

Supplementary Material

Palladium(II)-Catalyzed Copolymerization of Styrenes with Carbon Monoxide: Mechanism of Chain Propagation and Chain Transfer

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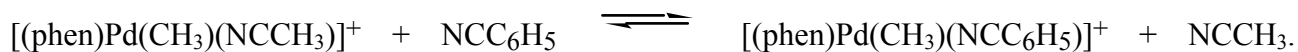
Kinetic Treatment: The following scheme describes the input into the Gear-Git program;

						k (min ⁻¹) ^a	
		4a	→	I		-0.01	
		4a	←	I		+1	
I	+	styrene	→	8a		+1	
		8a	→	5aσ,π		-0.01	
4a	+	styrene	→	9a	+	CO	+1
4a	+	styrene	←	9a	+	CO	+1.267 x 10 ⁸
8a	+	CO	→	3a	+	styrene	+8.45 x 10 ⁵
8a	+	CO	←	3a	+	styrene	+1

(a) A negative sign indicates that the rate constant was determined iteratively from the initial guess. A positive sign indicates a fixed rate constant. (b) **I** is the unsaturated intermediate "(phen)PdAc⁺" implicated in earlier studies. Fixed rate constants were arbitrarily fixed to larger values than the varying rate constants while maintaining the proper thermodynamic relationships (*vide supra*).

The initial concentrations of **4a**, **8a** and **5a** were estimated from standard single and double exponential curve fitting, appropriate for a simple A → B → C kinetic scheme. The initial concentrations of **9a** and **3a** were set at the observed values. The ratio [styrene]/[**4a**]₀ was used to calculate initial concentration of styrene. The initial concentration of CO was estimated from solving simultaneously the two equilibria represented by K₃ and K₄ for CO; it is essentially zero. The concentrations of palladium complexes were then normalized and the relative amounts of styrene and CO were input as initial values into the Gear-Git program: p**4a**₀ = 0.655; p**8a**₀ = 0.238; p**5a**₀ = 0.0366; p**9a**₀ = 0.0406; p**3a**₀ = 0.0297; pCO₀ = 1.21 x 10⁻⁶; pStyrene₀ = 9.6848; p**I**₀ = 1 x 10⁻⁸.

Equilibrium Constant Measurements: 3,5-(CF₃)₂Benzonitrile (2 μL; 4 μL) was added to a solution of CD₂Cl₂ (0.7 mL) and [(phen)Pd(CH₃)(NCC₆H₅)] [BArF] (10 mg, 7.6 x 10⁻⁶ mol) and the equilibrium constants determined at -66 °C: 2 μL, 1.2 equiv., K_{2μL} = 0.022; 4 μL: 2.51 equiv., K_{4μL} = 0.0223. K_{avg} = (0.0225 ± 0.0005) ΔG^o_{avg} = (1.56 ± 0.01) kcal/mol.



Benzonitrile (1 μL ; 1.5 μL) was added to a solution of CD_2Cl_2 (0.7 mL) and **1a** (7 mg, 5.6×10^{-6} mol) and the equilibrium constants determined at -66°C : 1 μL , 1.5 equiv., $K_{1\mu\text{L}} = 0.62$; 1.5 μL : 2.5 equiv., $K_{2\mu\text{L}} = 0.48$. $K_{\text{avg}} = (0.55 \pm 0.07)$ $\Delta G^\circ_{\text{avg}} = (0.25 \pm 0.05)$ kcal/mol.

Polymerizations

Poly(4-tert-Butylstyrene-*alt*-CO) prepared using 1a: The procedure for a typical TBS/CO copolymerization under 1 atmosphere of CO using **1a** will be presented here. A flame dried Schlenk flask was charged with 0.1 mM of **1a** and backfilled three times with CO. The catalyst was dissolved in CH_2Cl_2 (40 mL) to give a clear, colorless solution. Upon addition of 10 mL (0.055 M) of TBS, the solution turned clear light yellow. The polymerization rate was determined through measurement of CO uptake rates every fifteen minutes through the first two hours of the reaction. The reaction was stirred under 1 atm CO for 24 h and then precipitated in 1 L of methanol. The white powder was collected by suction filtration and washed five times with methanol. Solvent removal *in vacuo* gave 8.2 g (79 %) of syndiotactic copolymer with $M_n = 12,000$ and MWD = 1.7.

IR (CD_2Cl_2) $\nu_{\text{CO}} = 1708 \text{ cm}^{-1}$. ^1H NMR (400 MHz, CD_2Cl_2 , 20°C) δ 7.24 (d, $J = 8.4$ Hz, minor), 7.16 (d, $J = 8.4$ Hz, minor), 7.08 (2H, d, $J = 8.4$ Hz, major), 6.88 (d, $J = 8.4$ Hz, minor), 6.78 (d, $J = 8.4$ Hz, minor), 6.66 (2H, d, $J = 8.4$ Hz, major), 4.11 (br, m, CH), 3.06 (br dd, $J = 18, 7$ Hz), 2.64 (br dd), 1.24 (s, $\text{C}(\text{CH}_3)_3$). ^{13}C NMR (100 MHz, CD_2Cl_2 , 20°C) δ 206.9 (s, CO), 150.2 (s), 134.7 (s), 128.3 (d, $J_{\text{CH}} = 157$ Hz), 125.9 (d, $J_{\text{CH}} = 156$ Hz), 53.0 (d, $J_{\text{CH}} = 141$ Hz, CH), 43.4 (t, $J_{\text{CH}} = 128$ Hz, CH_2), 34.6 (s, $\text{C}(\text{CH}_3)_3$), 31.5 (q, $J_{\text{CH}} = 126$ Hz, $\text{C}(\text{CH}_3)_3$).

A similar procedure was used to generate Figure 1 and Table 1.

Poly(4-tert-Butylstyrene-*alt*-CO) prepared using 1a: The procedure for a typical TBS/CO copolymerization under high CO pressure using **1a** will be presented here. A solution of 0.2 mM of **1a** in 80 mL chlorobenzene was transferred under N_2 pressure to a Fisher-Porter reactor, where N_2 was replaced with CO. TBS (20 g, 124 mmol) was introduced, and the CO pressure was increased to 40 psi. During the reaction, which was allowed to continue at ambient temperature for 93 h, samples were withdrawn so that progress of the reaction, in terms of monomer conversion to polymer, could be determined. Polymers were collected and purified by methods outlined above. Percent conversion was determined by ^1H NMR spectroscopy, by integration of vinyl resonances of

the styrene and the three aliphatic absorptions of the polymer. These values were plotted against number-average molecular weights of the polymer isolated from these samples, as determined by gel permeation chromatography (Table 4). A similar procedure was used to generate Figure 2 and Table 5.

Table 1S. Molar Masses and Molar Mass Distributions as a Function of Conversion for TBS/CO Copolymerization Catalyzed by **1a** at 40 psi CO.

% conversion	Mn	Mw/Mn
9	9049	1.04
22	23223	1.04
24	26506	1.05
28	29498	1.05
41	40475	1.05
43	43105	1.05
50	44478	1.06
55	53186	1.06
57	55236	1.07
64	60149	1.08

Table 2S. Inverse Dependence of TOF on the Concentration of CO in the **1a** Catalyzed Copolymerization of TBS/CO. TOF was a Measure of Monomer Conversion at 26 °C in chlorobenzene.

Time (h)	% conv. (14.7 psia)	% conv. (40 psia)
21.5	30.4	10.3
29	38.1	13.5
45	51.4	19.2
52.5	54.5	22.1
70	62.5	28.6
77	65.5	30.6
96	70.2	35.1

Polymerization rate studies using substituted styrene monomers (Figure 3): In a typical copolymerization for this series of experiments, a flame dried 25 mL round bottom Schlenk flask was charged with 15 mg (0.012 mM) of **1a**. The Schlenk flask was backfilled three times with CO and the catalyst was dissolved in 8 mL of CH₂Cl₂. The reaction vessel was put in a water bath at 22 °C in order to maintain a constant temperature between runs. Styrene (4 mL, 0.035 mol) was syringed into the Schlenk flask and the solution was stirred at 500 r.p.m. Rate of CO uptake was taken every 15 min. for the first 2 h of the polymerization. Polymer was precipitated and isolated from methanol after 24 h. The conditions described are used for styrene, TBS, and 4-vinylanisole. In order to keep CO uptake rates rapid enough to measure every 15 min., the catalyst load was doubled for 4-chlorostyrene.

Table 3S. Rate of Copolymerization in a Series of Substituted Styrenes Versus σ^p

4-X-styrene	log(k _{obs})	σ^p
OMe	-0.489	-0.27
^t Bu	-0.551	-0.15
H	-0.729	0
Cl	-0.864	0.23

Rate of formation of **22 from **20a** (Figure 4):** A dry NMR tube was charged with 11 mg (8.1 x 10⁻⁶ M) of **20a** in the drybox and dissolved in 0.8 mL of CD₂Cl₂. TBS (14.7 μL) was syringed into the NMR tube at room temperature and the sample was immediately placed in the NMR probe and a spectrum was taken. Based on integration of signals from this spectrum, the exact number of equivalents of TBS in the sample was determined to be 12. Spectra were acquired approximately every 20 min. out to at least three half lives of **20a**. The rate of the reaction was followed through comparison of the integrals of the acyl methyl peak for both **20a** ($\delta = 2.50$) and the free enone **22** ($\delta = 2.32$). Similar experiments in which [**20a**] is held constant and [TBS] was varied were used to determine the effect of TBS concentration on the rate of free enone formation.

Table 4S. k_{obs} versus [TBS] for the formation of enone **22** from **20a**.

[TBS] (M)	k_{obs} (min^{-1})
0.07	0.0050
0.12	0.0108
0.13	0.0121
0.25	0.0235
0.35	0.0284
0.50	0.0376
0.67	0.0444
1.19	0.0899

Representative Copolymerization of TBS and CO in the presence of acetonitrile (Table 2 and Table 3). A 100-mL Schlenk flask was charged with **1a** (120.6 mg, 0.1 mmol) and vacuum degassed 3 times with CO. The white solid was dissolved in CO saturated CH_2Cl_2 (38.57 mL) and acetonitrile (1.43 mL, 27.3 mmol). To the homogenous solution TBS (10 mL, 54.6 mmol) was added and the reaction stirred for 20 h at ambient temperature. The reaction mixture was then poured into 500 mL of rapidly stirred methanol causing the precipitation of a white solid. The solid was collected, washed with methanol, and dried *in vacu* to afford 4.52 g of a white powder. GPC analysis: $M_n = 15,275$, $MWD = 1.57$.

