Supporting Information

Novel Cobalt-Catalyzed Carbonylation of 2-Aryl-2-Oxazolines

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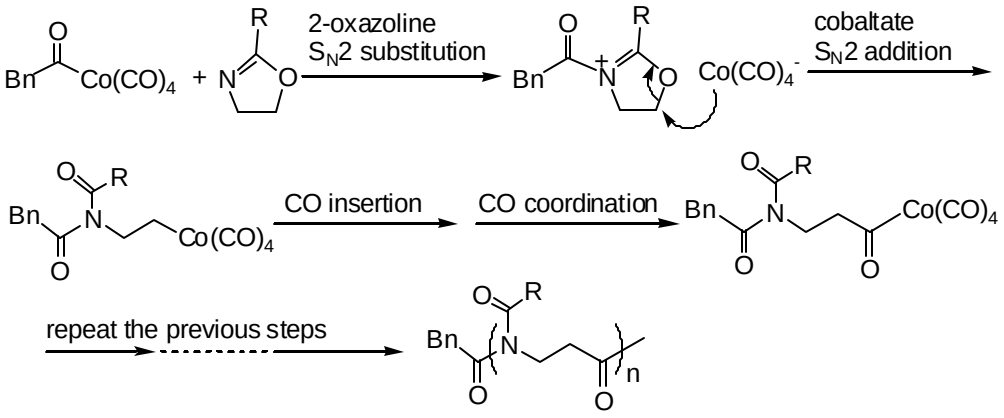
Mechanistic hypothesis for alternating copolymerization of CO and 2-oxazolines



Experimental

All manipulations were performed in a Vacuum Atmosphere DRI-LAB-08/85 dry box under a nitrogen atmosphere or using standard Schlenk line techniques. Diethyl ether, hexane and tetrahydrofuran (THF) were dried by refluxing over sodium/ benzophenone under nitrogen. Toluene was dried by refluxing over sodium under nitrogen. 2-Phenyl-2-oxazoline was purchased from Aldrich Chemicals. 2-(4-Tolyl)-2-oxazoline,[S1] 2-(2-Tolyl)-2-oxazoline,[S1] 2-(3-fluorophenyl)-oxazoline,[S1] 2-(2-furanyl)-oxazoline,[S1] 2-(2-thiophenyl)-2-oxazoline,[S1] 4-methyl-2-phenyl-2-oxazoline,[S2] 5-methyl-2-phenyl-2-oxazoline,[S2] and 2,5-diphenyl-oxazoline[S2, S3] were prepared following slightly modified literature procedures. The oxazolines are purified by standard techniques including reduced-pressure distillation, recrystallization, or sublimation. The liquid oxazolines were stored in Schlenk tubes over activated molecular sieves (4 Å) under nitrogen. The solid oxazolines were stored in the glove box. The pre-catalyst mixture of **1** and **2** were prepared by the literature procedure.[S4]

The ^{1}H NMR spectra and ^{13}C NMR spectra were recorded with an AMX 360 MHz or a DRX 500 MHz NMR spectrometer. Both the ^{1}H and ^{13}C chemical shifts were measured using the solvent resonances as internal references. GC/MS were obtained with a Hewlett Packard 5890 series instrument. The elemental analyses were performed by Galbraith Laboratories, Inc. HRFAB was obtained from the Biomedical and Bio-organic Mass Spectrometry Facility at Washington University in St. Louis.

General procedure of 2-oxazoline carbonylation. A 125 mL or 160 mL Parr bomb reactor was evacuated on a Schlenk line and backfilled with CO (1 atm). The 2-oxazoline substrate (7.6 mmol), the catalyst precursors **1** and **2** (0.38 mmol in 0.95 mL *n*-

hexane), and THF (50 mL) were transferred into the reactor with syringes under a gentle flow of CO. The reactor was immediately closed, and the pressure of CO was raised to 200 psi (1000 psi for the carbonylation of 2, 5-diphenyl-2-oxazoline). The reactor was heated in a 60 °C oil bath while being magnetically stirred for 48 h and then cooled to the ambient temperature. The CO pressure was slowly released in a hood, and the reactor was opened. The THF solution was transferred into a flask with a $CaCl_2$-drying tube attached to it and stirred for 2 h to allow aerobic decomposition and precipitation of the decomposed Co species. A mixture containing the crude carbonylation product and the starting material was obtained after removal of THF. The NMR-estimated yield of the reaction was obtained according to the ^{1}H NMR integration of the mixture at this point. The purification methods and spectroscopic information are described below.

***N*-Benzoyl-2-azetidinone.** The compound is isomeric to 2-phenyl-4,5-dihydro-1,3-oxazin-6-one. It was prepared following a literature procedure[S5] as a standard in order to rule out the possibility that the carbonylation product is the 4-member ring instead of the 6-member ring. ^{1}H NMR (20 ^{o}C, $CDCl_3$): ä 7.96 (d, J = 7.0 Hz, $C_6\underline{H}_5$), 7.56 (t, J = 7.0 Hz, 1H, $C_6\underline{H}_5$), 7.45 (t, J = 7.0 Hz, 2H, $C_6\underline{H}_5$), 3.77 (t, J = 5.5 Hz, 2H, $NC\underline{H}_2$), 3.10 (t, J = 5.5 Hz, 2H, $O{=}CC\underline{H}_2$). $^{13}C\{^1H\}$ NMR (20 ^{o}C, $CDCl_3$): ä 166.3, 163.9, 133.2, 131.9, 129.7, 128.2, 36.8, 35.1.

2-Phenyl-4,5-dihydro-1,3-oxazin-6-one. The carbonylation reaction was carried out following the aforementioned general procedure. The crude carbonylation product was extracted with *n*-hexane (50 mL). The volume of the solution was reduced to 20 mL. The solution was kept at –40 °C for crystallization. White needles were obtained after filtration. Isolated yield: 1.22 g (92%). ^{1}H NMR (20 ^{o}C, $CDCl_3$): ä 7.99 (d, J = 8.5 Hz,

2H, $C_6\underline{H}_5$), 7.49 (t, *J* = 8.5 Hz, 1H, $C_6\underline{H}_5$), 7.41 (t, *J* = 8.5 Hz, 2H, $C_6\underline{H}_5$), 3.87 (t, *J* = 7.0 Hz, 2H, $NC\underline{H}_2$), 2.69 (t, *J* = 7.0 Hz, 2H, $O{=}CC\underline{H}_2$). $^{13}C\{^1H\}$ NMR (20 ^oC, $CDCl_3$): ä 166.0, 154.0, 131.8, 130.4, 128.5, 127.6, 42.6, 28.3. MS: 175 (M^+). Anal. Calc. for $C_{10}H_9NO_2$: C, 68.56; H, 5.18; N, 8.00. Founded: C, 68.72; H, 5.61; N, 7.83. Comparison with the standard *N*-benzoyl-2-azetidinone prepared following the literature procedure of their NMR data rules out the possibility of *N*-benzoyl-2-azetidinone.

We further verified the identity of 2-phenyl-4,5-dihydro-1,3-oxazin-6-one by preparation and characterization of its derivative by methanolysis. The methanolyzed derivative, methyl 3-(benzoylamino)propionate, was prepared by dissolving 2-phenyl-4,5-dihydro-1,3-oxazin-6-one (1.0 g, 5.71 mmol) in methanol (50 mL) in a 100 ml Schlenk flask under nitrogen followed by stirring the solution for a day at the ambient temperature. After removal of methanol, the white crystalline product was obtained in quantitative conversion. The solid product was extracted with diethyl ether (50 mL). The solution was concentrated to 20 mL. Crystallization at –78 °C afforded a white crystalline solid. The analytically pure product was obtained after sublimation. Isolated yield: 0.95 g (80%). ^1H NMR (20 °C, $CDCl_3$): ä 7.75 (dt, *J* = 7.0, 1.5 Hz, 2H, $C_6\underline{H}_5$), 7.48 (tt, *J* = 7.0, 1.5 Hz, 1H, $C_6\underline{H}_5$), 7.41 (tt, *J* = 7.0, 1.5 Hz, 2H, $C_6\underline{H}_5$), 6.81 (br, 1H, $CON\underline{H}$), 3.73 (t, *J* = 7.0 Hz, 2H, $NC\underline{H}_2$), 3.70 (s, 3H, $OC\underline{H}_3$), 2.65 (t, *J* = 6.0 Hz, 2H, $C\underline{H}_2CO$). $^{13}C\{1H\}$ NMR (20 °C, $CDCl_3$): ä 173.3, 167.2, 134.3, 131.4, 128.5, 126.8, 51.8, 35.2, 33.6. MS: 207 (M^+). Anal. Calc. for $C_{11}H_{13}NO_3$: C, 63.76; H, 6.32; N, 6.76. Found: C, 63.96; H, 6.48; N, 6.64.

2-(*p*-Tolyl)-4,5-dihydro-1,3-oxazin-6-one. The carbonylation reaction was carried out following the aforementioned general procedure. The crude carbonylation product

was extracted with diethyl ether (50 mL). After removal of diethyl ether, the product was recrystallized from a mixture of toluene (10 mL) and hexane (20 mL) at -78 °C. The white crystalline compound collected after crystallization was further purified by sublimation at 50 °C. Isolated yield: 1.26 g (88%). ^{1}H NMR (20 °C, $CDCl_3$): ä 7.87 (d, *J* = 8.0 Hz, 2H, $CH_3C_6\underline{H}_4$), 7.21 (d, J = 8.0 Hz, 2H, $CH_3C_6\underline{H}_4$), 3.85 (t, *J* = 7.0 Hz, 2H, $NC\underline{H}_2$), 2.68 (t, *J* = 7.0 Hz, 2H, $O{=}C\underline{C}H_2$), 2.38 (s, 3H, $C\underline{H}_3$). ^{13}C{^{1}H} NMR (20 °C, $CDCl_3$): δ 166.1, 154.0, 142.2, 129.1, 127.5, 127.4, 42.5, 28.5, 21.4. MS: 189 (M^+). Anal. Calc. for $C_{11}H_{11}NO_2$: C, 69.83; H, 5.86; N, 7.40. Found: C, 69.91; H, 5.94; N, 7.40.

2-(*o*-Tolyl)-4,5-dihydro-1,3-oxazin-6-one. The carbonylation reaction was carried out following the aforementioned general procedure. The crude carbonylation product was extracted with diethyl ether (50 mL). The ether solution was evacuated to dryness, and the residual solid was washed with hexane (40 mL). Then, the solid was dissolved in diethyl ether (20 mL) again. The ether solution was kept at -78 °C for crystallization. The white product collected after crystallization was further purified by sublimation at 50 °C. Isolated yield: 0.13 g (9%). ^{1}H NMR (20 °C, $CDCl_3$): ä 7.69 (dd, *J* = 8.2, 1.5 Hz, 1H, $CH_3C_6\underline{H}_4$), 7.34 - 7.30 (m, 1H, $CH_3C_6\underline{H}_4$), 7.23 - 7.20 (m, 2H, $CH_3C_6\underline{H}_4$), 3.86 (t, J = 7.0 Hz, 2H, $NC\underline{H}_2$), 2.67 (t, *J* = 7.0 Hz, 2H, $O{=}CC\underline{H}_2$), 2.51 (s, 3H, $C\underline{H}_3$). ^{13}C{^{1}H} NMR (20 °C, $CDCl_3$): ä 166.0, 154.8, 138.0, 131.3, 130.6, 130.2, 129.1, 125.7, 42.8, 28.2, 21.4. MS: (189^+). Anal. Calc. for $C_{11}H_{11}NO_2$: C, 69.83; H, 5.86; N, 7.40. Found: C, 69.94; H, 5.95; N, 7.40.

2-(*m*-Fluorophenyl)-4,5-dihydro-1,3-oxazin-6-one. The carbonylation reaction was carried out following the aforementioned general procedure. The crude carbonylation

product was extracted with diethyl ether (50 mL). After removal of diethyl ether, the product was crystallized from a mixture of toluene (10 mL) and *n*-hexane (20 mL) at –78 °C. The crystallized product was further purified by sublimation at 50 °C. Isolated yield: 1.06 g (72%). ^{1}H NMR (20 °C, $CDCl_3$): 7.78 - 7.76 (m, 1H, $C_6\underline{H}_4F$), 7.70 - 7.67 (m, 1H, $C_6\underline{H}_4F$), 7.40 - 7.36 (m, 1H, $C_6\underline{H}_4F$), 7.20 - 7.16 (m, 1H, $C_6\underline{H}_4F$), 3.87 (t, J = 7.5 Hz, 2H, $NC\underline{H}_2$), 2.70 (t, J = 7.5 Hz, 2H, $O{=}CC\underline{H}_2$). $^{13}C\{^{1}H\}$ NMR (20 °C, $CDCl_3$): ä 165.5, 162.7 (d, $^{1}J_{C\text{-}F}$ = 246.6 Hz), 153.0 (d, $^{4}J_{C\text{-}F}$ = 3.5 Hz), 132.6 (d, $^{3}J_{C\text{-}F}$ = 8.0 Hz), 130.1 (d, $^{3}J_{C\text{-}F}$ = 8.0 Hz), 123.2 (d, $^{4}J_{C\text{-}F}$ = 3.0 Hz), 118.8 (d, $^{2}J_{C\text{-}F}$ = 21.4 Hz), 114.6 (d, $^{2}J_{C\text{-}F}$ = 24.0 Hz), 42.7, 28.2. MS: 193 (M^+). Anal. Calc. for $C_{10}H_8FNO_2$: C, 62.18; H, 4.17; N, 7.25. Found; C, 62.06; H, 4.26, N, 7.24.

2-(Furan-2-yl)-4,5-dihydro-1,3-oxazin-6-one. The carbonylation reaction was carried out following the aforementioned general procedure. The crude carbonylation product was extracted with diethyl ether (200 mL). The solvent was removed to result in a gray waxy solid. The solid was washed with *n*-hexane (40 mL) and was dissolved again in diethyl ether (30 mL). The ether solution was kept at -40 °C to afford a white crystalline solid, which was further purified by sublimation. Isolated yield: 0.40 g (32%). ^{1}H NMR (20 °C, $CDCl_3$, 360 MHz): ä 7.55 (d, J = 1.7 Hz, 1H, $C_4\underline{H}_3O$), 7.06 (d, J = 3.4 Hz, 1H, $C_4\underline{H}_3O$), 6.48 (dd, J = 3.4, 1.7 Hz, 1H, $C_4\underline{H}_3O$), 3.88 (t, J = 7.2 Hz, 2H, $NC\underline{H}_2$), 2.70 (t, J = 7.2 Hz, 2H, $O{=}CC\underline{H}_2$). $^{13}C\{^{1}H\}$ NMR (20 °C, $CDCl_3$): ä 165.0, 147.1, 146.0, 144.3, 114.8, 111.7, 42.6, 28.5. MS: 165 (M^+). Anal. Calc. for $C_8H_7NO_3$: C, 58.18; H, 4.27; N, 8.48. Found: C, 58.00; H, 4.37; N, 8.42.

2-(Thiophen-2-yl)-4,5-dihydro-1,3-oxazin-6-one. The carbonylation reaction was carried out following the aforementioned general procedure. The crude carbonylation

product was extracted with diethyl ether (50 mL). The solvent was removed, and the resulting solid was washed with *n*-hexane (40 mL). The product was then dissolved again in diethyl ether (30 mL). The solution was kept at -40 °C for crystallization. The crystallized product was further purified by sublimation at 50 °C. Isolated yield: 1.07 g (78%). ^{1}H NMR (20 °C, $CDCl_3$, 360 MHz): δ 7.61 (dd, *J* = 3.7 and 0.9 Hz, 1H, $C_4\underline{H}_3S$), 7.46 (dd, *J* = 5.0 and 0.9 Hz, 1H, $C_4\underline{H}_3S$), 7.07 (dd, *J* = 5.0 and 3.7 Hz, 1H, $C_4\underline{H}_3S$), 3.84 (t, *J* = 7.2 Hz, 2H, $NC\underline{H}_2$), 2.70 (t, *J* = 7.2 Hz, 2H, $O{=}CC\underline{H}_2$). $^{13}C\{^{1}H\}$ NMR (20 °C, $CDCl_3$): δ 165.4, 150.7, 134.2, 130.7, 130.1, 127.7, 42.6, 28.4. MS: 181 (M^+). Anal. Calc. for $C_8H_7NO_2S$: C, 53.02; H, 3.89; N, 7.73. Found: C, 52.68; H, 4.02; N, 7.66.

2-Phenyl-4-methyl-4,5-dihydro-1,3-oxazin-6-one. The carbonylation reaction was carried out following the aforementioned general procedure. The crude carbonylation product was extracted with *n*-hexane (50 mL). The volume of the solution was reduced to 20 mL. The solution was kept at -40 °C for crystallization. White needles were obtained after filtration. Isolated yield: 0.69 g (48%). ^{1}H NMR (20 °C, $CDCl_3$, 500 MHz): *ä* 8.00 (d, *J* = 7.5 Hz, 2H, $C_6\underline{H}_5$), 7.48 (t, *J* = 7.5 Hz, 1H, $C_6\underline{H}_5$), 7.41 (t, *J* = 7.5 Hz, 2H, $C_6\underline{H}_5$), 3.99 (m,1H, NCH), 2.77 (dd, *J* = 16.3, 5.5 Hz, 1H, $O{=}CC\underline{H}_2$), 2.40 (dd, *J* = 16.0, 9.0 Hz, 1H, $O{=}CC\underline{H}_2$), 1.38 (d, *J* = 7.0Hz, 3H, CH_3). $^{13}C\{^{1}H\}$ NMR (20 °C, $CDCl_3$): 166.1, 152.5, 131.7, 130.3, 128.4, 127.6, 49.0, 35.3, 21.4. MS: 189 (M^+). The above spectroscopic and analytical data are consistent with the literature report.[S6]

2-Phenyl-5-methyl-4,5-dihydro-1,3-oxazin-6-one. The carbonylation reaction was carried out following the aforementioned general procedure. The product was not isolated. NMR conversion: 8%. ^{1}H NMR (20 °C, $CDCl_3$, 500 MHz): *ä* 7.99-7.40 (m, 5H, C_6H_5), 3.90 (dd, *J* = 16.3Hz, 7.2Hz, 1H, NCH_2), 3.500 (dd, *J* = 16.0, 12.5 Hz, 1H,

NCH_2), 2.69 (m, 1H, COCHCH3), 1.32 (d, J = 7.0Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (20 °C, $CDCl_3$): 169.6, 154.0, 131.8, 130.4, 128.5, 127.5, 49.6, 33.4, 12.4. MS: 189 (M^+).

2,5-Diphenyl-4,5-dihydro-1,3-oxazin-6-one. The carbonylation reaction was carried out following the aforementioned general procedure expect that the CO pressure was 1000 psi. The crude product was extracted with diethyl ether (50 mL) at 0 °C. A white solid was obtained after removal of ether. The solid was sublimed at 80 °C to afford the desired product. Isolated yield: 1.15 g (60%). ^1H NMR (20 °C, $CDCl_3$): ä 8.02 (d, J = 8.5 Hz, 2H, $C_6\underline{H}_5CO$), 7.52 - 7.28 (m, 8H, 5H of 3-$C_6\underline{H}_5$ and 3H of $C_6\underline{H}_5CO$), 4.11 (dd, J = 16.3, 6.8 Hz, 1H, $COC\underline{H}C_6H_5$), 4.03 (dd, J = 16.3, 10.8 Hz, 1H, $NC\underline{H}_2$), 3.88 (dd, J = 10.8, 6.8 Hz, 1H, $NC\underline{H}_2$). $^{13}C\{^1H\}$ NMR (20 °C, $CDCl_3$): ä 167.2, 154.1, 134.1, 131.9, 130.2, 129.1, 128.5, 128.3, 128.2, 127.7, 49.6, 45.0. MS: 251 (M^+). Anal. Cacl. For $C_{16}H_{13}NO_2$: C, 76.48; H, 5.21; N, 5.57. Found: C, 76.41; H, 5.30; N, 5.55.

***trans*-*N*-Styrenyl-benzamide** (*trans*-PhCONHCH=CHPh). The title compound was the major byproduct of the carbonylation of 2, 5-diphenyl-oxazoline. A minor byproduct, which is presumably *cis*-PhCONHCH=CHPh, was not isolated or characterized. The ratio of the major byproduct and the desired product is a function of the CO pressure of the reaction. The ratio is 4 : 5 under 200 psi of CO and 13 : 83 under 1000 psi of CO. For the purpose of isolation and identification of the major byproduct, the reaction was carried out following the general procedure, i.e., under 200 psi of CO. The crude product was washed with diethyl ether (50 mL) at 0°C. The remaining solid after washing was dissolved in chloroform (15 mL). Diethyl ether (25 mL) was added into the chloroform solution as a poor solvent. The solution was then kept at -78 °C for crystallization. A

white powder was obtained after filtration. Isolated yield: 0.44 g (26%). The NMR data are consistent with literature report.[S7] MS: 223 (M^+).

High-Pressure NMR Tube Reaction

The pre-catalyst solution of **1** and **2** (7.6 μmol in 0.2 ml THF-d_8) and 2-phenyl-2-oxazoline (5μL, 38 μmol) was mixed in a 5 mm Wilmad high-pressure NMR tube in the glove box. The NMR tube was evacuated on a Schlenk line, pressurized with CO (200 psi), and heated in a 60 °C oil bath. The tube was shaken every ten minutes, and ^{1}H NMR was recorded every 1 or 2 hours. Toluene was observed as the reaction proceeded. A sample of toluene in THF-d_8 was prepared as the standard for comparison of the ^{1}H and ^{13}C chemical shifts with the spectra taken during the reaction.

Refereance

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