

Mechanistic Aspects of Metal-Catalyzed Alternating Copolymerization of Olefins with Carbon Monoxide

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The copolymers of olefins with carbon monoxide are of great interest from at least four standpoints.¹ First, as a monomer, carbon monoxide is particularly plentiful and inexpensive. Second, the presence of the carbonyl chromophore in the backbone makes these copolymers photodegradable.² A third reason for the interest in the olefin-carbon monoxide copolymers is that, because of the ease with which the carbonyl group can be chemically modified, the polyketones serve as excellent starting materials for other classes of functionalized polymers. In fact, about two dozen polymers incorporating a variety of functional groups have been previously synthesized¹ from the *random* ethylene-carbon monoxide copolymer ($C_2H_4:CO > 1$) made through radical-initiated polymerization. Since carbon monoxide does not homopolymerize, the *alternating* olefin-carbon monoxide copolymers (olefin:CO = 1) have the highest possible concentration of the reactive carbonyl groups. Additionally, the 1,4-arrangement of the carbonyl groups in the alternating olefin-carbon monoxide copolymers provides additional functionalization pathways.³ Finally, specific interest in the alternating ethylene-carbon monoxide copolymer stems from its high mechanical strength,⁴ which results from its high crystallinity.

Three different synthetic methods have been developed for the copolymerization of olefins with carbon monoxide.¹ The copolymerization may be initiated by free radicals or induced by γ -rays. A number of transition metal complexes are also effective catalysts for the copolymerization reaction. The metal-catalyzed copolymerization procedure has several noteworthy advantages over the other two.¹ First, the copolymerization occurs at significantly lower pressures and at or below ambient temperature. Second, the resultant polymers have a strictly alternating structure and high molecular weights.

Palladium(II)-Based Systems

Prior to our own work, all the transition metal systems capable of copolymerizing olefins with carbon monoxide were described in the patent literature.^{1a} The catalysts patented were either Ni(II) and Pd(II) cyanides or neutral tertiary phosphine complexes of Pd(II) and Pd(0). In our initial work,^{5,6} we were able to show that

cationic Pd(II) complexes of the type $[Pd(PR_3)_n(MeCN)_{4-n}](BF_4)_2$ were capable of copolymerizing olefins with carbon monoxide under conditions significantly milder than those described in the patents. Subsequently, in a series of patents,^{7,8} Drent and co-workers at Shell showed that the use of chelating bis(phosphines), in particular 1,3-bis(phosphino)propanes, results in significantly enhanced copolymerization rates and catalyst lifetimes. Additionally, the copolymerization of simple α -olefins, such as propylene, with carbon monoxide was achieved.⁸

Chain Propagation Mechanism. A rational mechanism for chain growth would involve the alternate insertions of carbon monoxide and olefin into a preformed Pd-alkyl bond (Scheme I).⁶ Two possible factors favor carbon monoxide insertion into a Pd-alkyl bond over the corresponding olefin insertion. First, since CO is a better π -acid compared to olefins, it will be expected to bind more readily to the Pd(II) center. In addition, carbon monoxide appears to have a greater inherent tendency to insert into transition metal-alkyl bonds than do olefins. Note that, in the absence of added carbon monoxide, the same catalyst system is effective for the dimerization of olefins under identical conditions.^{5,6} This clearly indicates that there is no thermodynamic barrier to olefin insertion into the Pd-alkyl bonds in this system; rather, the olefin insertion is too slow to compete with the corresponding carbon monoxide insertion. The formation of olefin dimers rather than polymers in the absence of carbon monoxide indicates the presence of a facile β -hydrogen abstraction pathway. This pathway was also found to be one of the chain termination/transfer steps in the alternating olefin-carbon monoxide copolymerization (*vide infra*).

In contrast to insertions involving Pd-alkyl bonds, insertions into Pd-acyl bonds are dictated by thermodynamics. As shown in Scheme II,^{9b} our work on α -keto acyl complexes of Pd(II) clearly indicates that carbon

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(1) Reviews: (a) Sen, A. *Adv. Polym. Sci.* 1986, 73/74, 125. (b) Sen, A. *CHEMTECH*, 1986, 48.

(2) Guillet, J. *Polymer Photophysics and Photochemistry*; Cambridge University: Cambridge, 1985; p 261.

(3) (a) Sen, A.; Jiang, Z.; Chen, J.-T. *Macromolecules* 1989, 22, 2012. (b) Jiang, Z.; Sen, A. *Macromolecules* 1992, 25, 880.

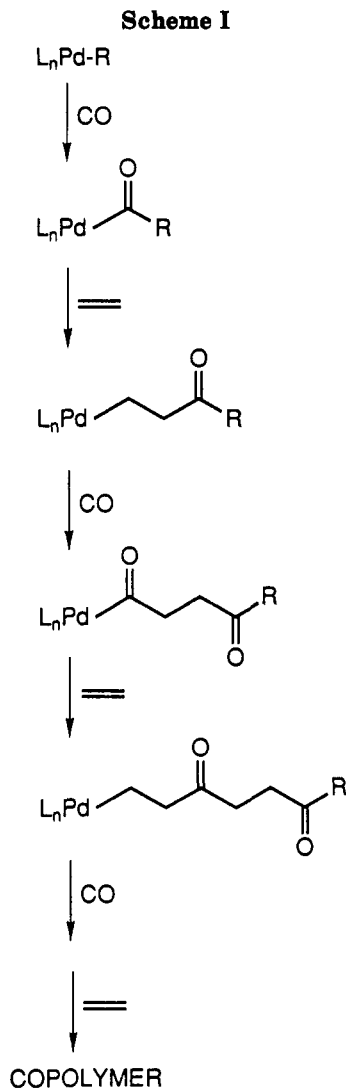
(4) Numerous patents by Shell. Representative examples: U.S. Patent 4,904,744 (1990); Eur. Pat. Appl. 400,719 (1990); Eur. Pat. Appl. 373,725 (1990); Eur. Pat. Appl. 360,358 (1990); Eur. Pat. Appl. 345,854 (1989).

(5) Sen, A.; Lai, T.-W. *J. Am. Chem. Soc.* 1982, 104, 3520.

(6) Lai, T.-W.; Sen, A. *Organometallics* 1984, 3, 866.

(7) Drent, E.; Van Broekhoven, J. A. M.; Doyle, M. J. *J. Organomet. Chem.* 1991, 417, 235 and references to patents therein.

(8) Representative examples: (a) Drent, E.; Wife, R. L. U.S. Patent 4,970,294 (1990). (b) Van Leeuwen, P. W. N.; Roobeek, C. F.; Wong, P. K. Eur. Pat. Appl. EP 393,790 (1990). (c) Wong, P. K. Eur. Pat. Appl. EP 384,517 (1990). (d) Van Deursen, J. H.; Van Doorn, J. A.; Drent, E.; Wong, P. K. Eur. Pat. Appl. EP 390,237 (1990). (e) Drent, E. Eur. Pat. Appl. EP 390,292 (1990).



monoxide insertion into a Pd-acyl bond is "uphill" from a thermodynamic standpoint.⁹ Thus, only olefin insertion into Pd-acyl bonds is observed.

We have studied the insertion of olefins into Pd(II)-acyl bonds in some detail.¹⁰ Olefins were found to insert readily into the Pd-acyl bond of $\text{Pd}(\text{PPh}_3)_2(\text{MeCN})(\text{COR})^+$. In most cases, the observed product was a vinyl ketone formed through a subsequent β -hydrogen abstraction step. However, in the case of norbornene derivatives, because of the steric inaccessibility of the available β -hydrogen atoms, stable organometallic derivatives could be isolated. The crystal structure of one such derivative is shown in Figure 1.^{10a} Several structural features are noteworthy. First, the exo, exo stereochemistry is consistent with the expected cis insertion of the olefin. Second, the organic fragment formed by insertion acts as a bidentate ligand due to coordination of the acyl oxygen. The weakly coordinating MeCN ligand is lost in the process, and a cis compound is formed. However, the binding of the acyl oxygen is not very strong. This can be seen by comparing the Pd-P bond distances for the two PPh_3

ligands. In the compound whose structure is shown in Figure 1, the Pd-P distance of 2.236 Å for the PPh_3 trans to the acyl oxygen is one of the shortest ever observed. In contrast, the Pd-P distance of 2.435 Å for the PPh_3 trans to the alkyl carbon is the longest known! Clearly, this difference reflects the very different trans influences of the σ -bonded alkyl and the dative-bonded acyl oxygen located trans to the respective PPh_3 ligands. A study of the kinetics of the insertion reaction revealed that actual insertion occurs from a four-coordinate intermediate formed by olefin displacement of the MeCN ligand.^{10a} More recently, the insertion of olefins into Pd-acyl bonds has also been reported by others.¹¹⁻¹³ In every case, the coordination of the carbonyl oxygen following olefin insertion is observed.

The insertion of norbornene derivatives into the Pd-acyl bond proceeds more slowly for the neutral compound $\text{Pd}(\text{PPh}_3)_2(\text{Cl})(\text{COR})$ than for the corresponding cationic species.^{10a} In the former case, too, the formed organic product acts as a chelating ligand due to coordination by the acyl oxygen. The only difference is that, in this case, one of the PPh_3 ligands is displaced by the incoming olefin prior to the insertion step. Consistent with this mechanism was the observation that the insertion reaction is significantly accelerated in the presence of a "phosphine sponge".^{10a}

The requirement of a ligand displacement step in the olefin insertion reaction nicely explains the observation^{5,6} that the cationic weakly solvated Pd(II) compounds (e.g., $\text{Pd}(\text{PPh}_3)_2(\text{R})(\text{solvent})^+$) are efficient catalysts for the copolymerization reaction while their neutral analogs (e.g., $\text{Pd}(\text{PPh}_3)_2(\text{R})(\text{X})$, X = halide) are inactive under the same conditions: it is clearly easier to displace a weakly bonded solvent molecule than a PPh_3 ligand. It should be noted that olefin insertion into the Pd-acyl bond is the rate-limiting step in the two-step chain growth sequence shown in Scheme I. Thus, β -hydrogen abstraction is a rare event in the copolymerization reaction (vide infra) although the catalytic dimerization (rather than polymerization) of olefins by the same system^{5,6} indicates that this is a facile step.

Chain Initiation and Termination Mechanisms. Figure 2¹⁴ shows the result of end-group analysis for a low molecular weight alternating propylene-carbon monoxide copolymer sample (average MW = 2400) formed in a methanol-nitromethane mixture using $[\text{Pd}(\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2)(\text{MeCN})_2](\text{BF}_4)_2$ as the catalyst. The majority of the oligomers contain 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 were 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

(11) Ozawa, F.; Hayashi, T.; Koide, H.; Yamamoto, A. *J. Chem. Soc., Chem. Commun.* 1991, 1469.

(12) Dekker, G. P. C. M.; Elsevier, C. J.; Vrieze, K.; van Leeuwen, P. W. N. M.; Roobeek, C. F. *J. Organomet. Chem.* 1992, 430, 357.

(13) Brookhart, M.; Rix, F. C.; DeSimone, J. M.; Barborak, J. C. *J. Am. Chem. Soc.* 1992, 114, 5894.

(14) (a) Jiang, Z.; Dahlen, G. M.; Houseknecht, K.; Sen, A. *Polym. Prepr.-Am. Chem. Soc., Div. Polym. Chem.* 1992, 33 (1), 1233. (b) Jiang, Z.; Dahlen, G. M.; Houseknecht, K.; Sen, A. *Macromolecules* 1992, 25, 2999.

(9) (a) Chen, J.-T.; Sen, A. *J. Am. Chem. Soc.* 1984, 106, 1506. (b) Sen, A.; Chen, J.-T.; Vetter, W. M.; Whittle, R. R. *J. Am. Chem. Soc.* 1987, 109, 148.

(10) (a) Brumbaugh, J. S.; Whittle, R. R.; Parvez, M. A.; Sen, A. *Organometallics* 1990, 9, 1735. (b) Vetter, W. M.; Sen, A. *J. Organomet. Chem.* 1989, 378, 485.

Scheme II

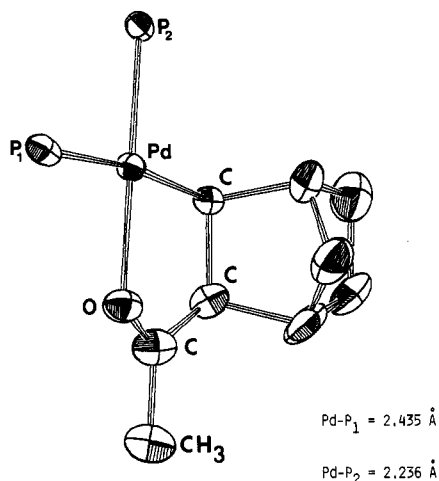
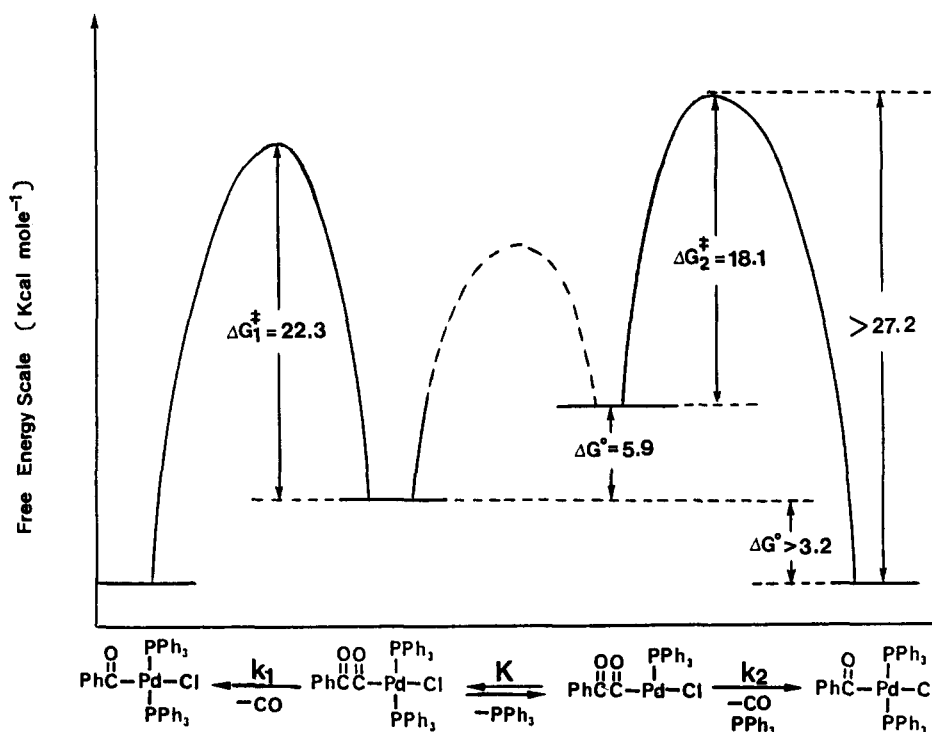


Figure 1. View of the inner coordination sphere of $[\text{Pd}(\text{PPh}_3)_2(\text{C}_7\text{H}_{10}\text{COCH}_3)](\text{BF}_4)$ including the entire chelating 2-acetylnorborn-1-yl ligand.^{10a}

Pd-acyl species or initiated by a Pd-methoxide and terminated by proton cleavage of a Pd-alkyl species. However, the latter oligomer *must* have formed through initiation by a Pd-methoxide and termination by β -hydrogen abstraction from a Pd-alkyl species. Likewise, the oligomers with methyl ether end-groups *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 was generated through β -hydrogen abstraction from a Pd-alkoxide generated in situ. The above conclusions regarding the initiation and termination steps in the formation of the propylene-carbon monoxide copolymer also appears to be applicable to the ethylene-carbon monoxide copolymer. For example,¹⁴ the ethylene-carbon monoxide copolymer formed using $[\text{Pd}(\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2)(\text{MeCN})_2](\text{BF}_4)_2$ in methanol-nitromethane showed small NMR resonances corresponding to terminal vinyl, methoxy-carbonyl, and ethyl groups. Drent,⁷ Consiglio,¹⁵ and

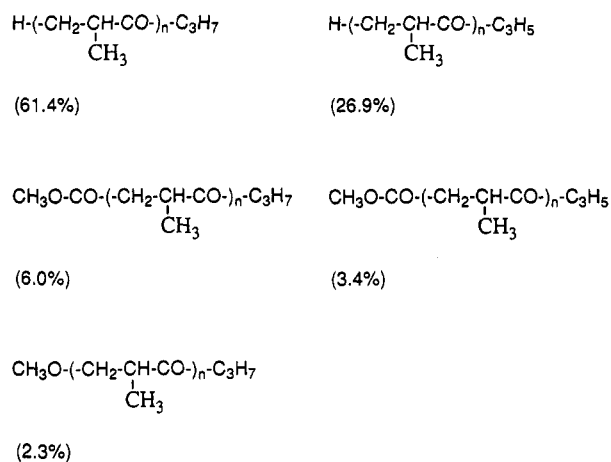


Figure 2. The low molecular weight alternating propylene-carbon monoxide polymers formed in nitromethane-methanol mixtures using $[\text{Pd}(\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2)(\text{CH}_3\text{CN})_2](\text{BF}_4)_2$ as catalyst.¹⁴

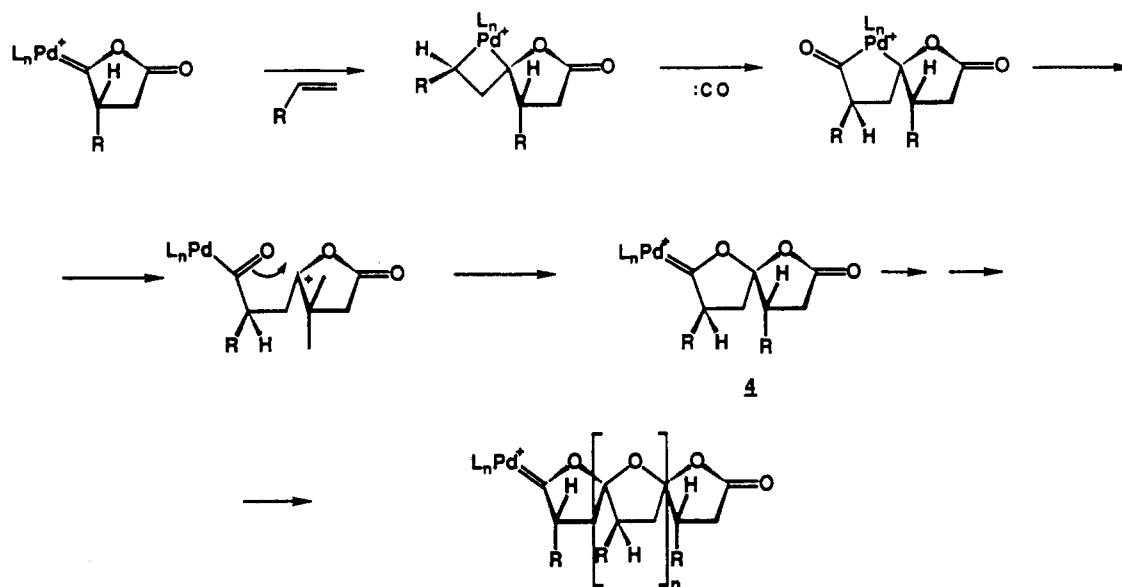
Chien¹⁶ have reached similar conclusions regarding the initiation and termination steps in recent publications.

A remarkable ligand effect was observed when the copolymerization was carried out in lower alcohols. For example, while a high molecular weight ethylene-carbon monoxide copolymer was formed in methanol using $[\text{Pd}(\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2)(\text{MeCN})_2](\text{BF}_4)_2$ as catalyst,^{7,14,16} only low oligomers ($\text{DP} < 10$) were observed when the corresponding PPh_3 derivative, $[\text{Pd}(\text{Ph}_3\text{P})_2(\text{MeCN})_2](\text{BF}_4)_2$, was employed.⁶ An examination of the structures of the oligomers formed in the latter case revealed them to be polyketo esters of the general formula $\text{MeO}-(\text{COCH}_2\text{CH}_2)_n\text{H}$, thereby indicating a facile termination step involving the methanolysis of the intermediate Pd-

(15) Barasacchi, M.; Consiglio, G.; Medici, L.; Petrucci, G.; Suter, U. *W. Angew. Chem., Int. Ed. Engl.* 1991, 30, 989.

(16) Zhao, A. X.; Chien, J. C. W. *J. Polym. Sci., Part A: Polym. Chem.* 1992, 30, 2735.

Scheme III



acyl species. Well-behaved Schultz-Flory plots were obtained for the polyketo esters formed using methanol and ethanol as solvents.⁶ From these plots it was determined that the termination rate is 1.7 times slower in methanol than ethanol, presumably due to the larger steric size of the latter. This was further supported by the observation that low molecular weight oligomers were not formed when the bulky *tert*-butyl alcohol was used as the solvent. Moreover, only methyl esters were formed in a 1:1 mixture (v/v) of methanol and *tert*-butyl alcohol, indicating a substantially higher termination rate for the smaller alcohol. As expected, the rate of alcoholysis of the Pd-acyls is also dependent on the nucleophilicity of the alcohol employed. Thus, lower oligomeric polyketo esters were not observed when CF₃CH₂OH was used as the solvent.

The initiation of copolymerization by Pd-hydrides and Pd-alkoxides formed in situ in alcohol-containing solvents is not too surprising. A more interesting question involves the nature of the initiator in aprotic media.¹⁴ In the copolymerization of ethylene and carbon monoxide by [Pd(Ph₂P(CH₂)₃PPh₂)(MeCN)₂](BF₄)₂ in THF-nitromethane, a long induction period followed by a slower copolymerization rate was observed.¹⁴ However, the induction period disappeared upon the addition of H₂. Given the high electrophilicity of the Pd(II) ion,¹⁷ the formation of a Pd-hydride by heterolytic cleavage of H₂ is not unexpected. That a Pd-hydride is the initiator in the presence of H₂ was also indicated by the observation of substantial deuteration of the terminal ethyl group of the copolymer when D₂ was used instead of H₂.¹⁴ Note that the deuteration of the methylene unit of the ethyl terminus is consistent with rapid *reversible* insertion of ethylene into the initial Pd-D bond. In the *absence* of added H₂, the Pd-hydride species forms from trace water via the water-gas shift reaction. Metal-hydrides are known to be intermediates in this reaction.¹⁸ Thus, we observed deuteration of the terminal ethyl group of the ethylene-carbon monoxide copolymer when the po-

lymerization was carried out in THF-nitromethane in the presence of added D₂O.¹⁴ 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 in the ethylene-carbon monoxide copolymer generated in THF-nitromethane.¹⁴

Alternative Mechanism. In a very recent paper,¹⁹ Consiglio has proposed a new chain growth mechanism involving cationic Pd-carbene species in order to account for the formation of polymers with spiroketal repeating units (Scheme III¹⁹). While this mechanism was proposed specifically for the alternating copolymerization of propylene with carbon monoxide, it was implied that other olefins may copolymerize with carbon monoxide through a similar series of steps. However, several pieces of evidence appear to rule out this mechanism, at least for the closely related systems examined by us and others. Specifically: (a) we have never observed the presence of spiroketal structures in any of our alternating olefin-carbon monoxide copolymers, including the propylene-carbon monoxide copolymer, although we have carried out the copolymerizations in a variety of protic and aprotic solvents;^{5,6,14,20} (b) the proposed mechanism for the generation of the Pd-carbene requires a protic solvent (specifically, an alcohol¹⁹) whereas our catalyst systems are equally effective in dry nonprotic solvents; and (c) we and others (especially Brookhart,¹³ *vide infra*) have already demonstrated the key steps in our chain growth sequence involving alternate insertions of olefin and carbon monoxide into an initial Pd-hydride bond (*vide supra*). We have now successfully carried out the alternating copolymerization of propylene with carbon monoxide *in the absence of any solvent* by starting with the Pd-alkyl compound [Pd(Ph₂P(CH₂)₃PPh₂)(MeCN)(Me)](BF₄).²¹ A copolymer with $M_w = 800\,000$ was obtained with a reaction rate comparable to that observed for solution-phase copolymerization using [Pd(Ph₂P(CH₂)₃PPh₂)(MeCN)₂](BF₄)₂ as catalyst. *The solid-state*¹³C-

(17) Sen, A. *Acc. Chem. Res.* 1988, 21, 421.

(18) Reviews: (a) Laine, R. M.; Wilson, R. B. In *Aspects of Homogeneous Catalysis*; Ugo, R., Ed.; D. Reidel: Dordrecht, 1984; p 217. (b) Ford, P. C. *Acc. Chem. Res.* 1981, 14, 31.

(19) Batistini, A.; Consiglio, G. *Organometallics* 1992, 11, 1766.

(20) (a) Sen, A.; Jiang, Z. *Polym. Mater. Sci. Eng.* 1992, 67, 102. (b) Sen, A.; Jiang, Z. *Macromolecules* 1993, 26, 911.

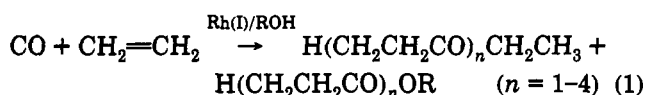
(21) Sen, A.; Sanganeria, S.; Dahlen, G. Unpublished.

NMR of this polymer revealed the complete absence of any spiroketal repeating units. On the basis of the above observations, we believe that the Pd(II)-catalyzed alternating olefin-carbon monoxide copolymerization proceeds through the chain growth sequence shown in Scheme I and that the spiroketal formation occurs subsequently under certain reaction conditions.

Rhodium(I)-Based Systems

Thus far, we have confined our discussions to Pd(II)-based systems. However, Ni(II)-catalyzed^{1a,22} and Rh(I)-catalyzed²³ alternating copolymerization and cooligomerization of olefins with carbon monoxide have also been reported. Indeed, any transition metal species that catalyzes the hydroformylation of olefins²⁴ should, in principle, also be an effective catalyst for the copolymerization reaction. The key intermediate in the hydroformylation mechanism is a metal-acyl species formed by successive insertions of olefin and carbon monoxide into an initial metal-hydride bond. The final step in hydroformylation is the conversion of this metal-acyl species to the aldehyde by hydrogenolysis.²⁵ However, under conditions of low hydrogen and high olefin and carbon monoxide concentrations, further successive insertions of olefin and carbon monoxide into the metal-acyl bond should occur, resulting in the alternating cooligomerization and copolymerization of the olefin with carbon monoxide.

In order to test this hypothesis, we have examined the reactions of a number of olefins with carbon monoxide in the presence of several known Rh(I) hydroformylation catalysts, such as Rh(PPh₃)₂(CO)(Cl), in the absence of added hydrogen.²⁶ As shown in eq 1,^{26b} a series of oligomeric polyketones and polyketo esters were formed, depending on the solvent system employed. Several features of the cooligomerization



reaction merit comment.^{26b} First, the extent of reaction, as determined by the overall change in pressure, decreased as the steric bulk of the alcohol increased. Second, the ketone-to-ester ratio increased with steric size of the alcohol in the following order: CH₃OH < CH₃CH₂OH < CH₃CH₂CH₂OH < (CH₃)₂CHOH << (CH₃)₃COH. This, of course, is not surprising in light of similar observations with the Pd(II)-based system⁶ (vide supra).

Chain Propagation Mechanism. A rational mechanism for the Rh(I)-catalyzed oligomerization reaction is shown in Scheme IV²⁶ and encompasses a single mode

(22) (a) Klabunde, U.; Tulip, T. H.; Roe, D. C.; Ittel, S. D. *J. Organomet. Chem.* 1987, 334, 141. (b) Klabunde, U.; Ittel, S. D. *J. Mol. Catal.* 1987, 41, 123.

(23) (a) Consiglio, G.; Studer, B.; Oldani, F.; Pino, P. *J. Mol. Catal.* 1990, 58, L9. (b) Iwashita, Y.; Sakuraba, M. *Tetrahedron Lett.* 1971, 2409.

(24) Review: Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 621.

(25) The mechanism of the final, aldehyde-forming step is controversial. Both oxidative addition of hydrogen to the metal-acyl species, followed by reductive elimination of aldehyde, and binuclear reductive elimination involving a metal-acyl and a metal-hydride species have been proposed. See ref 24 for a discussion.

(26) (a) Sen, A.; Brumbaugh, J. S. *J. Organomet. Chem.* 1985, 279, C5. (b) Sen, A.; Brumbaugh, J. S.; Lin, M. *J. Mol. Catal.* 1992, 73, 297.

of chain growth. The esters (E_n) and ketones (K_n) arise by the alcoholysis and hydrogenolysis of the intermediate metal-acyls (ME_n) and metal-alkyls (MK_n), respectively. The metal-acyl species are terminated by reaction with ROH (rate = *r*_{ta}) and are propagated by olefin insertion (rate = *r*_{pe}). *R*_e represents the mole fraction of a metal-acyl species that is propagated. Similar, *R*_k represents the mole fraction of a metal-alkyl species that is propagated. Using this terminology, it can be shown²⁶ that

$$\log X^{E_n} = \log(1-R_e) + (n-1) \log(R_e R_k)$$

and

$$\log X^{K_n} = \log(1-R_k) + \log R_e + (n-1) \log(R_e R_k)$$

where *X*^{E_n} and *X*^{K_n} represent respectively the mole fractions of E_n and K_n formed. It follows that a plot of the logarithm of the mole fractions of the esters and ketones formed versus (*n* - 1) should yield two parallel straight lines with a common slope of log(*R*_e*R*_k) and intercepts of log(1-*R*_e) and log(1-*R*_k) + log *R*_e, respectively, from which *R*_e and *R*_k can be evaluated. Where the oligomeric polyketones are the sole products, the second equation can be simplified to

$$\log X^{K_n} = \log(1-R_k) + (n-1) \log(R_k)$$

by substituting *R*_e = 1. This equation is now similar to the Schultz-Flory equation²⁷ which is applicable only to polymerization involving a single mode of propagation and a single mode of termination. *R* is identical to the quantity α, which is equal to the probability of chain growth in the Schultz-Flory equation.

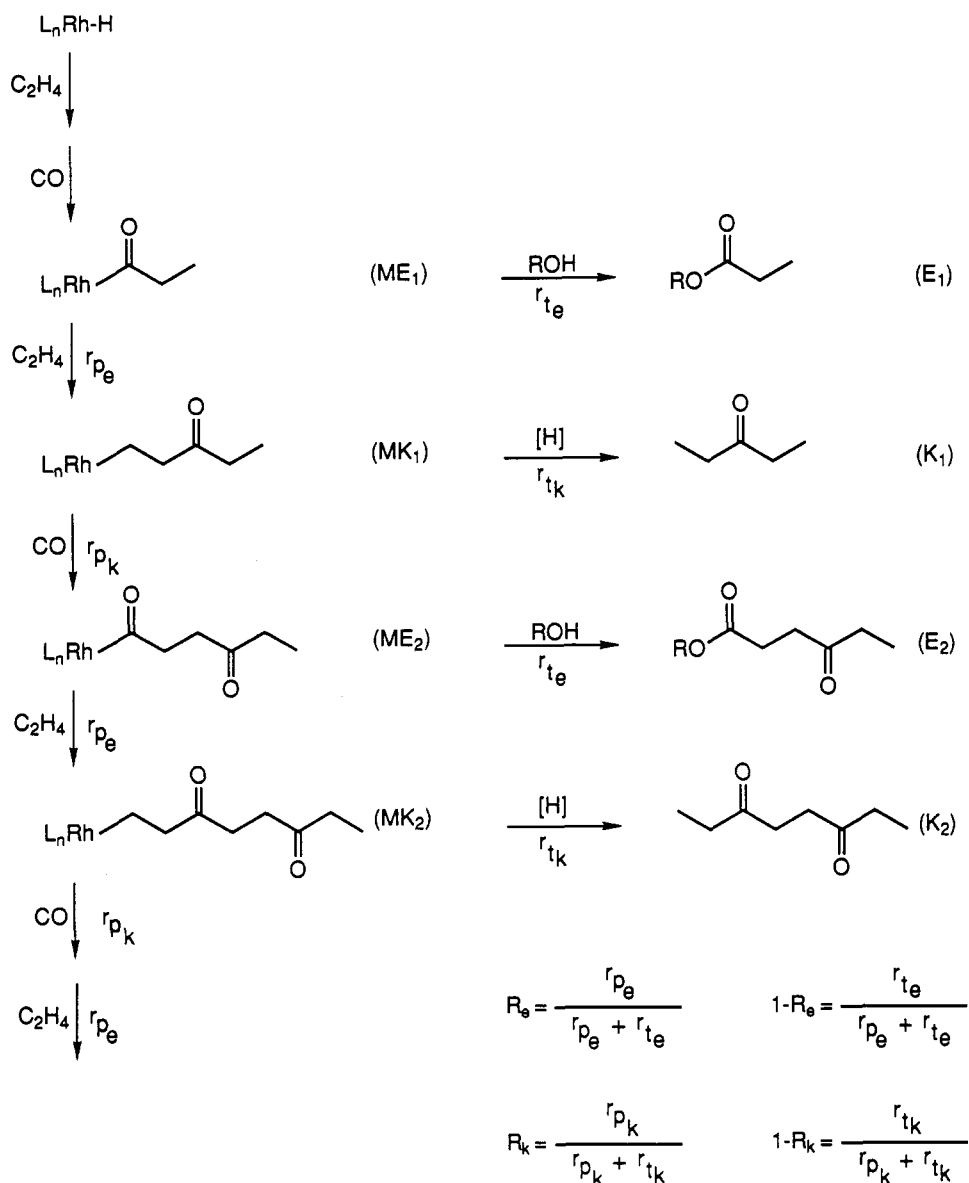
Using RhCl(CO)(PPh₃)₂ as catalyst, our results for the cooligomerization of ethylene with carbon monoxide in acetic acid-methanol mixture are shown in Figure 3.²⁶ Where both polyketones and polyketo esters were formed, two parallel straight lines are generated. For reasons not well-understood, an unusually low yield of diethyl ketone was produced in each case. The values of *R*_e and *R*_k obtained from the slopes and the intercepts are shown in Table I.²⁶ Table I clearly illustrates that *R*_e increases steadily with increasing steric bulk of the alcohol, reflecting the slower rate at which the intermediate metal-acyl complexes are terminated by the bulkier alcohols. On the other hand, as expected, the rate of hydrogenolysis of the corresponding metal-alkyls is alcohol independent.

Chain Initiation and Termination Mechanisms.

From a mass-balance standpoint, the esters H(CH₂CH₂CO)_nOR may be considered to be formed from *n* C₂H₄ units plus *n* CO units plus 1 alcohol molecule. On the other hand, the ketones H(CH₂CH₂CO)_nCH₂CH₃ must form from (*n* + 1) C₂H₄ units plus *n* CO units plus 2 H atoms (or H₂). Thus, it was necessary to examine the source for the two hydrogen atoms. Several pieces of experimental evidence indicated that these arise through a metal-catalyzed water-gas shift reaction.²⁶ For example, no reaction was observed in dry solvents. Additionally, the formation of ¹³CO₂ from ¹³CO was observed under similar reaction conditions. Note that the water-gas shift reaction involves a metal-hydride

(27) Henrici-Olive, G.; Olive, S. *Angew. Chem., Int. Ed. Engl.* 1972, 15, 136.

Scheme IV



intermediate.¹⁸ If this intermediate is intercepted by ethylene to form a metal-alkyl species, then the water-gas shift reaction would account for not only the source of hydrogen atoms but also the process of chain initiation.

Other Work

While the discussion, thus far, has focused mainly on work in our own laboratory, several recent publications emanating from other groups have served to significantly broaden the scope of the alternating copolymerization reaction. The synthesis of isotactic alternating propylene-carbon monoxide copolymer using a chiral bis(phosphine) Pd(II) complex as catalyst has been claimed by Consiglio.²⁸ Drent has demonstrated²⁹ that the simple substitution of the phosphine ligands on the Pd(II) ion by 1,10-phenanthroline leads to the formation of a catalyst that is effective for the alternating

copolymerization of styrene derivatives with carbon monoxide. Furthermore, Pino and Consiglio have shown that the resultant copolymers are highly syndiotactic (see Figure 4).³⁰ The mechanistic origin of the induced tacticity remains an open question. We have used [Pd(1,10-phenanthroline)(MeCN)₂](BF₄)₂ and related substituted phenanthroline derivatives as catalysts for the terpolymerization of ethylene, propylene, ω -undecylenyl alcohol, and ω -methylundecylenate with styrene and carbon monoxide.²⁰ Remarkably, at higher ratios of styrene to the second olefin, the terpolymers formed have structures consisting to syndiotactic alternating styrene-carbon monoxide blocks randomly separated by atactic spacers formed by the alternating second olefin-carbon monoxide units. The tactic styrene-CO blocks are lost with increasing content of the second olefin.²⁰

In a recent elegant study, Brookhart has demonstrated¹³ the *living* alternating copolymerization of styrene derivatives with carbon monoxide in noncoordinating solvents starting with the cationic species

(28) (a) Batistini, A.; Consiglio, G.; Suter, U. W. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 303. (b) Barasacchi, M.; Batistini, A.; Consiglio, G.; Suter, U. W. *Macromolecules* **1992**, *25*, 3604.

(29) (a) Drent, E. *Eur. Pat. Appl.* EP 229,408 (1986). (b) Drent, E. *U.S. Patent* 4,788,279 (1988).

(30) (a) Corradini, P.; De Rosa, C.; Panunzi, A.; Petrucci, G.; Pino, P. *Chimia* **1990**, *44*, 52. (b) Reference 28b.

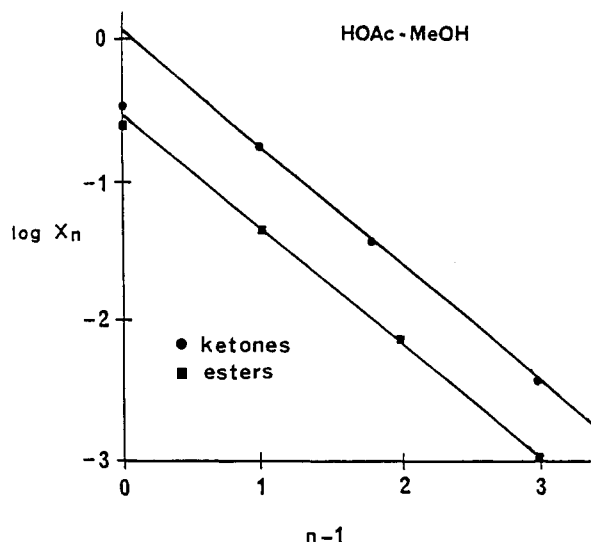


Figure 3. Plots of $\log X_n$ versus $n - 1$ for oligomeric polyketone esters and polyketones formed in acetic acid-methanol mixtures using $\text{Rh}(\text{PPh}_3)_2(\text{CO})\text{Cl}$ as catalyst.²⁸

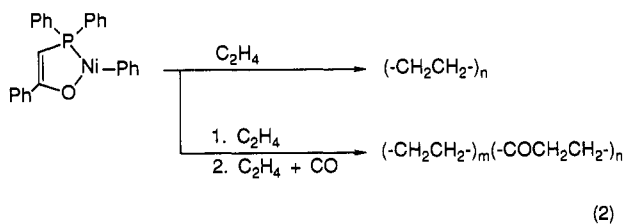
Table I. Calculated Values of R_p and R_x^a

solvent	R_p	R_x
HOAc-MeOH ^b	0.75	0.23
DOAc-MeOD ^b	0.83	0.23
HOAc-EtOH ^b	0.83	0.24
HOAc- <i>i</i> -PrOH ^b	0.88	0.23
acetone-H ₂ O ^c		0.11
<i>t</i> -BuOH-H ₂ O ^c		0.14

^a $[\text{Rh}(\text{PPh}_3)_2(\text{CO})(\text{Cl})] = 1 \times 10^{-2} \text{ M}$; reaction temperature = 110 °C; initial pressures, $P_{\text{CO}} = P_{\text{C}_2\text{H}_4} = 500 \text{ psi}$. ^b Acetic acid-alcohol = 1/1 (v/v). ^c Acetone-H₂O or *t*-BuOH-H₂O = 5/1 (v/v).

$[\text{Pd}(2,2'\text{-bipyridine})(\text{CO})(\text{COCH}_3)][\text{B}(3,5\text{-}(\text{CF}_3)_2\text{-C}_6\text{H}_3)_4]$. Apart from the synthesis of copolymers with narrow polydispersity, it was possible to monitor chain growth by NMR following sequential additions of styrene and carbon monoxide at -80 °C. Brookhart's observations¹³ further confirmed (a) the chain growth sequence shown in Scheme I, (b) the chelation of the carbonyl oxygen following olefin insertion into the Pd-acyl bond (cf. Figure 1), and (c) the olefin insertion into the Pd-acyl bond as the rate-limiting step. Clearly, the bis(phosphine)- and bis(amine)-Pd(II) systems follow closely analogous mechanistic pathways.

Finally, mention should be made of a very interesting Ni(II)-based catalytic system developed by the Du Pont group²² (see eq 2). Unlike the catalysts described above,



the Ni(II) species will homopolymerize ethylene. If carbon monoxide is added to the reaction mixture *after* the homopolymerization of ethylene has started, then a block copolymer with a polyethylene segment followed by an alternating ethylene-carbon monoxide segment is formed.

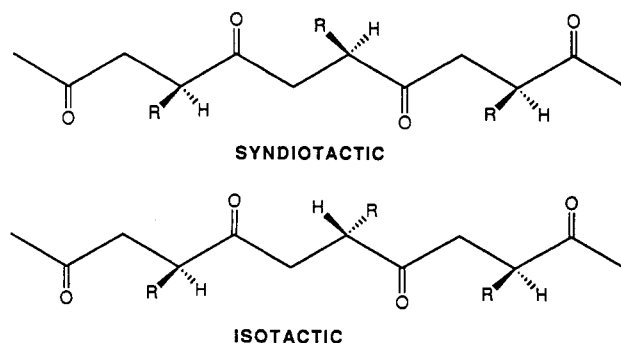


Figure 4. The syndiotactic and isotactic structures for the alternating copolymers of α -olefins with carbon monoxide.

Conclusion

It is clear from the above discussions that interest in the alternating copolymerization of olefins with carbon monoxide is driven both by the fascinating aspects of the copolymerization mechanism and the practical utility of the resultant polymers and oligomers. While significant progress has been made, several key questions remain unanswered. Perhaps the most intriguing of these is the mechanistic origin of the induced tacticity (see Figure 4) observed in some copolymers^{13,20,28,30} (vide supra). It should be noted in this context that, at the high molecular weight limit, a *syndiotactic* alternating α -olefin-carbon monoxide copolymer chain will always show vanishingly small optical activity since the chiral sense of the asymmetric centers in the backbone *alternate* (i.e., ...*RSRSRS*...). On the other hand, the asymmetric centers in the individual chains of an *isotactic* alternating α -olefin-carbon monoxide copolymer sample have the *same* chiral sense (i.e., ...*RRRRRR*... or ...*SSSSSS*...), and thus, the synthesis of optically active isotactic alternating α -olefin-carbon monoxide copolymers should be possible.²⁸

The second important goal in the area is the synthesis of block copolymers using a living copolymerization system. While the living copolymerization of styrene derivatives with carbon monoxide using a bis(amine)-Pd(II)-based system has been demonstrated by Brookhart,¹³ the synthesis of block copolymers has not been reported. More importantly, there exists no comparable living copolymerization system that is based on bis(phosphine)-Pd(II) complexes. The latter complexes are significantly better catalysts than the bis(amine) analogs for the copolymerization of aliphatic α -olefins with carbon monoxide.

The third important objective is the copolymerization of functional vinyl monomers with carbon monoxide. The resultant highly functionalized materials are likely to be of considerable practical importance given the varied applications of the presently known functional polymers.³¹ One of the advantages of using a late transition metal, such as Pd(II), as catalyst is that it is unlikely to be poisoned or deactivated by the presence of oxygen, nitrogen, or halogen functionalities, either in the solvent or in the substrate. Indeed, functional vinyl monomers, such as methyl acrylate, are known to insert readily into the Pd-acyl bonds of $\text{Pd}(\text{Ph}_2\text{P}-$

(31) Recent reviews: (a) Akelah, A.; Moet, A. *Functionalized Polymers and Their Applications*; Chapman & Hall: New York, 1990. (b) *Functional Polymers*; Bergbreiter, D. E., Martin, C. R., Eds.; Plenum: New York, 1989. (c) Sherrington, D. C.; Hodge, P. *Syntheses and Separations using Functional Polymers*; Wiley: New York, 1988.

$(\text{CH}_2)_n\text{PPh}_2(\text{solvent})(\text{COR})^+$ species.^{11,12} That such complexes do not catalyze the corresponding copolymerization reaction is presumably, therefore, due to the slow insertion of carbon monoxide into the resultant Pd-alkyl bond.

Finally, from an environmental standpoint, it would be most desirable to carry out the copolymerization reaction in the absence of a solvent. As described above, we have achieved the solventless synthesis of high molecular weight propylene-carbon monoxide copolymers by starting with $[\text{Pd}(\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2)(\text{MeCN})-$

$(\text{Me})](\text{BF}_4)$.²⁰ However, the scope of such a solventless copolymerization procedure needs to be fully explored.

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