec-8-en-4-ylmethyl ester (17).** **7** (0.30 g, 1.45 mmol), *N*-(*tert*-butoxycarbonyl)-L-alanine (0.27 g, 1.45 mmol), DCC (0.30 g, 1.45 mmol), and DMAP (0.03 g, 0.22 mmol) were stirred in $CH_2Cl_2$ (18 mL) for 12 hours. The solution was filtered and the solvent removed *in vacuo*. The residue was subjected to column chromatography twice (EtOAc, followed by EtOAc/hex, 8/2) to give 0.33 g (61 % yield) of **17** as a sticky solid. $^1$H NMR ($CD_3Cl$, 500 MHz) δ 6.29 (2H, s), 4.99 (1H, bs), 4.11-4.32 (3H, bm), 3.75-3.79 (2H, m), 3.29 (2H, d, J = 10.1 Hz), 2.71 (2H, s), 1.52-1.54 (1H, m), 1.43 (9H, s), 1.35 (3H, d, J = 7.2 Hz), 1.27-1.29 (1H, m). $^{13}$C NMR ($CDCl_3$, 300 MHz) δ 177.89, 173.33, 155.33, 137.79, 79.87, 61.69, 49.33, 47.83, 45.22, 42.73, 37.49, 28.31, 18.39. IR (NaCl plate): 3366.2, 2977.5, 2936.6, 1747.1, 1696.0, 1506.7, 1450.4, 1389.1, 1363.5, 1327.7, 1251.0, 1164.0, 1061.7, 990.1, 775.3, 719.0, 642.3 cm$^{-1}$. $[\alpha]_D^{23}$ = -19.0. HRMS (DCI/$NH_3$) calcd for $(MH)^+$ 379.1869 found 379.1871.

**[(Bicyclo[2.2.1]hept-5-ene-*endo*-2-carbonyl)-amino]-acetic acid methyl ester (19).** Triethylamine (1.41 mL, 10.14 mmol) and glycine methyl ester hydrochloride (0.64 g, 5.06 mmol) were added to a solution of *endo* **18** (0.70 g, 5.06 mmol) in $CH_2Cl_2$ (75 mL). HOBT (1.03 g, 7.62 mmol) was added, and the solution was stirred until all solids had dissolved. Then a solution of EDC (0.97 mg, 5.06 mmol) and triethylamine (1.41 mL, 10.14 mmol) in $CH_2Cl_2$ (25

mL) was added and the mixture was stirred for 24 h. The organic layer was washed successively with 10% citric acid, $H_2O$, sat. $NaHCO_3$, and brine, dried over $MgSO_4$, and the solvent removed *in vacuo*. The crude product was subjected to column chromatography (ether) resulting in 0.70 g (66% yield, 11% *exo*) of **19** as a white solid. $^1H$ NMR ($CD_2Cl_2$, 300 MHz) δ 6.17-6.19 (1H, m), 5.94-5.97 (1H, m), 3.92 (2H, d, J = 5.7 Hz), 3.70 (3H, s), 3.14 (1H, bs), 2.87-2.92 (2H, m), 1.85-1.93 (1H, m), 1.28-1.43 (3H, m). $^{13}C$ NMR ($CD_2Cl_2$, 300 MHz) δ 174.62, 171.16, 138.03, 132.73, 52.58, 50.39, 46.77, 44.80, 43.26, 41.46, 29.84. IR (NaCl plate) : same as for **20** (*vide infra*).

**[(Bicyclo[2.2.1]hept-5-ene-*exo*-2-carbonyl)-amino]-acetic acid methyl ester (20).** The same procedure as for **19** was followed with 1.40 mL (10.06 mmol) triethylamine, 0.54 g (4.30 mmol) glycine methyl ester hydrochloride, 0.57 g (4.10 mmol) *exo* **18**, 0.83 g (6.14 mmol) HOBT, and 0.79 g (4.10 mmol) EDC in 40 mL of $CH_2Cl_2$ resulting in 0.63 g (73%) of **20** as an off-white solid. $^1H$ NMR ($CDCl_3$, 400 MHz) δ 6.10-6.13 (2H, m), 6.01 (1H, bs), 4.05 (2H, dd, J = 4.8 Hz, 17.9 Hz), 3.75 (3H, s), 2.96 (1H, s), 2.91 (1H, s), 2.06-2.08 (1H, m), 1.90-1.95 (1H, m), 1.67 (1H, d, J = 8.0 Hz), 1.34 (2H, d, J = 9.2). $^{13}C$ NMR ($CD_2Cl_2$, 300 MHz) δ 175.92, 170.97, 138.48, 136.25, 52.43, 47.48, 46.45, 44.49, 41.94, 41.42, 30.59. IR (NaCl plate): 3315.1, 3059.3, 2957.1, 2865.0, 1747.1, 1644.8, 1532.3, 1440.2, 1404.4, 1368.6, 1327.7, 1204.9, 1097.5, 1046.4, 1010.6, 898.0, 852.0, 790.6, 719.0 $cm^{-1}$. HRMS (EI) calcd for $(M)^+$ 209.1052 found 209.1048.

**[(Tricyclo[4.2.1.$0^{2,5}$]non-7-ene-*exo*-3-carbonyl)-amino]-acetic acid methyl ester (23).** Same procedure as for **19** was followed with 0.97 mL (6.98 mmol) triethylamine, 0.44 g (3.49 mmol) glycine methyl ester hydrochloride, 0.57 g (3.49 mmol) **22**, 0.71 g (5.22 mmol) HOBT, and 0.67 g (3.49 mmol) EDC in 30 mL $CH_2Cl_2$. The crude product was subjected to column

chromatography (ether) to provide 0.53 g (65%) of **23** as a white solid. $^1$H NMR ($CDCl_3$, 300 MHz) δ 5.90-5.98 (2H, m), 4.04 (2H, d, J = 5.1 Hz), 3.74 (3H, s), 2.71 (1H, s), 2.65 (1H, s), 2.31-2.36(2H, m), 2.14 (1H, t, J = 7.2 Hz), 1.99 (1H, t, J = 7.8 Hz), 1.54-1.66 (2H, m), 1.32 (1H, d, J = 9.3 Hz). $^{13}$C NMR ($CDCl_3$, 300 MHz) δ 175.68, 170.59, 135.75, 134.39, 52.22, 43.97, 43.85, 41.16, 40.35, 40.28, 38.70, 34.12, 23.68. IR (NaCl plate): 3287.8, 3062.8, 2966.4, 2355.9, 1754.9, 1647.8, 1540.7, 1433.6, 1369.3, 1203.3, 1048.0, 989.0, 699.9, 507.1 cm$^{-1}$. HRMS (DEI) calcd for ($M^+$) 235.1208 found 235.1201.

**Polymer Synthesis.**

**General Synthesis for Polymers with one pendent amino acid or $EO_5$.** In a nitrogen-filled dry box, a solution of **1** in $CH_2Cl_2$ was added to a solution of monomer $CH_2Cl_2$ (or $CD_2Cl_2$ for NMR reactions) to give an initial monomer concentration of 0.7-0.75 M. The initial $[M]_0/[C]_0$ was 100/1. The reaction mixture was stirred at room temperature for 15 min to 3 h before quenching with ethyl vinyl ether and stirring for an additional 15-30 minutes. The polymers were precipitated into ether or hex, stirred for 15 min, and subjected to centrifugation. The solvent was removed and the solids dried under vacuum. The polymers were all white to tan powders. Deviations from this literature procedure are noted in specific cases below. (Data not reported within the text is also reported below.)

**Poly(9).** $^1$H NMR ($CDCl_3$, 300 MHz) δ 6.06, 5.79 (*trans* & *cis*, 2H, bs), 4.91-4.97, 4.44-4.53 (*cis* & *trans*, 2H, bm), 4.20 (*trans* & *cis*, 2H, bs), 3.74 (*trans* & *cis*, 3H, s), 3.40 (*trans* & *cis*, 2H, bs). $^{13}$C NMR ($CDCl_3$, 300 MHz) δ 174.77, 167.05, 130.94, 130.71, 80.74, 53.32, 52.84,

52.34, 39.37. IR (NaCl plate): 3662.0, 3468.5, 2998.0, 2957.1, 2854.8, 1782.9, 1752.2, 1711.3, 1419.8, 1368.6, 1322.6, 1220.3, 1169.1, 1020.8, 974.8, 918.5, 734.4 $cm^{-1}$.

**Poly(10).** The solvent was either $CH_2Cl_2$ or benzene. $^1H$ NMR ($CD_2Cl_2$, 300 MHz) δ 6.08, 5.83 (*trans* & *cis*, 2H, bs), 4.87-4.97, 4.74-4.76 (*cis* & *trans*, 1H, bm), 4.48 (*trans* & *cis*, 2H, bs), 3.71, 3.70 (*trans* & *cis*, 3H, s), 3.37 (*trans* & *cis*, 2H, bs), 1.57 (*trans* & *cis*, 3H, bd, J = 7.5 Hz).

**Poly(11).** $^1H$ NMR ($CD_2Cl_2$, 400 MHz) δ 6.06, 5.78 (*trans* & *cis*, 2H, bs), 5.25, 5.16 (*cis* & *trans*, 1H, bs), 4.91-5.00, 4.47 (*cis* & *trans*, 2H, bm, bs), 4.29 (*trans* & *cis*, 2H, bs), 4.15-4.19 (*trans* & *cis*, 1H, bm), 3.75 (*trans* & *cis*, 2H, bs), 3.35 (*trans* & *cis*, 2H, bs), 1.38 (*trans* & *cis*, 9H, s), 1.30 (*trans* & *cis*, 3H, bd, J = 7.3 Hz). $^{13}C$ NMR ($CDCl_3$, 300 MHz) δ 175.42, 173.22, 155.08, 130.99, 130.89, 80.63, 79.83, 61.41, 53.30, 52.28, 49.12, 38.20, 28.31, 18.12. IR (NaCl plate): 3528.3, 3372.6, 2967.9, 2936.8, 2874.5, 1778.3, 1742.0, 1705.7, 1513.7, 1451.4, 1425.5, 1394.3, 1363.2, 1332.1, 1249.1, 1160.8, 1119.3, 1067.5, 1025.9, 911.8, 730.2 $cm^{-1}$.

**Poly(12).** $[M]_0$ was 0.6 M. $^1H$ NMR ($CD_2Cl_2$, 300 MHz) δ 6.06, 5.79 (*trans* & *cis*, 2H, bs), 4.92, 4.47 (*cis* & *trans*, 2H, bs), 4.60 (*trans* & *cis*, 2H, s), 4.32 (*trans* & *cis*, 2H, bs), 3.80 (*trans* & *cis*, 2H, bs), 3.73 (*trans* & *cis*, 3H, s), 3.38 (*trans* & *cis*, 2H, bs). $^{13}C$ NMR ($CD_2Cl_2$, 300 MHz) δ 176.04, 175.91, 168.38, 155.15, 131.78, 131.49, 131.38, 81.36, 81.30, 81.24, 77.81, 65.24, 64.07, 54.76, 54.40, 52.92, 38.30. IR (NaCl plate): 4202.5, 3631.2, 3537.9, 3468.0, 3013.2, 2954.9, 2850.0, 2302.0, 2197.1, 1754.6, 1707.9, 1433.9, 1393.1, 1119.1, 1031.7, 973.4, 915.1, 850.9, 781.0, 705.2, 676.0, 629.4, 565.3 $cm^{-1}$.

**Poly(13).** $[M]_0$ was 0.5 M. $^1H$ NMR ($CD_2Cl_2$, 400 MHz) δ 7.03 (*trans* & *cis*, 1H, bs), 6.03, 5.79 (*trans* & *cis*, 2H, bs), 4.96, 4.48 (*trans* & *cis*, 2H, bs), 3.93 (*trans* & *cis*, 2H, bs), 3.66 (*trans* & *cis*, 3H, s), 3.47 (*trans* & *cis*, 2H, bs), 3.37 (*trans* & *cis*, 2H, bs), 2.23 (*trans* & *cis*, 2H,

bs), 1.85 (*trans* & *cis*, 2H, bs). $^{13}$C NMR ($CD_2Cl_2$, 300 MHz) δ 176.01, 173.21, 172.91, 135.87, 135.54, 135.24, 82.46, 81.56, 81.26, 55.10, 52.57, 48.23, 41.77, 41.55, 39.16, 38.49, 34.69, 34.21, 25.21. IR (NaCl plate): 3578.3, 3330.0, 3081.6, 2947.1, 2854.0, 1749.2, 1702.7, 1666.5, 1542.3, 1433.6, 1397.4, 1366.4, 1211.2, 1159.4, 1118.0, 1030.1, 973.2, 916.3, 771.4, 704.1, 564.4 $cm^{-1}$.

**Poly(15).** $^1$H NMR ($CD_2Cl_2$, 300 MHz) δ 5.74, 5.53 (*trans* & *cis*, 2H, bs), 4.17 (*trans* & *cis*, 2H, bs), 3.72, 3.71 (*trans* & *cis*, 3H, s), 3.45, 3.09 (*cis* & *trans*, 2H, bs), 2.84, 2.76 (*cis* & *trans*, 2H, bs), 2.13-2.21 (*trans* & *cis*, 1H, bm), 1.61-1.76 (*trans* & *cis*, 1H, bm). $^{13}$C NMR ($CDCl_3$, 300 MHz) δ 177.47, 167.32, 131.89, 131.76, 52.67, 51.04, 50.93, 45.87, 45.73, 41.91, 41.07, 39.06. IR (NaCl plate): 2994.4, 2954.0, 2853.7, 1779.4, 1751.4, 1704.5, 1413.6, 1366.7, 1324.5, 1216.6, 1169.7, 972.7, 916.4, 766.3, 733.5, 616.2 $cm^{-1}$.

**Poly(16).** $^1$H NMR ($CD_2Cl_2$, 300 MHz) δ 5.74-5.78, 5.57-5.59 (*trans* & *cis*, 2H, br m), 4.76 (*trans* & *cis*, 1H, br q, J = 7.5 Hz), 3.74, 3.71 (*trans* & *cis*, 3H, s), 3.19-3.25, 3.07-3.14 (*cis* & *trans*, 2H, br m), 2.76 (*trans* & *cis*, 2H, br s), 2.10-2.22 (*trans* & *cis*, 1H, br m), 1.82-1.90, 1.60-1.75 (*cis* & *trans*, 1H, br m), 1.55 (*trans* & *cis*, 3H, d, J = 7.2 Hz). $^{13}$C NMR ($CDCl_3$, 300 MHz) δ *trans* & *cis*: 177.43, 177.23, 169.70, 133.40, 132.01, 131.77, 52.75, 52.28, 50.77, 47.71, 45.78, 45.65, 41.93, 41.84, 40.87, 14.23, 14.02. IR (NaCl plate): 3003.8, 2947.5, 2863.1, 1774.8, 1742.0, 1704.5, 1451.2, 1390.2, 1357.3, 1310.4, 1230.7, 1197.9, 1118.1, 1071.2, 972.7, 911.7, 785.1, 733.5, 625.6 $cm^{-1}$.

**Poly(17).** $^1$H NMR ($CDCl_3$, 300 MHz) δ 5.73, 5.49 (*trans* & *cis*, 2H, bs), 5.17, 5.07 (*cis* & *trans*, 1H, bs), 4.22-4.28 (*trans* & *cis*, 3H, bm), 3.70 (*trans* & *cis*, 2H, bm). 2.96-3.05 (*trans* & *cis*, 2H, bm), 3.23, 2.70 (*cis* & *trans*, 2H, bs), 2.05-2.27 (*trans* & *cis*, 1H, bm), 1.55-1.67 (*trans* & *cis*, 1H, bm), 1.40 (*trans* & *cis*, 9H, s), 1.32 (*trans* & *cis*, 3H, d, J = 7.2 Hz). $^{13}$C NMR

($CDCl_3$, 300 MHz) δ 177.91, 173.09, 155.04, 131.87, 131.75, 79.77, 61.65, 51.65, 50. 78, 49.12, 47.55, 45.59, 42.19, 40.79, 37.73, 28.32, 18.27. IR (NaCl plate): 3439.0, 3364.9, 2973.2, 2930.9, 2867.4, 1766.8, 1745.6, 1703.3, 1512.7, 1449.2, 1422.7, 1391.0, 1364.5, 1332.8, 1248.1, 1163.4, 1115.7, 1068.1, 1020.5, 972.8, 914.6, 729.4 $cm^{-1}$.

**Poly(19).** The reaction time was 26 h. $^1H$ NMR ($CD_2Cl_2$, 300 MHz) δ 5.40-5.59 (*trans* & *cis*, 2H, bm), 3.89-4.02 (*trans* & *cis*, 2H, bm), 3.74 (*trans* & *cis*, 3H, s), 2.66 (*trans* & *cis*, 2H, bs), 2.48 (*trans* & *cis*, 1H, bs), 1.57-1.98 (*trans* & *cis*, 2H, bm), 1.10-1.45 (*trans* & *cis*, 2H, bm). $^{13}C$ NMR ($CD_2Cl_2$, 300 MHz): same as for Poly(**20**) (*vide infra*). IR (NaCl plate): same as for Poly(**20**) (*vide infra*).

**Poly(20).** $^1H$ NMR ($CDCl_3$, 400 MHz) δ 6.40, 6.03 (*cis* & *trans*, 1H, bs), 5.18-5.55 (*trans* & *cis*, 2H, bm), 3.88-4.08 (*trans* & *cis*, 2H, bm), 3.72 (*trans* & *cis*, 3H, s), 3.01, 2.65 (*cis* & *trans*, 2H, bs), 2.47, 2.38 (*cis* & *trans* 1H, bs), 2.17 (*trans* & *cis*, 1H, bs), 1.94, 1.84 (*cis* & *trans*, 1H, bs), 1.57-1.61 (*trans* & *cis*, 1H, bm), 1.15-1.20 (*trans* & *cis*, 1H, bm). $^{13}C$ NMR ($CD_2Cl_2$, 300 MHz) δ 176.12, 175.49, 171.97, 171.16, 170.79, 135.54, 134.96, 133.87, 133.04, 131.78, 128.77, 52.46, 51.76, 51.17, 50.86, 49.43, 48.30, 43.62, 42.99, 42.36, 41.48, 37.75, 37.55, 37.01, 36.73, 36.36, 36.15. IR (NaCl plate): 3300.0, 3082.1, 2947.2, 2843.4, 1752.4, 1648.6, 1534.4, 1437.7, 1404.7, 1363.2, 1259.4, 1202.4, 1181.6, 1031.1, 968.9, 844.3, 797.6, 750.9, 704.2 $cm^{-1}$.

**Poly(23).** $[M]_0$ was 0.6 M. $^1H$ NMR ($CD_2Cl_2$, 300 MHz) δ 6.43-6.81 (*trans* & *cis*, 1H, bs), 5.08, 5.31 (*trans* & *cis*, 2H, bs), 3.93 (*trans* & *cis*, 2H, bs), 3.67 (*trans* & *cis*, 3H, bs), 2.76 (*trans* & *cis*, 2H, bs), 2.36-2.60 (*trans* & *cis*, 2H, bm), 2.09 (*trans* & *cis*, 1H, bs), 1.82 (*trans* & *cis*, 1H, bs), 1.15-1.43 (*trans* & *cis*, 3H, bm). $^{13}C$ NMR ($CD_2Cl_2$, 300 MHz) δ 176.10, 175.98, 171.19, 171.10, 133.66, 133.34, 132.58, 54.50, 52.66, 42.98, 44.27, 41.70, 35.14, 32.11, 28.23,

28.27, 25.76, 23.19, 14.42. IR (NaCl plate): 3301.9, 3073.5, 2921.2, 2856.0, 1753.7, 1650.4, 1536.2, 1438.3, 1405.7, 1373.1, 1210.0, 1188.2, 1035.9, 1003.3, 965.3, 845.6, 704.3, 671.6 $cm^{-1}$.

**Polymer Stereoisomers**

**Using Initiator 1.** The polymerization of monomers **15**, **20**, and **21** with initiator **1** are described above.

**Using Initiator 2.** Monomers **15**, **20**, and **21** were polymerized with initiator **2** under identical conditions as with **1**, except that the mixtures were heated in a sealed dram in a 55 °C oil bath during polymerization. The *trans* to *cis* ratios were determined from the $^1H$ NMR spectra by integrating the peaks corresponding to the olefinic protons of the *trans* and *cis* polymers.