Nonterminating Alternating Copolymerization of Ethene with Carbon Monoxide and the Synthesis of Graft Polymers with *alt*-Ethene–Carbon Monoxide Blocks

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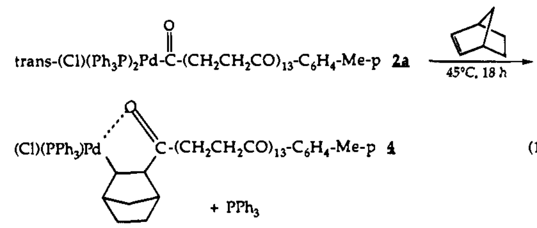
Received June 26, 1995

We and others have previously reported on the palladium(II)-catalyzed alternating copolymerization of olefins with carbon monoxide.[1] These polymers are of interest due to low monomer costs, potential photodegradability,[2] and the presence of carbonyl groups capable of further functionalization.[3] Specific interest in the alternating ethene–carbon monoxide copolymer (E–CO copolymer) stems from its high mechanical strength[4] and melting point, which result from its high crystallinity.[5] Its commercial production is projected to start in 1996.[6] Every system described thus far for the E–CO copolymer synthesis suffers from the presence of chain termination steps, such as β-hydrogen abstraction and protonolysis of Pd–alkyl intermediates, and alcoholysis of Pd–acyl intermediates.[1] Herein, we describe a well-defined palladium(II) system that operates in aprotic solvents at ambient temperature to generate E–CO copolymers without chain termination. Furthermore, for the first time, it becomes possible to synthesize graft polymers with *alt*-E–CO blocks. We note that nonterminating alternating copolymerization of styrene and norbornene derivatives with carbon monoxide has been reported using chelating bis(amine) ligand based catalyst systems.[7] However, these systems are not effective for ethene, the simplest and the most important olefinic monomer.

The complex *trans*-$Pd(PPh_3)_2(Cl)(COC_6H_4Me$-*p*),[8] **1**, was found to convert to *trans*-$Pd(PPh_3)_2(Cl)[(COCH_2CH_2)_x(COC_6H_4$-Me-*p*)] ($x \approx 8$),[9] **2a**, upon reaction with C_2H_4 (200 psi) and CO (200 psi) in $CDCl_3$ at ambient temperature for 18 h. The species **2a** was fully characterized by ^{1}H-, ^{13}C-, and ^{31}P-NMR spectroscopy. For example, in the ^{1}H-NMR spectra (see Figure 1), the CH_2CH_2 unit adjacent to the original COC_6H_4Me-*p* group was present as two triplets (at 3.25 and 2.88 ppm) downfield of the main $(COCH_2CH_2)_x$ resonance (2.73 ppm). Conversely, the $COCH_2CH_2$ unit next to the Pd consisted of two broad resonances (at 1.26 and 2.32 ppm) upfield of the main $(COCH_2CH_2)_x$ resonance. The chemical shift of the $PdCOCH_2$ protons was similar to that of corresponding protons in *trans,trans*-$Pd(PPh_3)_2(Cl)[COCH_2CH_2CH_2CO]Pd(PPh_3)_2(Cl)$,[8] **3**, (1.38 ppm). The ^{31}P-NMR resonance of the new acyl compound, **2a**, (19.6 ppm) was close to that of the original species, **1** (19.3 ppm). Most importantly, there were no ^{1}H-NMR resonances ascribable to either vinylic or ethyl end groups, confirming that chain termination had not occurred. The lack of chain termination was also shown by the ability of **2a** ($x \approx 13$ used) to undergo insertion of norbornene into the Pd–acyl bond (eq 1). The inserted product,[10] **4**, was found to have NMR parameters that matched those of analogous compounds reported previously[11] (in particular, ^{31}P-NMR ($CDCl_3$): 38.6 ppm (s)). The reverse reaction, i.e., the growth of an *alt*-E–CO chain starting with a norbornene inserted product, has also been accomplished; see eq 2.



(1)

When **1** was allowed to react with C_2H_4 and ^{13}CO, the species *trans*-$Pd(PPh_3)_2(Cl)[(^{13}COCH_2CH_2)_x(COC_6H_4Me$-*p*)] ($x \approx 7$), **2b**, was formed in which the acyl carbonyl resonated at 235.5 ppm in the ^{13}C-NMR spectrum. This resonance was significantly downfield of the other carbonyl groups of the $(^{13}COCH_2CH_2)_x$ segment (207.7 ppm) but was comparable to the corresponding carbonyl resonance of *trans,trans*-$Pd(PPh_3)_2(Cl)[CO(CH_2)_{10}CO]Pd(PPh_3)_2(Cl)$ (236.6 ppm),[8] **5**. When species **2b** was allowed to react with C_2H_4 and ^{12}CO, the resonance at 235.5 ppm disappeared as a "diblock" (with blocks of isotopomers) polymeric species, *trans*-$Pd(PPh_3)_2(Cl)[(^{12}COCH_2CH_2)_y(^{13}COCH_2CH_2)_x(COC_6H_4Me$-*p*)] ($x \approx 7$, $y \approx 5$), **2c**, was formed. As expected, the CH_2 groups in the $(^{13}COCH_2CH_2)_x$ block appeared as a doublet in the ^{13}C-NMR spectra due to coupling with the neighboring ^{13}CO, whereas the CH_2 groups in the $(^{12}COCH_2CH_2)_x$ block appeared as a singlet.

The species **2a–c** were quite stable since their NMR spectra did not change upon isolation as solids followed by redissolution in $CDCl_3$. Upon further exposure to C_2H_4 and CO in solution at ambient temperature for 18 h, high molecular weight E–CO copolymer precipitated out. The latter polymer is known to be insoluble in all but the most strongly acidic solvents in which the polymer chain is expected to cleave off the metal. In sharp contrast to the neutral Pd–acyl compounds, the use of the corresponding cationic species, *trans*-$(Ph_3P)_2Pd(solv)(COR)^+$, resulted in rapid polymer formation under the same conditions. However, upon isolation, the resultant E–CO copolymer chains were invariably found to have end groups consistent with a β-hydrogen abstraction step.[1a,b] Since ligand substitutions in these square-planar complexes tend to proceed by an associative mechanism,[12] the lack of chain termination in the neutral complex is presumably due to the blocking of one of the

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(8) All starting complexes of the type *trans*-$Pd(PPh_3)_2(Cl)(COR)$ were synthesized by the reaction of $Pd(PPh_3)_4$ with the appropriate acyl chloride.

(9) ^{1}H-NMR ($CDCl_3$) (300 MHz. 25 °C)(ppm): 1.26 (m, 2H); 2.18 (t, J = 7 Hz, 2H); 2.32 (m, 2H); 2.40 (s, 3H); 2.48 (t, J = 7 Hz, 2H); 2.73 (s, 20H); 2.88 (t, J = 7 Hz, 2H); 3.25 (t, J = 7 Hz, 2H); 7.65–7.82 (m, 30H); 7.85 (d, J = 7 Hz, 2H). ^{31}P{^{1}H}-NMR ($CDCl_3$) (121 MHz, 25 °C)(ppm): 19.6 (s).

(10) ^{1}H-NMR ($CDCl_3$) (300 MHz, 25 °C)(ppm): −0.03 (m, 1H); 0.80 (m, 1H); 1.06 (m, 2H); 1.38 (m, 2H); 1.69 (m, 4H); 2.20 (m, 1H); 2.40 (s, 3H); 2.51 (m, 1H); 2.73 (bs, 46H); 2.88 (t, J = 6 Hz, 2H); 3.23 (t, J = 6 Hz, 2H); 7.40 (m, 9H); 7.70 (m, 6H). ^{31}P{^{1}H}-NMR ($CDCl_3$) (121 MHz, 25 °C)(ppm): 38.6 (s).

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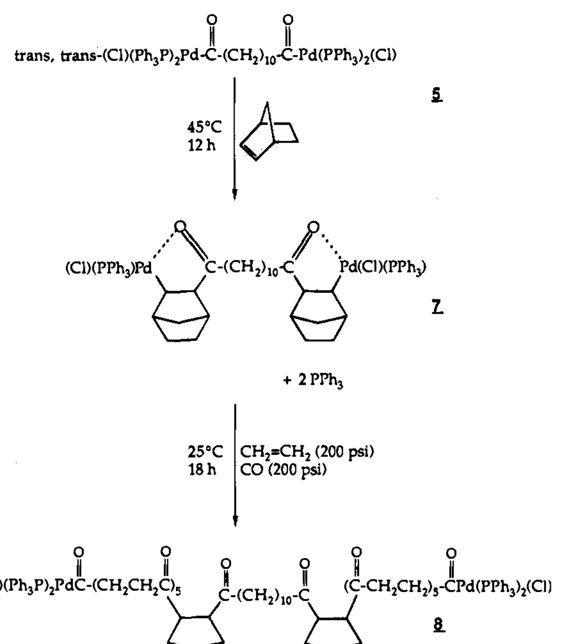
coordination positions by the Cl^- ion. Preliminary experiments indicate that this is a general phenomenon, and the complex *cis*-Pd[$PPh_2(CH_2)_3PPh_2$](Cl)(COMe) behaved analogously. Note that, in contrast to previous reports on the insertion of other olefins into Pd(II)−acyl bonds,[7,11,13] there is *no* evidence in the present instances for the coordination of the acyl oxygen following insertion of ethene (e.g., the insertion products have the same trans structures as the starting Pd(II)−acyl complexes).

The ability to grow an *alt*-E−CO block starting with a well-defined Pd−acyl complex opens up the possibility of synthesizing graft polymers. The possibility of synthesizing such polymers was explored in two prototype reactions. In the first reaction, the species *trans,trans*-$Pd(PPh_3)_2(Cl)[COCH_2O(CH_2CH_2O)_aCH_2CO]Pd(PPh_3)_2(Cl)$ ($a \approx 13$),[8] **6** (50 mg in 2 mL of $CHCl_3$), was allowed to react with C_2H_4 (300 psi) and CO (300 psi) in $CHCl_3$ at 50 °C for 50 h. At the end of this period, the precipitated polymer was isolated (98 mg), subjected to Soxhlet extraction for 24 h with $CHCl_3$ to remove Pd(II) species and residual poly(ethene oxide) (12 mg), dissolved in CF_3CO_2H, and analyzed by NMR spectroscopy. A symmetrical graft triblock polymer, $(COCH_2CH_2)_bCOCH_2O(CH_2CH_2O)_aCH_2CO(CH_2CH_2CO)_b$ ($a \approx 13$, $b \approx 24$), was indicated from the spectra (e.g., ^{1}H-NMR ($CDCl_3-CF_3CO_2H$) (300 MHz, 25 °C)(ppm): 2.88 (bs, 192H, $COCH_2CH_2$); 3.78 (bs, 52H, CH_2CH_2O). The overall transformation represents a near quantitative yield based on **6**.

The sequence of steps involved in the second prototype transformation is shown in eq 2. The compound, *trans,trans*-$Pd(PPh_3)_2(Cl)[CO(CH_2)_{10}CO]Pd(PPh_3)_2(Cl)$,[8] **5**, was not very stable. Accordingly, we first synthesized compound **7**[14] by the



(2)

insertion of norbornene into the two terminal Pd−acyl bonds (cf. eq 1). Compound **7** could be isolated as a solid, and its NMR parameters matched those of analogous compounds, including **4** (^{31}P-NMR ($CDCl_3$): 38.3 ppm (s)). Compound **7**, *generated in situ*, was found to react with C_2H_4 and CO to form

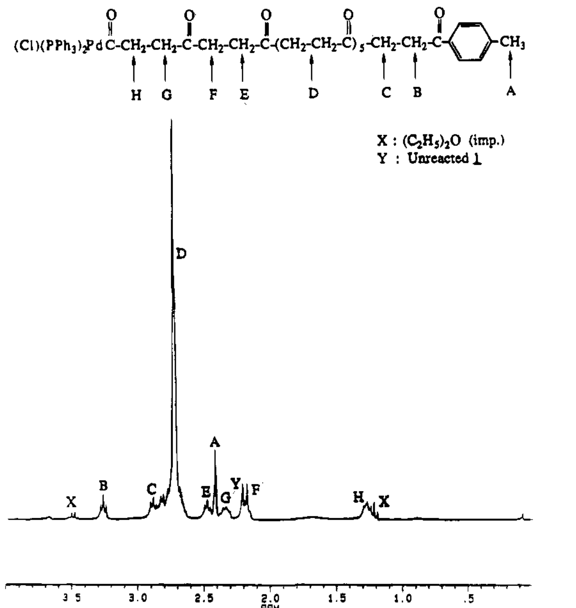


Figure 1. ^{1}H-NMR ($CDCl_3$) (300 MHz, 25 °C) spectrum (0−5 ppm) of *trans*-$Pd(PPh_3)_2(Cl)[(COCH_2CH_2)_x(COC_6H_4Me\text{-}p)]$ ($x \approx 8$), **2a**.

8,[15] in which ~5 E−CO units were added to each Pd−C bond of **7**. The *trans*-$Pd(PPh_3)_2(Cl)[(COCH_2CH_2)_x$ end segments of **8** exhibited NMR resonances similar to those for **2a−c** (e.g., ^{31}P-NMR ($CDCl_3$): 19.6 ppm (s)). *Pure* **7** reacted readily with C_2H_4 and CO and precipitated a polymer in which E−CO copolymer blocks were appended to the two ends of the original hydrocarbon chain. Substantial decomposition of the Pd species was also observed in this reaction. The reason that the well-defined species, **8**, was not observed in the latter reaction is that the isolation of pure **7** resulted in the removal of two PPh_3 molecules formed concomitantly.[11] These were necessary for the formation of **8**.

In conclusion, we have demonstrated for the first time (a) the nonterminating alternating copolymerization of C_2H_4 with CO and (b) a procedure for the synthesis of graft polymers with *alt*-C_2H_4−CO blocks. The only related polymer reported previously was formed by a nickel(II) sytem that is specific for diblock (polyethene)(*alt*-ethene−carbon monoxide) polymer.[16] Our results show that *alt*-C_2H_4−CO blocks can be grafted on to *any* carboxy-terminated polymer.

Acknowledgment. This research was supported by a grant from the U.S. Department of Energy, Office of Basic Energy Sciences (DE-FG02-84ER13295).

Supporting Information Available: Experimental procedures and characterization data not included in the paper (5 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA952085N

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(14) ^{1}H-NMR ($CDCl_3$) (300 MHz, 25 °C)(ppm): −0.05 (m, 2H); 0.80 (m, 2H); 1.05 (m, 4H); 1.23 (s, 12H); 1.72 (m, 8H); 2.32 (m, 2H); 2.65 (m, 6H); 2.42 (t, $J = 7$ Hz, 4H); 7.28−7.91 (m, 30H). ^{13}C{^{1}H}-NMR ($CDCl_3$) (75 MHz, 25 °C)(ppm): 24.5 (s); 28.8 (s); 29.0 (s); 29.1 (s); 29.2 (s); 35.3 (s); 36.2 (s); 39.8 (s); 43.2 (s); 43.5 (s); 54.0 (s); 70.8 (s); 128.3−134.9; 235.1 (s). ^{31}P{^{1}H}-NMR ($CDCl_3$) (121 MHz, 25 °C)(ppm): 38.3 (s).

(15) ^{1}H-NMR ($CDCl_3$) (300 MHz, 25 °C)(ppm): 1.14 (d, $J = 8$ Hz, 4H); 1.25 (bs, 6H); 1.59 (m, 4H); 2.04 (m, 1H); 2.19 (t, $J = 6$ Hz, 4H); 2.32 (m, 7H); 2.47 (m, 11H); 2.56 (bs, 7H); 2.70 (bs, 36H); 7.43 (m, 24H); 7.70 (m, 36H). ^{13}C{^{1}H}-NMR ($CDCl_3$) (75 MHz, 25 °C)(ppm): 24.0 (s); 24.4 (s); 29.1 (s); 29.2 (s); 29.4 (s); 29.5 (s); 36.0 (s); 36.2 (s); 39.5 (s); 39.8 (s); 41.1 (s); 42.7 (s); 42.9 (s); 59.3 (s); 128.3−135.2; 208.1 (s). ^{31}P-{^{1}H}-NMR ($CDCl_3$) (121 MHz, 25 °C)(ppm): 19.6 (s).

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