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Inhibitory Role of Carbon Monoxide in Palladium(II)-Catalyzed Nonalternating Ethene/Carbon Monoxide Copolymerizations and the Synthesis of Polyethene-*block*-poly(ethene-*alt*-carbon monoxide)

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Summary: We report the first well-defined palladium-based system for the living homopolymerization of ethene, as well as the living copolymerization of ethene with carbon monoxide. We demonstrate this by the synthesis of polyethene-block-poly-(ethene-alt-carbon monoxide). In addition, it has been possible to monitor chain growth by sequential insertions of carbon monoxide and ethene into palladium−carbon bonds. The mechanistic studies have also allowed us to pinpoint the hitherto not well-understood reason for the general failure to obtain alkene/carbon monoxide copolymers with low carbon monoxide content.

The palladium-catalyzed *alternating* copolymerization of ethene with carbon monoxide (CO) has been widely studied.[1] The processing of the resultant polyketone (*alt*-PK) is problematic due to its insolubility in common solvents and its very high melting point (~265 °C), both of which result from high crystallinity brought about by dipolar interactions between carbonyl groups present at 50 mol % in the copolymer. The problem of processibility can be circumvented by lowering the CO content in the copolymer by producing *nonalternating* copolymers. It has been suggested that as low as 5−10 mol % CO incorporation into polyethene would be sufficient to impart such desirable properties as adhesion, paintability, and hardness without sacrificing the processibility associated with polyethene.[1] However, traditional catalysts for the production of alkene/CO copolymers do not yield materials with <50 mol % CO even at high alkene:CO feed ratios.[1] There are several reasons for the strict alternation observed with conventional catalysts: CO binds more strongly to the active palladium species and inserts more readily into the Pd−alkyl bond than ethene does; however, successive insertions of CO (i.e., insertion of CO into a Pd−acyl bond) are thermodynamically disfavored.

Recently, a system that generates nonalternating ethene/CO copolymers (*nonalt*-PK) with as little as 35 mol % CO has been reported, and it employs the anionic phosphine ligand (P~SO_3^-) shown below.[2,3] Additionally, the same system polymerizes ethene to linear polyethene (PE) unlike conventional phosphine- or imine-ligated palladium systems. A key unanswered mechanistic question is why copolymers with the full range of CO incorporation from 0 to 50 mol % cannot be synthesized using this system by simply raising the alkene:CO feed ratio. Herein, we address this question and demonstrate that it is possible to produce *nonalt*-PK with as low as 10 mol % CO, albeit in low yields. Further, using a well-defined palladium complex with this ligand, we demonstrate the first catalytic system for the living polymerization of *both* PE and *alt*-PK, thereby allowing the synthesis of the block copolymer: polyethene-*block*-poly-(ethene-*alt*-carbon monoxide).

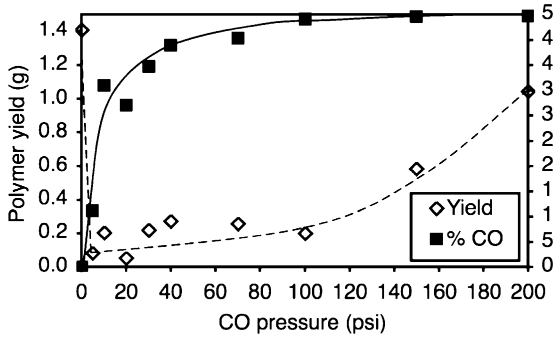
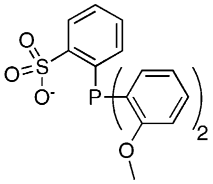


Figure 1. Effect of carbon monoxide pressure on polymer yield and composition. Curves merely guide the eye. Reaction conditions: $Pd_2(dba)_3$, 10 μmol; (P~SO_3H), 20 μmol; C_2H_4, 300 psi; CH_2Cl_2, 20 mL, 75 °C, 3 h.



P~SO_3^- ligand

The addition of small amounts of CO to the monomer feed during ethene homopolymerization using the original (P~SO_3^-)-based system caused a dramatic reduction in activity despite the system's ability to produce PE, *nonalt*-PK, and *alt*-PK. However, it was possible to produce *nonalt*-PK incorporating as little as 10 mol % CO by adding only 5 psi (35 kPa) CO into an autoclave with 300 psi (2070 kPa) ethene (see Figure 1). This lowered the melting point of the copolymer to 118 °C, as determined by DSC. The activity of the system could be improved by increasing the CO pressure but not without restoring the near-alternating character of the resulting copolymer. The relationship between CO pressure, yield, and composition is consistent with the mechanism originally proposed for

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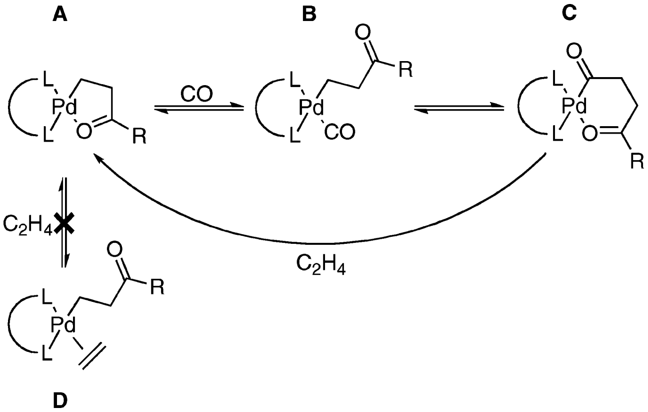
Scheme 1. General Catalytic Cycle for Ethene/Carbon Monoxide Copolymerization[1,4]



the classical alternating copolymerization system (see Scheme 1).[1,4] As shown, a chelate resting state (**A**) exists in the catalytic cycle and, unlike CO, the more weakly coordinating ethene is less able to disrupt the chelate (**A** → **D**), a requirement for sequential ethene insertions; note that this issue does not arise in ethene *homo*polymerization. However, CO binding is strong enough to disrupt the chelate, leading to further insertions (**A** → **B** → **C** → **A**). Thus, with conventional alternating copolymerization catalysts, CO is required for the alkene insertion step to proceed.

We sought to look for a stable chelate similar to **A** in Scheme 1 for the present system in order to confirm that it proceeds via the same general mechanism as bis-phosphine-ligated systems. The active species in the original catalytic system reported by Drent and Pugh (prepared *in situ* from $Pd(OAc)_2$ and $P{\sim}SO_3H$) was not well-defined.[2] Therefore, we used a model compound with a methyl group and pyridine occupying two coordination sites, *cis*-$(P{\sim}SO_3)Pd(Me)(Py)$, **1**. This species was synthesized and characterized by ^1H and ^{31}P NMR and IR spectroscopy and single-crystal X-ray diffraction as described in the Supporting Information. The ORTEP structure is shown in Figure 2. All reactions were carried out in dichloromethane to maintain solubility of the products. When **1** in CD_2Cl_2 was exposed to 100 psi (690 kPa) ethene at 25 °C, PE was produced. The ethene polymerization has living characteristics under these conditions, and the chain growth was monitored by ^1H NMR spectroscopy. The growth of the PE peak at 1.3 ppm was not accompanied by any signals in the vinyl region that would indicate chain termination by β-hydrogen abstraction. Also, CH_2 groups α and β to the Pd center were seen respectively as multiplets at 0.8 and 0.6 ppm, along with the methyl end group at 0.9 ppm.

When **1** was exposed to a mixture of 50 psi (345 kPa) CO and 50 psi (345 kPa) ethene in CD_2Cl_2 at 25 °C, *alt*-PK was formed. As with ethene homopolymerization, it was possible to observe stepwise insertion of CO (or ^{13}CO for ^{13}C NMR experiments) and ethene into the growing, methyl-terminated co-oligomer. To accomplish this, **1** was first exposed to 15 psi (105 kPa) CO, causing the immediate formation of *cis*-$(P{\sim}SO_3)Pd(COMe)(Py)$, **2**. The ^1H NMR signal for $Pd{-}CH_3$ at 0.2 ppm was replaced by the $Pd{-}COCH_3$ signal at 1.8 ppm. Also, the ^{31}P signal at 23 ppm was replaced by a signal at 11 ppm and a ^{13}C carbonyl signal appeared at 227 ppm. IR analysis showed a carbonyl absorption at 1695 cm^{-1}. Single-crystal X-ray diffraction data were also collected as described in the Supporting Information. The ORTEP structure is shown in Figure 2. The Pd−carbon bond in both **1** and **2** is found *cis* to the coordinated phosphine moiety, presumably because of the stronger *trans* effect of phosphorus compared to oxygen. The insertion of CO into the Pd−C bond of **1** was found to be reversible, as shown by the following experiment. First, $(P{\sim}SO_3)Pd(^{13}COMe)(Py)$ was formed by the insertion of ^{13}CO, as confirmed by a strong carbonyl ^{13}C NMR signal at 227 ppm. The solvent and excess ^{13}CO were removed under vacuum, and the product was redissolved in CD_2Cl_2 before being exposed to 50 psi (345 kPa) of regular ^{12}CO. After 18 h, ^{13}C NMR analysis showed a lack of ^{13}C enrichment in the Pd complex, indicating slow decarbonylation of ^{13}CO followed by rapid insertion of ^{12}CO as predicted by Ziegler.[5]

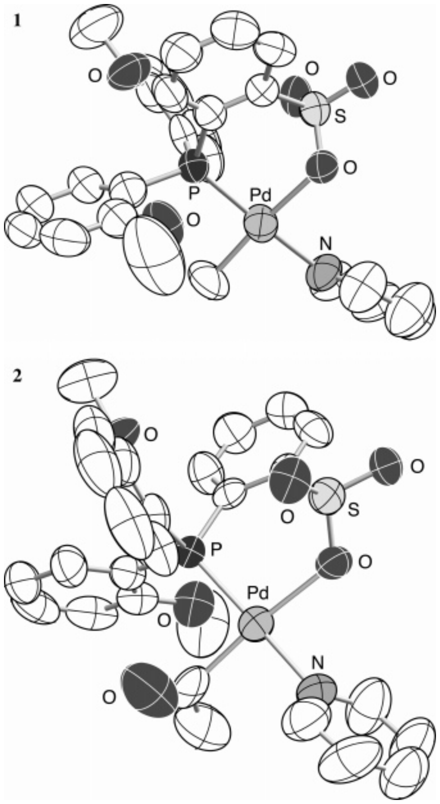


Figure 2. ORTEP structures of *cis*-$(P{\sim}SO_3)Pd(Me)(Py)$ (**1**) and *cis*-$(P{\sim}SO_3)Pd(COMe)(Py)$ (**2**). Hydrogen atoms are omitted for clarity.

When a solution of **2** in CD_2Cl_2 was exposed to 100 psi (690 kPa) ethene at 0 °C, slow insertion of ethene into the Pd−acyl bond occurred to give a mixture of $(P{\sim}SO_3)Pd(CH_2CH_2COMe)$, **3**, and unreacted **2** but *not* PE. NMR analysis showed a new terminal methyl ^1H NMR signal at 1.9 ppm, and the CH_2 groups α and β to the metal appeared as a doublet of triplets at 1.3 ppm and as a broad multiplet at 2.1 ppm, respectively. Also, a new ^{31}P signal appeared at 25 ppm and a broad ^{13}C carbonyl signal appeared at 216 ppm. IR analysis showed a new carbonyl absorption at 1643 cm^{-1}, which is consistent with the formation of a five-membered chelate like structure **A**, Scheme 1.[6,7]

Low-temperature ^1H NMR analysis suggests that the five-membered chelate **3** is likely in equilibrium with the open-chain pyridine-coordinated analogue, **3·Py**, and that the former is favored at low temperatures. At −80 °C, a doublet due to the

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ortho-hydrogens of the free pyridine is observed at 8.7 ppm. Additionally, the doublet of triplets at 1.3 ppm and the multiplet at 2.1 ppm from the CH_2 groups α and β to the metal, respectively, split into unique proton signals at 0.80, 1.01, and 1.55 ppm with the fourth obscured by the methyl signal, suggesting the presence of a rigid chelate ring structure.

In contrast to **1** and **2**, the chelated species **3** was unreactive toward ethene alone at 100 psi (690 kPa) and 25 °C, consistent with the notion that the alkene is too weakly binding to easily disrupt the chelate (or displace the coordinated pyridine) and give consecutive ethene insertions under these conditions. Under the more forcing conditions used to generate the data for Figure 1, ethene insertion does occur slowly, resulting in *nonalt*-PK. However, unlike *alt*-PK formation, the yield of *nonalt*-PK is low because of the sluggishness of this step. We hypothesize that the step **A** → **D** of Scheme 1 does proceed in the present *neutral* system, albeit slowly, because the carbonyl group in species **A** binds less strongly to the metal unlike in the traditional *cationic* palladium systems used for alternating ethene/CO copolymerizations.

Compound **3**, when redissolved in CD_2Cl_2 and exposed to 50 psi (345 kPa) CO at 25 °C, formed $(P{\sim}SO_3)Pd(COCH_2CH_2COMe)$, **4**, which corresponds to structure **C** in Scheme 1 (or its open-chain pyridine-coordinated analogue). The ^1H NMR signals for the CH_2 groups α and β to the metal in **4** were shifted to 1.9 and 2.5 ppm, respectively. The ^{31}P signal at 25 ppm was replaced by a peak at 12 ppm, and the ^{13}C carbonyl signal at 216 ppm was replaced by two carbonyl signals at 207 and 228 ppm. Compound **4**, in turn, was exposed to 100 psi (690 kPa) ethene at 0 °C for 18 h. The ^{31}P NMR signal for the Pd-acyl species was shifted to 22 ppm, indicating that it underwent ethene insertion to form a Pd-alkyl species (similar to **3**).

Finally, the living nature of the ethene homopolymerization and ethene/CO copolymerization allows the formation of PE and *alt*-PK blocks in a single chain. Block cooligomers were synthesized to demonstrate this, while maintaining the solubility of the products in CD_2Cl_2. First, **1** in CD_2Cl_2 was exposed to 100 psi (690 kPa) ethene at 25 °C for 2 h to grow a PE block with an average of four ethene units. The solvent and excess ethene was removed under vacuum, and the redissolved system was then exposed to a mixture of 50 psi (345 kPa) ethene and 50 psi (345 kPa) CO for 9 h to grow a second *alt*-PK block. The PE and *alt*-PK blocks were identified by their characteristic ^1H NMR chemical shifts at 1.3 and 2.7 ppm, respectively. The connectivity between the two blocks was observed as two CH_2 signals at 1.5 and 2.4 ppm. The assignment of the connecting CH_2 groups was established by comparing with the ^1H NMR shifts of 3-hexanone. The protons labeled *a* and *b* in $Et\text{-}C(O)\text{-}C^bH_2\text{-}C^aH_2\text{-}Me$ are observed at 1.6 and 2.4 ppm, respectively.

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Supporting Information Available: Experimental procedures, characterization data for all new compounds, X-ray crystal structure coordinates, and files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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