

Palladium-Catalyzed Nonalternating Copolymerization of Ethene and **Carbon Monoxide: Scope and Mechanism**

Rong Luo, David K. Newsham, and Ayusman Sen*

Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802

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A series of nonalternating ethene/carbon monoxide copolymers with very low carbon monoxide content were synthesized using a neutral palladium catalyst bearing a phosphine-sulfonate ligand. The ratio of the binding affinities of carbon monoxide and ethene to the palladium chelate complex ($P^{\circ}SO_{3}$)-

 $PdCH_2CH_2C(O)CH_3$ has been determined by NMR spectroscopy to be ~50:1 at 25 °C. The migratory insertions of ethene and carbon monoxide into the palladium methyl complex (P^{SO}3)- $PdCH_3(py)$ have also been examined by NMR spectroscopy, giving the following activation parameters: $\Delta G^{\dagger}(25 \,^{\circ}\text{C}) = 21.7 \,\text{kcal mol}^{-1} \,(\Delta H^{\ddagger} = 17.7(1) \,\text{kcal mol}^{-1} \,\text{and} \,\Delta S^{\ddagger} = -13.6(4) \,\text{eu})$ for ethene insertion; $\Delta G^{\ddagger}(25 \,^{\circ}\text{C}) = 13.0 \,\text{kcal mol}^{-1} \,(\Delta H^{\ddagger} = 16.6(8) \,\text{kcal mol}^{-1} \,\text{and} \,\Delta S^{\ddagger} = 20(434) \,\text{eu})$ for carbon monoxide insertion. Our study suggests that the unusually small difference in ethene and carbon monoxide binding affinities plays an important role in determining the copolymer composition.

Introduction

The palladium-catalyzed alternating copolymerization of ethene and carbon monoxide (CO) has been studied extensively over the last three decades.¹⁻⁵ The resultant polyketone is difficult to process because of its insolubility in common solvents and its high melting point (~ 260 °C) brought about by the interchain dipolar interaction between carbonyl groups present at 50 mol % in the copolymer. The problem of processability can be circumvented by lowering the carbon monoxide content in the copolymer. It has been suggested that incorporating as little as $\sim 5-10 \mod \%$ carbon monoxide into polyethene would be sufficient to impart such desirable properties as adhesion, paintability, and hardness without sacrificing its processability.¹ However, such materials are not attainable using conventional cationic palladium catalysts, which bear either a bidentate diphosphine ligand such as 1,3-bis(diphenylphosphino)propane (dppp) or a bidentate diimine ligand such as 1,10phenanthroline (phen), and produce strictly alternating ethene/carbon monoxide copolymers even at high ethene: carbon monoxide ratios.¹ While these catalysts are capable of oligomerizing⁶ or polymerizing⁷ ethene, consecutive ethene insertions are not observed in the presence of carbon monoxide due to the formation of a stable five-membered

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chelate following sequential carbon monoxide and ethene insertions, which can be opened by the strongly coordinating carbon monoxide, but not by ethene, as shown in Scheme $1.^{8-12}$ Consecutive carbon monoxide insertions are not observed for thermodynamic reasons.^{13,14}

Recently, first Drent¹⁵ and then we⁸ and others¹⁶ have reported on neutral palladium complexes with anionic phosphine-sulfonate ligands ($P^{\cap}SO_3^{-}$) that are able to form nonalternating ethene/carbon monoxide copolymers. The cause of consecutive ethene insertions has been ascribed to stereoelectronic destabilization of the five-membered chelate, which can then be disrupted by ethene,¹⁵ and to decarbonylation of the six-membered chelate (Scheme 1).^{17,18}

Herein, we report on the copolymerization of ethene with carbon monoxide to obtain copolymers with the full range of carbon monoxide incorporation: 1-50 mol %. Furthermore, we have examined, in detail, the mechanism of the

^{*}Corresponding author. E-mail: asen@psu.edu.

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 ${}^{a}R$ represents the growing polymer chain, and $L^{\cap}L$ represents a bidentate ligand.

nonalternating copolymerization through a combination of monomer-binding thermodynamics and monomer-insertion kinetics. These results show several key differences and similarities with traditional cationic alternating copolymerization catalysts^{10,19} and provide a more detailed explanation for the observed nonalternation in the phosphine-sulfonate-coordinated palladium system.



P^{SO_3} ligand

Results and Discussion

Bulk Polymerization. The combination of $P^{\circ}SO_{3}H$ and palladium acetate (Pd(OAc)₂) in situ yields an active catalyst for the copolymerization of ethene with carbon monoxide as summarized in Table 1. The copolymer composition can be controlled by varying the ethene:carbon monoxide feed ratio and temperature. Entries 2, 3, and 6 were conducted under the same reaction conditions with different carbon monoxide pressures. Increasing the pressure from 15 psig to 25 psig increased the carbon monoxide content in the final product from 6 mol % to 32 mol %. However, as noted previously,⁸ the copolymer yield decreased with decreasing carbon monoxide content. Entries 3, 4, and 5 were conducted

under the same reaction conditions, but at different temperatures. Increasing the reaction temperature from 80 °C to 110 °C decreased the carbon monoxide content of the copolymer from 28 mol % to 8 mol %. This temperature dependence was anticipated by Ziegler and co-workers on the basis of theoretical calculations for the ethene and carbon monoxide binding constants and the rate of decarbonylation.^{17,18}

Polymer Characterization. The nonalternating structure of the copolymers was confirmed by ¹H and ¹³C NMR spectroscopy, as shown in Figures 1 and 2. In the ¹H NMR spectra, the peak at 2.7 ppm was assigned to CH₂ in alternating copolymer segments. The peaks at 2.4 and 1.6 ppm were assigned to the CH₂ groups α and β to the carbonyl, respectively, for double ethene insertions. The peak at 1.3 ppm was assigned to ethene units not adjacent to a carbonyl group. In the ¹³C NMR spectra, multiple peaks near 210 ppm indicated multiple chemical environments for the carbonyl groups in the final product. Double, triple, and quadruple ethene insertions were also indicated by signals between 20 and 45 ppm. The chemical shift assignments are in good agreement with those previously reported for nonalternating copolymers of ethene with carbon monoxide.¹⁵

Differential scanning calorimetry showed a single melting point for all of the copolymers of ethene with carbon monoxide (Figure 3), confirming the formation of true copolymers. In copolymers with low carbon monoxide contents, the melting point decreased with increasing carbon monoxide incorporation, presumably due to the disruption of polyethene crystallinity. For example, increasing carbon monoxide content from 1 mol % to 28 mol % decreased the melting point from 125.3 °C to 115.9 °C.

It has been noted previously that the infrared spectra for solid samples of the alternating copolymer of ethene with carbon monoxide show an abnormally low carbonyl stretching frequency ($\nu_{\rm C=O} \approx 1695 \text{ cm}^{-1}$).²⁰ This phenomenon was attributed to the presence of intra- and interchain dipolar interactions between the carbonyl groups. Infrared spectra were collected for a series of copolymer samples with carbon monoxide incorporation ranging from 1 to 49 mol %. The corresponding carbonyl stretching frequency was observed to decrease from 1717 cm⁻¹ to 1689 cm⁻¹ with increasing carbon monoxide incorporation, consistent with dipolar interactions increasing with carbonyl concentration in the copolymer chain.

Mechanistic Study. In order to better understand the reactivity of the phosphine-sulfonate-based catalyst, we constructed a complete catalytic cycle for the nonalternating copolymerization of ethene with carbon monoxide, using the well-defined, square-planar model complex ($P^{\cap}SO_3$)Pd-CH₃(py), **1**.

Complex 1 was exposed to carbon monoxide at 50 psig in dichloromethane- d_2 and immediately formed palladium-acyl complex 2. Exposure of a solution of 2 in dichloromethane- d_2 to ethene at 80 psig and 50 °C for 5 min resulted in slow insertion of ethene into the palladium-acyl bond to give a mixture of the five-membered chelate (P^{SO}3)-

 $PdCH_2CH_2C(O)CH_3$, 3, and unreacted 2.

Exposure of **3** to ethene generated an equilibrium mixture of **3** and its open-chain, ethene-coordinated analogue, **4**. The

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Table 1. Copolymerization of Ethene with Carbon Monoxide Using the Catalyst Formed in Situa

entry	temp (°C)	CO (psig)	yield (g)	activity (g mmol·Pd ⁻¹ h ⁻¹)	$\begin{array}{c} \text{CO incorp.} \\ (\text{mol } \%)^b \end{array}$	$T_{\rm m}$ (°C)	$M_{\rm n}$	PDI ^c
1	90	0	0.657	4.38	0	125.4		
2	90	15	0.423	2.82	6	120.8		
3	90	20	0.327	2.18	10	117.9	4460	3.5
4	80	20	0.172	1.15	28	115.9		
5	110	20	0.696	4.64	8	120.2		
6	90	25	0.206	1.37	32	97.2	37555	2.1
7	110	25	0.740	4.94	9	118.8		

^{*a*} Reaction conditions: ethene, 300; Pd(OAc)₂, 0.1 mmol; $P^{O}SO_{3}H$, 0.1 mmol; $CH_{2}Cl_{2}$, 10 mL; 1.5 h. ^{*b*} Determined by ¹H NMR spectroscopy. ^{*c*} Determined by high-temperature GPC using polystyrene standards.



Figure 1. ¹H NMR spectrum of nonalternating polyketone with 10 mol % carbon monoxide incorporation in tetrachloroethane- d_2 .



Figure 2. ¹³C NMR spectrum of nonalternating polyketone with 10 mol % carbon monoxide incorporation (above) and an expansion of the methylene region (below) in tetrachloroethane- d_2 .



Figure 3. Melting transitions of copolymers of ethene and carbon monoxide.

presence of 4 was confirmed by ¹H NMR spectroscopy, which showed that the signal of the terminal methyl group shifted from 1.9 ppm to 1.4 ppm, and those of the CH₂ groups α and β to the metal center shifted from 1.3 ppm and 2.1 ppm to broad peaks at 0.8-1.1 and 1.5-1.7 ppm, respectively. As expected,⁹ coordinated ethene was not observed in the presence of excess monomer. The ³¹P NMR signal at 23.6 ppm was shifted to 27.0 ppm, and the ¹³C NMR carbonyl signal at 216 ppm was shifted to 201 ppm. The temperature-dependent equilibrium between 3 and 4 in dichloromethane- d_2 was monitored by ${}^{13}C$ NMR spectroscopy from -90 to -70 °C. The van't Hoff plot (see Supporting Information) gives $\Delta H^{\circ} = 0.68(7)$ kcal mol⁻¹ and $\Delta S^{\circ} =$ -1.1(3) eu. The calculated equilibrium constant K_1 at 25 °C is $0.548 \text{ L} \text{ mol}^{-1}$. Because impure 3 was used as a starting material, it is possible that residual 2 could influence the observed equilibrium by reaction with ethene to give 3, which would result in slight underestimation of K_1 if the rate of insertion were fast relative to ring-opening of the chelate. However, the rate of insertion is negligible in this temperature range.



Exposure of 3 to carbon monoxide generated an equilibrium mixture of 3 and its open-chain, carbon

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monoxide-coordinated analogue, 5. The presence of 5 was confirmed by ¹H NMR spectroscopy, which showed that the signal of the terminal methyl group shifted from 1.9 ppm to 1.4 ppm, and those of the CH₂ groups α and β to the metal center shifted from 1.3 and 2.1 ppm to broad peaks at 0.8–1.1 and 1.5–1.7 ppm, respectively. The ³¹P NMR signal at 23.6 ppm was shifted to 26.6 ppm, and the ¹³C NMR carbonyl signal at 216 ppm was shifted to 201 ppm. The temperature-dependent equilibrium between 3 and 5 in dichloromethane- d_2 was monitored by ${}^{13}C$ NMR spectroscopy from -90 to -70 °C. The van't Hoff plot (see Supporting Information) gives $\Delta H^{\circ} = 3.2(2)$ kcal mol⁻¹ and $\Delta S^{\circ} = 17.2(12)$ eu. The calculated equilibrium constant K_2 at 25 °C is 27.4 L mol⁻¹. In this case, although impure 3 was used as a starting material, the presence of the palladium-acyl complex 2 had no influence on the equilibrium because carbon monoxide is unreactive toward 2.



The rate of migratory insertion of ethene into palladiummethyl complex 1, $k_{\rm E}$, to give palladium-propyl complex 6 was determined by ¹H NMR spectroscopy. The presence of 6 was confirmed by ¹H NMR spectroscopy, which showed that the PdCH₃ signal shifted from 0.2 ppm to 1.0 ppm and was accompanied by the appearance of CH_2 groups α and β to the metal center at 0.8 and 1.3 ppm, respectively. The ³¹P NMR signal at 22.7 ppm was broadened and shifted to 27.1 ppm. First-order kinetics were observed under excess ethene, and the rate is zero-order in ethene. This indicates that migratory insertion is the rate-limiting step rather than coordination or pyridine displacement. The Eyring plot (see Supporting Information) gives activation parameters of $\Delta H^{\ddagger} = 17.7(1)$ kcal mol⁻¹ and $\Delta S^{\ddagger} = -13.6(4)$ eu, which are somewhat higher than those reported by Brookhart and co-workers for the analogous cationic dppp-ligated system $(\Delta H^{\ddagger} = 15.2(7) \text{ kcal mol}^{-1}, \Delta S^{\ddagger} = -6.2(29) \text{ eu}).^{19} \text{ Our observation is consistent with the suggestion by Rieger that}$ a higher energy barrier for ethene insertion may account for the low activity of the neutral phosphine-sulfonate system compared to the traditional cationic systems.¹⁶ Unlike the dppp system, β -H elimination of propene was not observed.



The rate of migratory insertion of carbon monoxide into palladium-methyl complex 1, k_{CO} , to give palladium-acyl complex 7 was also determined by ¹H NMR spectroscopy. The presence of 7 was confirmed by ¹H NMR spectroscopy, which showed that the PdCH₃ signal at 0.2 ppm was replaced

by PdC(O)CH₃ at 1.8 ppm. The ³¹P NMR signal at 22.7 ppm was broadened and shifted to 11.4 ppm. Second-order kinetics were observed under excess carbon monoxide, and the rate is first-order in carbon monoxide. The Eyring plot (see Supporting Information) gives activation parameters of $\Delta H^{\ddagger} = 16.6(8)$ kcal mol⁻¹ and $\Delta S^{\ddagger} = 20.0(434)$ eu, which are again somewhat higher the parameters for the analogous cationic dppp-ligated system reported by Brookhart and coworkers ($\Delta H^{\ddagger} = 14.8(7)$ kcal mol⁻¹ and $\Delta S^{\ddagger} = 0.1(4)$ eu).¹⁹ The rate law also differs from the cationic dppp system, which was observed by Brookhart and co-workers to be first-order overall and zero-order in carbon monoxide.19 This suggests that, unlike the conversion of 1 to 6, the rate-limiting step is not the migratory insertion of the monomer, but rather the associative displacement of pyridine from 1.



These results suggest that the principal difference between the neutral phosphine-sulfonate system and the traditional cationic systems is the unusually small difference in the binding affinity of carbon monoxide and ethene in the former.^{10,19} The ratio of the carbon monoxide and ethene binding constants (K_2 : K_1) is ~50:1 at 25 °C, compared to ~10⁴:1 for cationic palladium complexes bearing a bidentate nitrogen ligand¹⁰ or a bidentate phosphine ligand.¹⁹ As discussed by others,^{18,19} the extent of double ethene insertion is controlled, in part, by the equilibrium ratio of the palladium-alkyl carbonyl (**8**) to palladium-alkyl olefin (**9**) complexes, K_{eq} , and the relative rates of migratory insertion for these two species, K_{CO} and K_E , respectively. The factors controlling the ratio of alternating to nonalternating propagation are illustrated by Scheme 2 and eq 1.

$$\frac{\text{alternation}}{\text{nonalternation}} = K_{\text{eq}} \left(\frac{k_{\text{CO}}}{k_{\text{E}}} \right)$$

$$\approx \left(\frac{[\mathbf{8}]}{[\mathbf{9}]} \right) \left(\frac{k_{\text{CO}}}{k_{\text{E}}} \right)$$

$$= \left(\frac{K_2 \times [\text{CO}]}{K_1 \times [\text{C}_2\text{H}_4]} \right)$$

$$\times \left(\frac{(1730 \text{ L mol}^{-1} \text{ s}^{-1}) \times [\text{CO}]^1}{(6.11 \times 10^{-4} \text{ s}^{-1}) \times [\text{C}_2\text{H}_4]^0} \right)$$

$$= \left(\frac{(27.4 \text{ L mol}^{-1}) \times (7.3 \times 10^{-3} \text{ mol } \text{ L}^{-1})}{(0.584 \text{ L mol}^{-1}) \times (0.11 \text{ mol } \text{ L}^{-1})} \right)$$

$$\times \left(\frac{(1730 \text{ L mol}^{-1} \text{ s}^{-1}) \times (7.3 \times 10^{-3} \text{ mol } \text{ L}^{-1})}{(6.11 \times 10^{-4} \text{ s}^{-1})} \right)$$

$$= 6.4 \times 10^4 \tag{1}$$

Equation 1 shows the estimation of the ratio of alternating to nonalternting propagation during copolymerization of ethene with carbon monoxide (conditions: 0.5 atm ethene, 0.5 atm carbon monoxide, 25 °C; monomer concentrations are those reported by Rix and co-workers¹⁰).

Scheme 2. Kinetics of Nonalternating Copolymerization of Ethene with Carbon Monoxide^{*a*}



 a R represents the growing polymer chain, and P^OO represents the phosphine-sulfonate ligand.

The equilibrium constant, K_{eq} , was estimated from the ratio of [8]:[9] multiplied by the ratio of [CO]:[C₂H₄] in dichloromethane at 25 °C with a partial pressure of 0.5 atm for each monomer. The propagation rates were extrapolated from the Eyring plots obtained from the kinetics of migratory insertion of carbon monoxide and ethene. From eq 1, it is apparent that the favorable K_{eq} is offset by the slow rate of ethene insertion since one would expect a double ethene insertions under these conditions. Although this is more frequent than either the ~10⁵ reported for the bidentate diphosphine system.¹⁰ it is still effectively alternating.

Although this model system has previously shown functional group tolerance and polymerization activity similar to the system prepared in situ,^{8,21} these results indicate that significant differences exist between the two. We propose three likely reasons for this discrepancy. First, the presence of the pyridine ligand may affect the apparent K_{eq} by establishing an equilibrium between the pyridine- and monomer-coordinated palladium species. Second, the rates of monomer insertion observed for palladium-methyl complex 1 may differ significantly from those of complexes 8 and 9. In particular, the kinetics of ethene insertion into the Pd-CH₃ bond of 1 is unlikely to be representative of ethene insertion into the palladium-carbon bond of a growing polymer chain. These first two concerns could be circumvented by working with pure samples of complex 3. However, while 3 has been reported,²² we were unable to isolate a sample pure enough for NMR studies. Finally, eq 1 assumes that decarbonylation occurs to a negligible extent. The reversibility of carbon monoxide insertion has been addressed by Ziegler and co-workers, ^{17,18} who calculated that the deinsertion of carbon monoxide from the copolymer chain (PdC(O)R) followed by ethene coordination and insertion leads to decreased incorporation of carbon monoxide.

Previously, we observed decarbonylation in compound 2.⁸ However, we did not determine conclusively whether the $(P^SO_3)PdC(O)CH_2CH_2C(O)CH_3$ species exists in its open or chelate form because the presence of monomer is sufficient to disrupt the chelate. A direct comparison of the rates of decarbonylation of the palladium-acyl species in the neutral, phosphine-sulfonate complex $(P^SO_3)Pd^{13}C(O)CH_3(py)$ and its cationic analogue (dppp) $Pd^{13}C(O)CH_3(py)^+BF_4^$ was performed. The rate of decarbonylation, $k_{obs(CO)}^{-1}$, was measured by using ¹³C NMR spectroscopy to observe the loss of ¹³C enrichment in the palladium-acyl species, 7, and its dppp-bearing analogue in the presence of natural carbon monoxide.

The neutral phosphine-sulfonate system was found to have an approximate $k_{obs(CO)}^{-1}$ of 5.6 × 10⁻⁶ s⁻¹, while the cationic diphosphine system was found to have an approximate $k_{obs(CO)}^{-1}$ of 2.8× 10⁻⁵ s⁻¹. Thus, the classic cationic system actually undergoes decarbonylation with exchange more readily than the phosphine-sulfonate system. However, again, our model system differs from the system acting in situ because the rate of decarbonylation in the cationic diphosphine system may be reduced by the formation of six-membered chelates (see Scheme 3). Ziegler and coworkers showed that, unlike the cationic diphosphine system, the neutral, sterically demanding metal center of the phosphine-sulfonate system does not readily form a sixmembered chelate with the growing polyketone chain. In this scenario, decarbonylation of a neutral phosphine-sulfonate complex would not require the disruption of a chelate and, consequently, would have a lower ΔH^{\dagger} . Furthermore, because a decarbonylation event can affect the copolymer composition only if it is followed by exchange between carbon monoxide and ethene $(8 \rightarrow 9)$ and the subsequent insertion of the latter, the higher relative binding affinity of ethene in the phosphine-sulfonate system (i.e., low K_{eq}) may enhance the effective rate of decarbonylation. Ultimately, further study will be required to fully quantify the effect of decarbonylation on the catalytic cycle.

The very different coordinating abilities of the two ends of the phosphine-sulfonate ligand pose an interesting mechanistic problem. It has been shown that the removal or the substitution of the sulfonate group by a carboxylate functionality strongly attenuates²³ catalysis. According to Ziegler,¹⁷ because of the stronger *trans* effect of the phosphine, the complex is most stable when the Pd-C bond in the growing polymer chain is located *cis* to the phosphine. As discussed previously, the crystal structures of 1 and 2 bear this out.⁸ However, the insertion barrier is much lower when the Pd-C bond in the growing polymer chain is located *trans* to the phosphine. Thus, the overall polymerization may proceed through the following series of steps: (a) coordination of a monomer to the complex with the Pd-C bond cis to the phosphine, (b) isomerization to the complex with the Pd-C bond trans to the phosphine, and (c) migratory insertion of the monomer to re-form the complex with the Pd-C bond *cis* to the phosphine. As shown in Scheme 4, the *cis-trans* isomerization may be viewed as a pseudorotation, and the ability of the sulfonate group to coordinate through multiple oxygens may to aid this process. We are currently investigating this possibility.

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Scheme 3. Decarbonylation of a Copolymer Chain^a



^{*a*} If a six-membered chelate is formed between the metal center and the growing polymer chain, it acts as a trapping ligand and must be disrupted before decarbonylation can proceed. R represents the growing polymer chain, and $L^{\cap}L$ represents a bidentate ligand.

Scheme 4. Possible Mechanism for the Isomerization of the Catalytic Species from the Complex with the Pd-C Bond *cis* to the Phosphine to the Complex with the Pd-C Bond *trans* to the Phosphine That Begins with a Pseudorotation of the Phosphine-Sulfonate Ligand^a



^a R represents the growing polymer chain, and L represents a coordinated monomer.

Conclusions

We have demonstrated the synthesis of a series of nonalternating copolymers of ethene with carbon monoxide using a neutral palladium catalyst bearing a phosphinesulfonate ligand. It is possible to control the degree of carbon monoxide incorporation from 0-50 mol % by varying the monomer feed ratio and reaction temperature.

By examining the kinetic and thermodynamic parameters, we found that the catalyst displays an unusually small difference in its binding affinities for ethene and carbon monoxide. However, the difference in monomer binding affinity alone is not sufficient to explain the degree of nonalternation actually observed in this system. It appears that decarbonylation also plays a significant role in the nonalternation. Unlike the traditional cationic palladium complexes that catalyze the alternating copolymerization, the neutral complex formed from the anionic ligand disfavors the formation of Pd-O chelates by coordination of the carbonyl group on the growing polymer chain. This, in turn, facilitates ethene coordination to the metal and subsequent insertion. We also found that the rate of decarbonylation in the traditional cationic diphosphine system is higher than in the neutral phosphine-sulfonate system when chelation is absent.

Experimental Procedures

Chemical manipulations, with the exception of polymer workup and analysis, were performed under a dry nitrogen atmosphere using a glovebox or Schlenk techniques. All solvents, with the exception of NMR solvents, were distilled over CaH₂ and degassed using the freeze-pump-thaw technique. Ultra-high-purity ethene and ultra-high-purity carbon monoxide were obtained from MG Industries and used without further purification. Deuterated NMR solvents and ¹³CO were obtained from Cambridge Isotope Laboratories and used without further purification. Palladium acetate (99%) was purchased from Johnson Matthey and used as received. The phosphinesulfonate ligand was synthesized by following the literature procedure.¹⁵ Palladium-methyl complex **1** was synthesized by following the literature procedure.⁸

Nuclear magnetic resonance spectroscopy was performed using a Bruker DPX-300 spectrometer equipped with a variable-temperature, multinuclear probe at 300.13 MHz for ¹H, 121.49 MHz for ³¹P, or 75.4 MHz for ¹³C NMR spectra. ³¹P and ¹³C spectra were obtained with proton decoupling. Quantitative ¹³C experiments were performed using a *zgig* pulse sequence and a delay of 120 s before each scan. High-pressure NMR tubes were obtained from Wilmad with a Quick Pressure Valve, 5 mm diameter, 0.77 mm wall thickness, and an 8 in. length.

NMR data for 1: ¹HNMR (CD₂Cl₂): δ (ppm) 0.22 (d, 3H, PdCH₃); 3.68 (s, 6H, OCH₃); 6.99 (dd, 2H, Ar); 7.06 (b, 2H, Ar); 7.36 (m, 2H, Ar); 7.50 (m, 3H, Ar); 7.58 (t, 2H, Ar); 7.92 (t, 1H, Ar); 8.06 (dd, 1H, Ar); 8.75 (dd, 2H, Py). 31 P NMR (CD₂Cl₂): δ 23.4 ppm. 2: ¹H NMR (CD₂Cl₂): δ (ppm) 1.84 (s, 3H, PdC-(O)CH₃); 3.78 (s, 6H, OCH₃); 7.03 (dd, 2H, Ar); 7.10 (m, 2H, Ar); 7.34 (m, 2H, Ar); 7.53 (m, 3H, Ar); 7.60 (m, 2H, Ar); 7.77 (m, 2H, Ar); 7.95 (t, 1H, Ar); 8.09 (dd, 1H, Ar); 8.81 (d, 2H, Py); ³¹P NMR (CD₂Cl₂): δ 11.0 ppm. ¹³C NMR (CD₂Cl₂): δ 227 ppm (PdC(O)CH3). 3: ¹H NMR (CD₂Cl₂): δ (ppm) 1.30 (m, 2H, PdCH₂CH₂C(O)CH₃); 1.89 (s, 3H, PdCH₂CH₂C(O)CH₃); 2.11 (b, 2H, PdCH₂CH₂C(O)CH₃); 3.70 (s, 6H, OCH₃); 7.02 (dd, 2H, Ar); 7.09 (dd, 2H, Ar); 7.34 (m, 2H, Ar); 7.50 (dd, 3H, Ar); 7.59 (t, 2H, Ar); 7.67 (b, 2H, Ar); 7.90 (t, 1H, Ar); 8.09 (m, 1H, Ar); 8.79 (d, 2H, Py). ³¹P NMR (CD₂Cl₂): δ 23.6 ppm. ¹³C NMR (CD₂Cl₂): δ 216 ppm (PdCH₂CH₂C(O)CH₃). 4: ¹H NMR $(CD_2Cl_2, -70 \text{ °C}): \delta$ (ppm) 0.8–1.1 (b, 2H, $(PdCH_2CH_2 C(O)CH_3$; 1.4 (s, 3H, PdCH₂CH₂C(O)CH₃); 1.5-1.7 (b, 2H, PdCH₂CH₂C(O)CH₃); 3.6 (b, 3H, OCH₃); 3.8 (b, 3H, OCH₃); 5.4 (s, free ethene); 6.7-8.0 (17H, Ar); 8.7 (b, 1H, Py); 8.8 (b, 1H, Py). ³¹P NMR (CD₂Cl₂, -70 °C): δ 27.0 ppm. ¹³C NMR (CD₂Cl₂, -70 °C): δ 201 ppm (PdCH₂CH₂C(O)CH₃). **5**: ¹H NMR (CD₂Cl₂, -70 °C): δ (ppm) 0.8–1.1 (b, 2H, (PdCH₂-CH₂C(O)CH₃); 1.4 (s, 3H, PdCH₂CH₂C(O)CH₃); 1.5-1.7 (b, 2H, PdCH₂CH₂C(O)CH₃); 3.6 (b, 3H, OCH₃); 3.8 (b, 3H, OCH₃); 6.7–8.0 (17H, Ar); 8.7, 8.8 (b, 2H, Py). ³¹P NMR (CD₂Cl₂, -70 °C): δ 26.6 ppm. ¹³C NMR (CD₂Cl₂, -70): δ 201 (PdCH₂CH₂C(O)CH₃). 6: ¹H NMR (CD_2Cl_2): δ (ppm) 0.8 (b, 2H, PdCH₂CH₂CH₃) 1.0 (b, 3H, PdCH₂CH₂CH₃) 1.3 (b, 2H, PdCH₂CH₂CH₃) 3.7 (s, 6H, OCH₃); 5.5 (s, free ethene); 6.9–8.2 (17H, Ar); 8.8, 8.9 (b, 2H, Py). ³¹P NMR (CD₂Cl₂): δ 27.1 ppm. 7: ¹H NMR (CD₂Cl₂): δ (ppm) 1.76 (s, 3H, PdC(O)CH₃); 3.73 (s, 6H, OCH₃); 7.00 (dd, 2H, Ar); 7.09 (b, 2H, Ar); 7.34 (dd, 2H, Ar); 7.50 (m, 3H, Ar); 7.60 (t, 2H, Ar); 7.93 (t, 1H, Ar); 8.03 (dd, 1H, Ar); 8.73 (d, 2H, Py). ³¹P NMR (CD₂Cl₂): δ 11.4 ppm. ¹³C NMR (CD₂Cl₂): δ 227 ppm $(PdC(O)CH_3).$

Differential scanning calorimetry was performed by heating 3 mg of copolymer samples at a rate of 20 $^{\circ}$ C min⁻¹ from 40 to 300 $^{\circ}$ C using a TA Instruments model DSC Q100.

Infrared spectroscopy was performed using a Varian FTS 7000 series DigiLab FT-IR spectrometer equipped with a ceramic IR source, KBr beamsplitter, deuterated triglycine sulfate detector, and 632.8 nm HeNe laser with a 5 kHz laser modulation frequency. The sample chamber was flushed with dry nitrogen, and data were collected from 4000 to 900 cm⁻¹ with a resolution of 1 cm⁻¹.

Bulk polymerization reactions were carried out in an open 50 mL serum bottle placed in a 125 mL autoclave with magnetic stirring. The bottle was charged with 22 mg (0.10 mmol) of Pd(OAc)₂, 40 mg (0.10 mmol) of P $^{\circ}$ SO₃H ligand, and 10 mL of dichloromethane. The bottle was placed in the autoclave and removed from the glovebox. The autoclave was then charged with the desired amounts of ethene and carbon monoxide. The autoclave was placed in an oil bath with magnetic stirring for 1.5 h. At the end of this period, the autoclave was cooled to room temperature, vented to the atmosphere, and opened. The resulting polymer was precipitated into acidified methanol, collected by vacuum filtration, and dried under high vacuum overnight before analysis. Polymers were dissolved in tetrachloroethane- d_2 at 100 °C for NMR analysis. Carbon monoxide incorporation was determined by the integration of the CH₂

protons using the formula

$$[CO] = \frac{A+B}{2A+2B+C+D}$$
(2)

where A is the integral of the peak at 2.7 ppm corresponding to ethene units adjacent to two carbonyl units; B and C are the integrals of the peaks at 2.4 and 1.6 ppm corresponding to CH₂ protons α and β to the carbonyl, respectively, in ethene units adjacent to one carbonyl unit (double insertion); and D is the integral of the peak at 1.3 ppm corresponding to ethene units not adjacent to a carbonyl unit (multiple insertion).

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Supporting Information Available: Thermodynamic and kinetic data and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.