Communications to the Editor

Palladium(II)-Catalyzed Alternating Copolymerization of Carbon Monoxide with α-Olefins: Synthetic and Mechanistic Aspects

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The metal-catalyzed alternating copolymerization of carbon monoxide with ethylene[1] and the properties of the resultant ethylene–carbon monoxide copolymer (E–CO copolymer)[1] have been described in detail by us[2] and others.[3] In contrast, very little is known regarding the alternating copolymers of α-olefins with carbon monoxide.[1] The metal-catalyzed copolymerization of carbon monoxide with propylene has very recently been revealed in the patent literature.[4] However, neither the structure of the resultant propylene–carbon monoxide copolymer (P–CO copolymer) nor the mechanism by which they are generated has been reported. Herein, we describe (a) a highly active catalyst system for the synthesis of alternating copolymers of carbon monoxide with ethylene, α-olefins, and α,ω-dienes, (b) the structures of the resultant copolymers including the end groups, and (c) the initiation and termination mechanisms.

The compound [Pd(Ph$_2$P(CH$_2$)$_3$PPh$_2$)(MeCN)$_2$](BF$_4$)$_2$ (1)[5] was prepared in situ by codissolving a 1:1 (molar ratio) mixture of [Pd(MeCN)$_4$](BF$_4$)$_2$ and Ph$_2$P(CH$_2$)$_3$PPh$_2$ (dppp) in an appropriate solvent. In a number of solvents, 1 was found to be a highly active catalyst for the alternating copolymerization of CO with olefins. For example, in a nitromethane/methanol (2:1, v/v) mixture, using 500 psi each of C$_2$H$_4$ and CO, the E–CO copolymer was formed at the *initial* rate of 3.6 kg of copolymer/(g of Pd·h) when the reaction was carried at 66 °C (productivity over 19 h at 70 °C: 28 kg/g of Pd). The addition of water (49 mol equiv/Pd) and 2,6-di-*tert*-butylpyridine (8 equiv/Pd) did not affect the reaction rate. No decomposition of the catalyst was observed at the end of the reaction, and the catalyst could be used repeatedly. The E–CO copolymer[6] was a white crystalline solid insoluble in common organic solvents but soluble in strong acids, such as 1,1,1,3,3,3-hexafluoroisopropyl alcohol and trifluoroacetic acid (¹H NMR (CF$_3$COOD) δ 3.02 (s); ¹³C{¹H} NMR (CF$_3$COOD) δ 217.02, 38.03).

The choice of solvent had a dramatic effect on the rate of reaction. A polar solvent system with an alcohol as one component, such as methanol/nitromethane, appeared to be optimal. In the absence of alcohol, a long induction period followed by a slower rate was observed. For example, in a THF/nitromethane mixture, a 2-h induction period was observed.

Compound 1 was also found to catalyze the copolymerization of carbon monoxide with α-olefins and α,ω-dienes, such as propylene, 1-heptene, and 1,7-octadiene. Starting with approximately 30 g of C$_3$H$_6$ and 600 psi of CO, the P–CO copolymer was formed at the *average* rate of 48 g

of copolymer/(g of Pd·h) at 50 °C in a 2:1 (v/v) mixture of methanol/nitromethane. The copolymerization of CO with 1-heptene or 1,7-octadiene was performed following a similar procedure employed for propylene. 1-Heptene showed a significantly lower reactivity than propylene in the copolymerization reaction due to the following reasons. First, because of its greater steric bulk, 1-heptene would be expected to insert more slowly into the intermediate metal–acyl species in the chain-growth sequence. Second, 1-heptene was found to be isomerized in the absence of CO to form internal olefinic isomers[7] that were no longer able to copolymerize with CO under the same reaction conditions as demonstrated by control experiments. The alternating copolymers of carbon monoxide with propylene[6] and 1-heptene[6] had molecular weights of (3.1–2.4) × 10⁴ and 1 × 10³, respectively, versus standard polystyrene. Both copolymers were soluble in common organic solvents such as CH$_2$Cl$_2$, CHCl$_3$, and THF.

The P–CO copolymer[6] was an atactic alternating copolymer with a mixture of head-to-tail and head-to-head repeating units. The characterization of the copolymer was accomplished by IR and ¹H and ¹³C NMR spectroscopy and supported by elemental analysis. A strong IR absorption (neat) at 1710 cm⁻¹ was ascribed to the carbonyl group. The ¹H NMR (CDCl$_3$) spectrum of the copolymer exhibited three broad resonances at 2.89–3.16 ppm (2 H), 2.33–2.50 ppm (1 H), and 1.01–1.10 ppm (3 H) corresponding to the CH$_2$, CH, and CH$_3$ groups, respectively. The ¹³C{¹H} NMR (CDCl$_3$) spectrum displayed multiplets at 215.46, 211.91, 207.70, 44.62, 40.29, and 16.34 ppm. The first three resonances are due to the carbonyl group, and the latter were attributed to the CH, CH$_2$, and CH$_3$ groups, respectively. The multiplicity of the resonances was caused by the lack of tacticity and the presence of a mixture of head-to-tail and head-to-head repeating units in the polymer backbone. We assign the absorptions at 215.46, 211.91, and 207.70 ppm to carbonyl groups flanked by head-to-head, head-to-tail, and tail-to-tail propylene units based on the ¹³C NMR resonances of the carbonyl groups of model compounds as shown in Figure 1. The intensity ratios of the carbonyl resonances of the P–CO copolymer indicates that the copolymer has 60% head-to-tail, 20% head-to-head, and 20% tail-to-tail arrangements.

As expected, cross-linked polymers were obtained in the reaction of α,ω-dienes with CO. For example, the 1,7-octadiene–CO copolymer was a white solid that was totally insoluble in organic solvents but swellable in solvents such as THF. ¹³C{¹H} NMR spectra[8] revealed the presence of carbonyl groups, unreacted terminal vinyl groups, internal double bonds, and methoxycarbonyl groups in addition to the alkyl groups. The internal double bonds were likely formed through the isomerization of the pendant vinyl groups, while the methoxycarbonyl groups were formed due to chain initiation by Pd–methoxide (vide infra).

Owing to the versatility of the present catalyst systems, it was possible to prepare different kinds of olefin–carbon monoxide copolymers in one pot or to incorporate more than one olefin into the copolymer chains. For example, one-pot synthesis of the E–CO and the P–CO copolymers
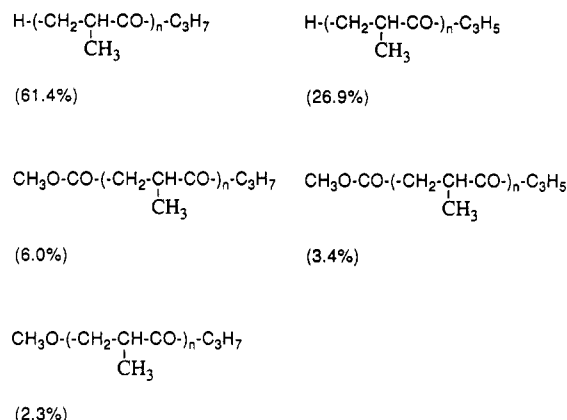
206 ppm

211 ppm

218 ppm

207.7 ppm
tail-to-tail

211.9 ppm
head-to-tail

215.5 ppm
head-to-head
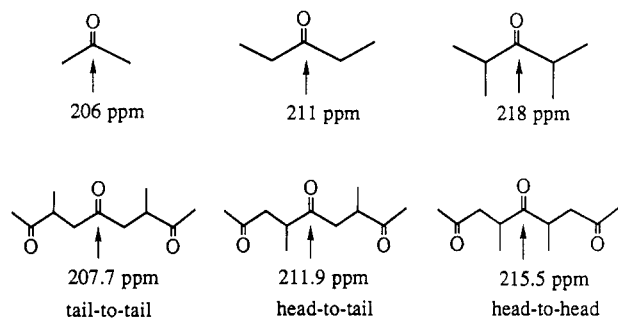
Figure 1. Comparison of the ^{13}C NMR resonances for the carbonyl groups in model compounds and in the repeating units of the alternating propylene–carbon monoxide copolymer.

H-(-CH$_2$-CH-CO-)$_n$-C$_3$H$_7$
        CH$_3$

(61.4%)

H-(-CH$_2$-CH-CO-)$_n$-C$_3$H$_5$
        CH$_3$

(26.9%)

CH$_3$O-CO-(-CH$_2$-CH-CO-)$_n$-C$_3$H$_7$
              CH$_3$

(6.0%)

CH$_3$O-CO-(-CH$_2$-CH-CO-)$_n$-C$_3$H$_5$
              CH$_3$

(3.4%)

CH$_3$O-(-CH$_2$-CH-CO-)$_n$-C$_3$H$_7$
              CH$_3$

(2.3%)

Figure 2. Low molecular weight alternating propylene–carbon monoxide oligomers formed in a nitromethane/methanol mixture.

was accomplished by the following procedure. A solution containing 1.13 × 10^{-2} mmol of the catalyst in 1.2 mL of 2:1 (v/v) nitromethane/methanol was exposed to a mixture of C_2H_4 (500 psi) and CO (500 psi) at room temperature for 20 h. At the end of this period, the gases were expelled and the apparatus (with its contents untouched) was recharged with a mixture of C_3H_6 (30 g) and CO (600 psi) at 50 °C. After 3 days, 12.4 g of solid was obtained, which was separated into pure E–CO copolymer (6 g, insoluble) and pure P–CO copolymer (6.4 g, soluble) by extraction with CH_2Cl_2 and identified by NMR spectroscopy. On the other hand, a terpolymer containing *both* alternating E–CO and alternating P–CO units[9] was formed when the catalyst solution in nitromethane/THF was exposed to a mixture of C_2H_4, C_3H_6, and CO. The ^1H NMR (CF_3COOD) spectrum of the polymer showed absorptions at 2.93 (s), 3.2–2.6 (br), and 1.19 (d, $J = 6.5$ Hz) ppm due to the $-CH_2CH_2-$ group of the E–CO units and $-CH_2CH-$ and $-CH_3$ groups of the P–CO units, respectively. The terpolymer had 14% P–CO units and was insoluble in common organic solvents but appeared to swell in CH_2Cl_2. Interestingly, only the E–CO copolymer was formed when the reaction was performed in nitromethane/methanol rather than in nitromethane/THF. Thus, it was possible to tailor catalyst selectivity by the appropriate choice of the solvent.

Since the copolymerization of the α,ω-dienes with CO led to the formation of cross-linked materials, they were good candidates as cross-linking reagents for the copolymerization of CO with α-olefins. Thus, when 1,7-octadiene was added during the copolymerization of C_3H_6 and CO, a cross-linked P–CO copolymer was obtained. This polymer had a low solubility in organic solvents and formed a gel in $CHCl_3$.

By using [Pd(PPh$_3$)$_2$(MeCN)$_2$](BF$_4$)$_2$ and related compounds as catalysts, we had earlier demonstrated that, for the E–CO copolymer, the chain growth occurred by alternate insertions of C_2H_4 and CO into an initial Pd–H bond.[2c] There was no compelling reason to postulate a different chain-growth mechanism for the copolymerization of CO with α-olefins. However, it was important to establish the steps by which the polymer chains were initiated and terminated since these may vary with the particular catalyst and solvent system employed. In order to examine these steps, the end groups of the P–CO copolymer were determined in the following way. A low molecular weight P–CO copolymer sample (average MW = 2400) that was synthesized using a nitromethane/methanol solvent mixture was heated at 140 °C under 2.5 × 10^{-5} mmHg, and the oligomers that distilled over were trapped in a liquid-nitrogen trap. A $CHCl_3$ solution of the oligomers was analyzed by GC–MS and identified as shown in Figure 2. The structures of the oligomers were

further confirmed by ^1H NMR spectroscopy. The majority of the oligomers contained alkyl–alkyl or alkyl–propenyl end groups. These oligomers were clearly formed as a result of reactions initiated by a Pd–hydride and terminated by either proton cleavage of or β-hydrogen abstraction from the final Pd–alkyl species. A relatively smaller number of the oligomers was found with methoxycarbonyl-alkyl or methoxycarbonyl–propenyl end groups. The former could have been initiated by a Pd–hydride and terminated by methanolysis of a Pd–acyl species (as was observed previously[2c]) *or* initiated by a Pd–methoxide and terminated by proton cleavage of a Pd–alkyl species. However, the latter oligomers *must* have formed through initiation by a Pd–methoxide and termination by β-hydrogen abstraction from a Pd–alkyl species. Likewise, the oligomers with a methyl ether end group *must* also be initiated by a Pd–methoxide. In short, both a Pd–hydride *and* a Pd–methoxide must act as initiators. The initial Pd–hydride could be generated through β-hydrogen abstraction from a Pd–alkoxide[10] generated in situ. In support of this assumption, we observed the formation of acetone from isopropyl alcohol at ambient temperature in the presence of 1 in CD_3NO_2. Additionally, the copolymerization yield was significantly lower in a *tert*-butyl alcohol/nitromethane mixture when compared to methanol/nitromethane or isopropyl alcohol/nitromethane solvent mixtures presumably because of the absence of β-hydrogens in Pd–*tert*-butoxide. The initiation of the copolymerization by a Pd–alkoxide is also feasible since the insertion of CO and olefins into Pd–OR bonds is well documented.[10] Depending on whether CO or C_3H_6 inserted first, the copolymer would either have methoxycarbonyl or methyl ether terminal groups; both were observed. Finally, by switching from a methanol/nitromethane to a isopropyl alcohol/nitromethane mixture, isopropoxide end groups were formed as detected by ^1H NMR spectroscopy of the isolated copolymer.[11] The above conclusions regarding the initiation and termination steps in the formation of the P–CO copolymer also appear to be applicable to the E–CO copolymer. The E–CO copolymer formed using 1 in nitromethane/methanol showed three small ^1H NMR (CF_3COOD) resonances at 5.83, 3.75, and 1.22 ppm due to the terminal vinyl, methoxycarbonyl, and methyl (or ethyl) end groups. Scheme I outlines some of the principal steps involved in the copolymerization reaction in the presence of methanol.[12]

The initiation of copolymerization by Pd–hydride and Pd–alkoxide formed in situ in alcohol-containing solvents is, perhaps, not too surprising. A more interesting question involves the nature of the initiator in aprotic media. As described earlier, in the absence of alcohol, such as in ni-
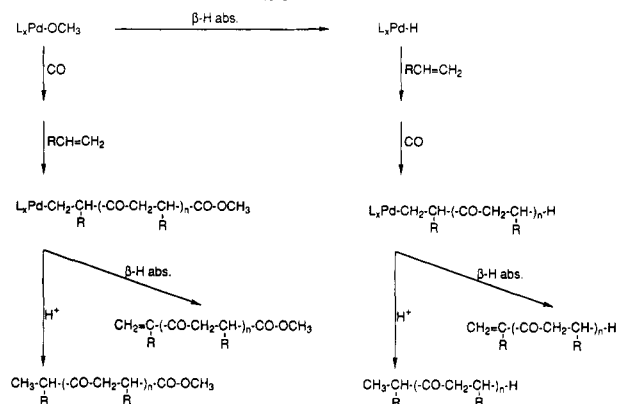
Scheme I

tromethane/THF, a long induction period followed by a slower copolymerization rate was observed. The induction period for the copolymerization of C_2H_4 with CO in a nitromethane/THF mixture disappeared upon the addition of 200 psi of H_2. Given the high electrophilicity of the Pd(II) ion,[13] the formation of a Pd–hydride by heterolytic cleavage of H_2 is not unexpected. That a Pd–hydride was the initiator in the presence of H_2 was also indicated by the following observation. The ^2H NMR spectrum (in CF_3COOH) of the E–CO copolymer formed in nitromethane/THF in the presence of D_2 showed substantial deuteration of the terminal ethyl group (CH_2, 2.70 ppm; CH_3, 1.18 ppm). The deuteration of the methylene unit of the ethyl terminus was consistent with a rapid *reversible* insertion of C_2H_4 into the initial Pd–D bond. In the *absence* of added H_2, the Pd–hydride species may form from trace water via the water–gas shift reaction.[14] Metal-hydrides are known to be intermediates in this reaction. In support of the above hypothesis, we observed deuteration of the terminal ethyl group of the E–CO copolymer when the polymerization was carried out in nitromethane/THF in the presence of added D_2O. One termination step in an aprotic solvent appears to be β-hydrogen abstraction from the final Pd–alkyl species. This was indicated by the presence of a terminal vinyl resonance at 5.82 ppm in the E–CO copolymer generated in nitromethane/THF.

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