GRANT #DE-FG02-84ER13295

PROGRESS REPORT

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SUMMARY

Work on several different facets of organotransition metal chemistry, homogeneous and heterogeneous catalysis that was carried out during the current grant period is summarized. We have discovered several cationic palladium(II) complexes incorporating bulky phosphine or pyridine ligands that are highly selective catalysts for the linear dimerization of vinyl monomers (styrene, ethylene, and propylene) and the linear polymerization of p-divinylbenzene, the reactions proceeding through a carbocationic mechanism. We have continued our studies in the area of alternating olefin-carbon monoxide copolymers. The scope and the mechanism of the copolymerization reaction, as well as the reactivity of the copolymers, were examined. New catalytic systems for the alternating copolymerization of α-olefins with carbon monoxide were discovered. In the case of styrene derivatives, highly tactic copolymers were obtained. Novel poly(ethylenepyrrolediyl) derivatives were synthesized in one-step from the alternating ethylene-carbon monoxide copolymer and were found to become electronic conductors upon doping with iodine. A new catalytic system for the synthesis of polyureas and polyoxamides directly from carbon monoxide and diamines was also discovered. In the area of oxidation chemistry, metallic platinum was found to be an active catalyst for the oxidation of ethers, esters, and amines to the corresponding carboxylic acids and the oxidation of olefins to the corresponding 1,2-diols in aqueous medium. Dioxygen was the oxidant in all cases. In another project, the anaerobic and aerobic decomposition of molybdenum(VI)-oxoalkyl compounds were studied as possible models for the heterogeneous oxidation of alkanes and olefins on Mo(VI)-oxide surfaces. Finally, the results of an ongoing effort directed toward the synthesis of polymer-trapped metal, metal oxide, and metal sulfide nanoclusters (size <1-10 nm) is described.

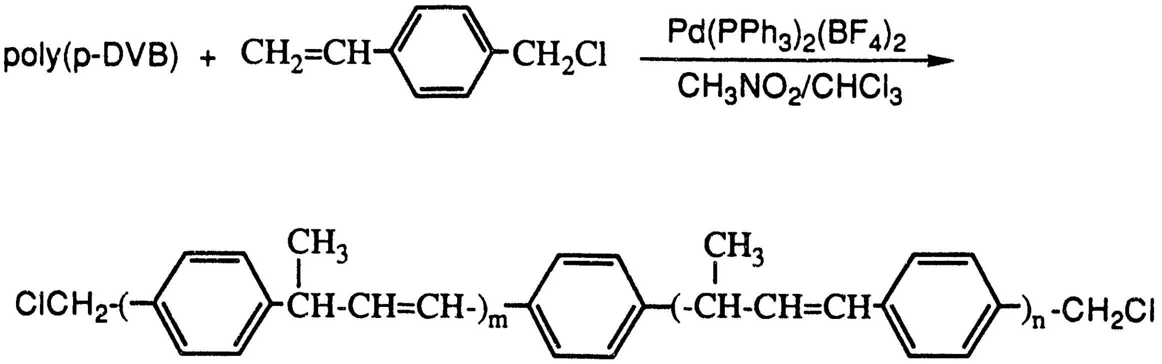
PROGRESS REPORT

Current Grant Period: December 1, 1989 - November 30, 1992.
Total Funding: $ 284,036 ($ 204,167 in direct costs).

This progress report summarizes the work performed in the first 2.5 *years* of the current grant period. During this time, we have investigated several different facets of organotransition metal chemistry, homogeneous and heterogeneous catalysis. It is gratifying to note that the principal goals stated in the previous proposal were achieved. These were (a) the discovery of new catalytic systems for the alternating copolymerization of α-olefins with carbon monoxide;[5,6,7] in the case of styrene derivatives, highly tactic copolymers were obtained,[7] (b) the discovery of a new catalytic system for the synthesis of polyureas and polyoxamides directly from carbon monoxide and diamines,[10] and (c) the discovery of a new catalytic system for the direct oxidation of organic substrates by dioxygen under mild conditions.[11,12] Our results in these and other areas are summarized below.

Building on our previous study of the interaction of highly electrophilic, weakly ligated, transition metal complexes with olefins, we have succeeded in developing catalysts for the dimerization and polymerization of vinyl monomers with selectivity that is unprecedented in carbocationic chemistry.[2,3] We had earlier shown that the cationic Pd(II) species, $Pd(CH_3CN)_4(BF_4)_2$,[1] was an effective catalyst for the oligomerization of simple olefins, such as ethylene and propylene, and the polymerization of styrene derivatives. These reactions were shown to proceed through a carbocationic pathway initiated by the electrophilic (heterolytic) cleavage of the C-C π-bond of the olefin by the metal resulting in the formation of an incipient carbocation. A key advantage that transition metal electrophiles have over the traditional Lewis acids is the ability to tailor their activity and selectivity by a rational choice of ligands. Indeed, highly selective catalysts have resulted from replacement the some of the weakly coordinating CH_3CN ligands in the parent compound by the more basic phosphine or pyridine derivatives.[2,3] For example, the compounds, $Pd(2,6\text{-}^tBu_2\text{-pyridine})_2(CH_3CN)_2(BF_4)_2$, $Pd(PPh_3)_2(BF_4)_2$, and $Pd(Ph_2PCH_2CH_2PPh_2)(BF_4)_2$, were found to be highly selective catalysts for the linear dimerization of vinyl monomers (styrene, ethylene, and propylene) and the linear polymerization of p-divinylbenzene, the reactions proceeding through a carbocationic mechanism (cf., Scheme 1). One manifestation of the high selectivity was the ability to catalyze the dimerization of ethylene in the presence of propylene and styrene in the presence of α-methylstyrene even though the second member of each pair is normally significantly more reactive in reactions involving carbocationic intermediates. The abnormal reactivity pattern was due to greater steric congestion in the latter Pd(II) compounds which prevented the bulkier olefins from readily approaching the electrophilic metal center. The linear polymerization of p-divinylbenzene involved a novel step-growth mechanism (Scheme 2). The synthesis of a telechelic polymer through cross-coupling between the the terminal vinyl groups of linear poly(p-divinylbenzene) and the vinyl group of a functionalized styrene derivative was also achieved (eq. 1).

The reaction rates for the linear dimerization of styrene and the linear polymerization of p-divinylbenzene obeyed the following rate law (eq 2).[3] Mathematical modeling indicated that the fractional order in the catalyst concentration was due to preequilibria involving anion dissociation from the metal center and the actual catalytic species in the case of $Pd(PPh_3)_2(BF_4)_2$ was found to be the dication, $Pd(PPh_3)_2(solv)_2^{2+}$.

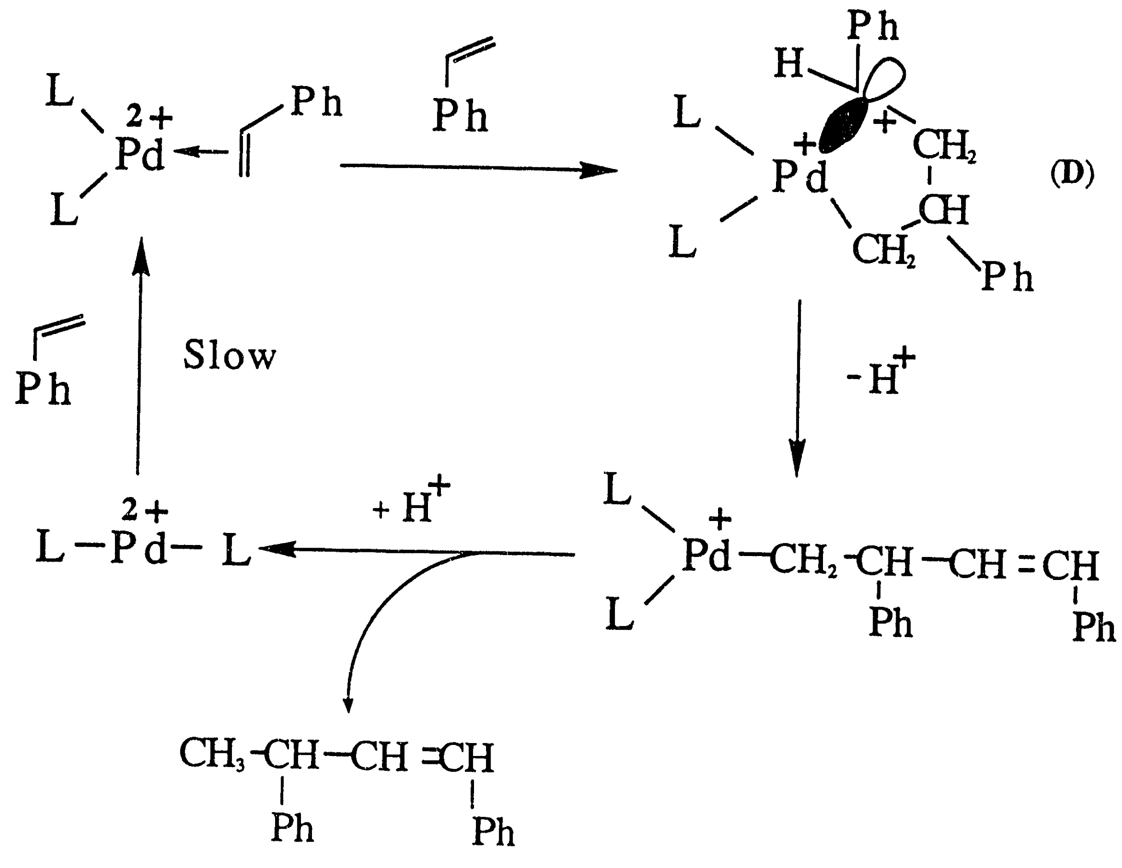


(1)

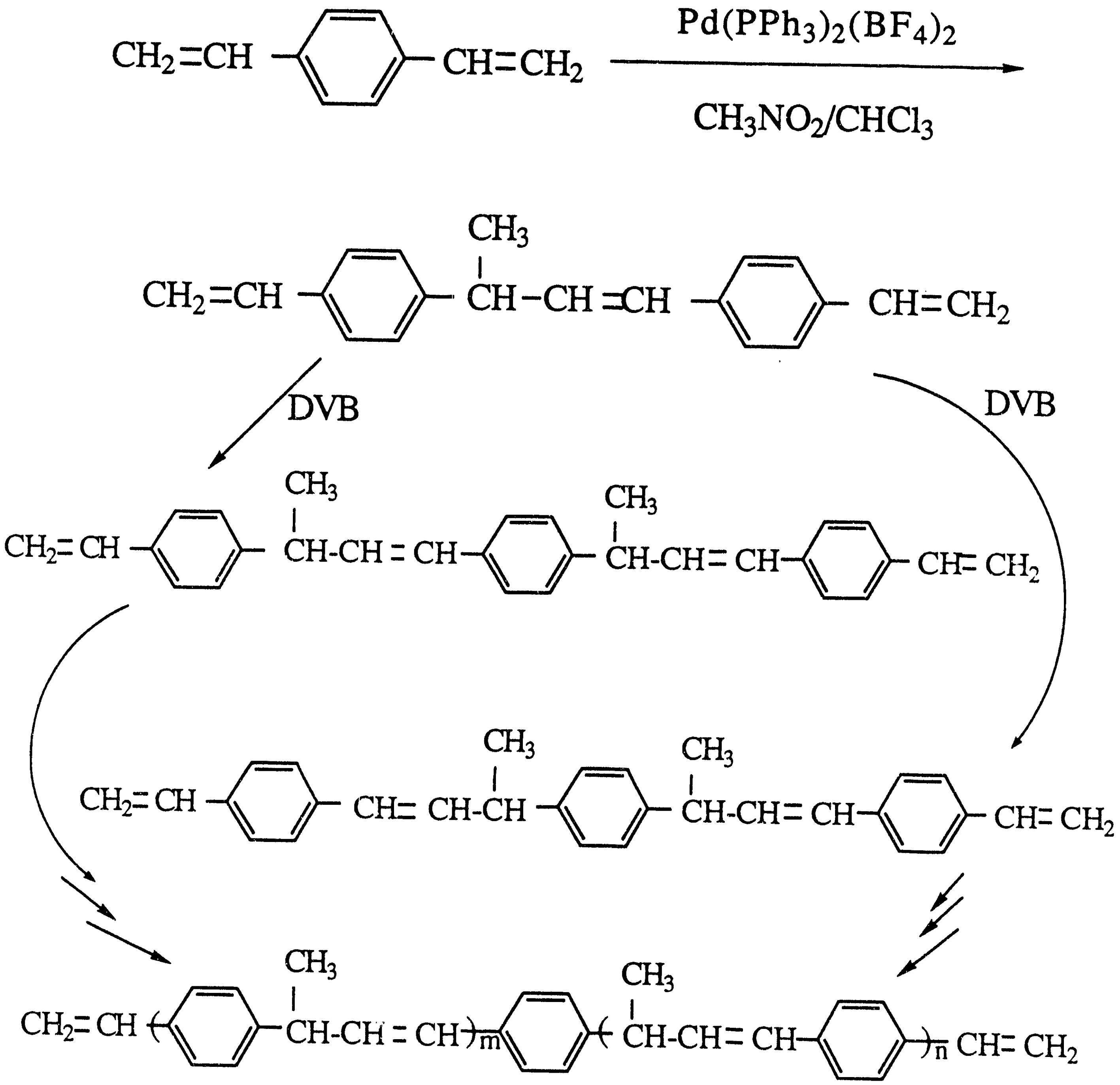
$$-d[\text{vinyl}]/dt = k[\text{Pd(II)}]^{0.7}[\text{vinyl}]^{1}$$

(2)

Scheme 1



Scheme 2


CH2=CH
CH=CH2
Pd(PPh3)2(BF4)2
CH3NO2/CHCl3
CH3
CH2=CH
CH-CH=CH
CH=CH2
DVB
DVB
CH3
CH3
CH2=CH
CH-CH=CH
CH-CH=CH
CH=CH2
CH3
CH3
CH2=CH
CH=CH-CH
CH-CH=CH
CH=CH2
CH3
CH3
CH2=CH
CH-CH=CH
m
CH-CH=CH
n
CH=CH2

We have continued our studies in the area of alternating olefin-carbon monoxide copolymers. The scope and the mechanism of the copolymerization reaction, as well as the reactivity of the copolymers, were examined.[4-9] The high interest in these polymers stem from (a) the low cost of carbon monoxide, (b) their superior mechanical properties, (c) their photodegradability due to the presence of the carbonyl chromophore in the backbone, and (d) their ready chemical transformation to other classes of functionalized polymers. Indeed, Shell plans to start the commercial production of the alternating ethylene-carbon monoxide copolymer using a catalyst system closely analogous to that developed by us.

We have studied the insertion of olefins into Pd(II)-acyl bonds.[4] This is the rate determining step in the chain growth sequence observed for the Pd(II) catalyzed alternating copolymerization of olefins with carbon monoxide. The reaction of norbornene with the cationic Pd(II)-acyl species, $[Pd(PPh_3)_2(CH_3CN)(COR)]BF_4$, resulted in the formation of $[Pd(PPh_3)_2(C_7H_{10}COR)]BF_4$. The crystal structure for R = Me is shown in Fig. 1. The phosphines occupy cis positions and the 2-acetylnorborn-1-yl residue acts as a chelating ligand by coordinating through the norbornyl carbon and the carbonyl oxygen. In case of olefins that have an accessible β-hydrogen atom, a stable organometallic species was not formed; rather, a vinylketone formed by β-hydrogen abstraction from the inserted product was observed. An examination of the mechanism indicated that the insertion proceeded through a four-coordinate intermediate formed by olefin displacement of the CH_3CN ligand. In the case of neutral Pd(II) compounds of the type, $Pd(PPh_3)_2(Cl)(COR)$, olefin insertion proceeded more slowly through a four-coordinate intermediate formed by olefin displacement of the PPh_3 ligand. Consistent with this mechanism was the observation that the insertion was significantly accelerated in the presence of a "phosphine sponge". Our study[4] allowed, for the first time, an assessment of the relative importance of the presence of a easily displaced ligand versus electrophilicity of the metal center in an insertion reaction. In this case, it is clear that the facile coordination of the olefin by ligand displacement was of primary importance.

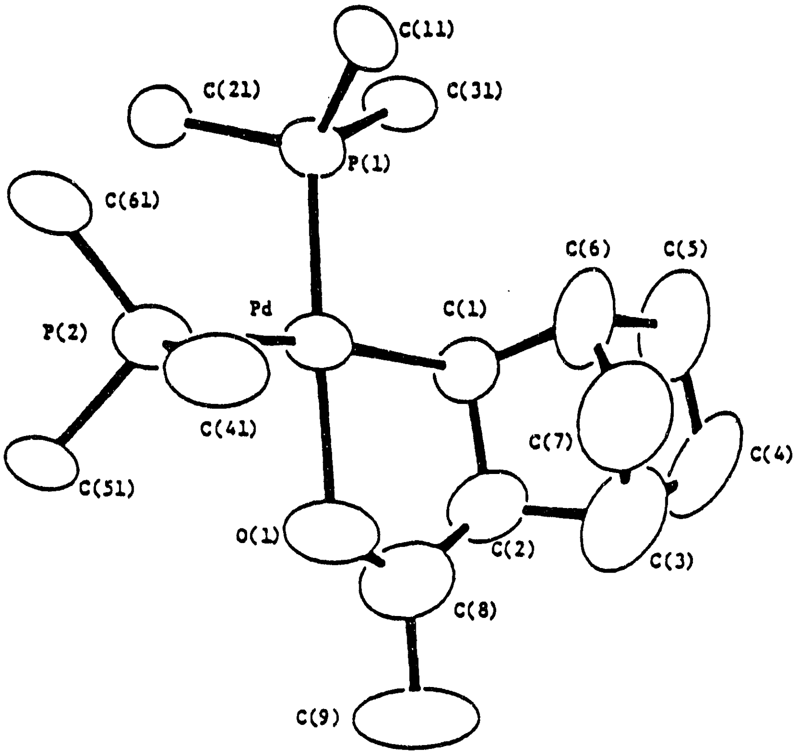
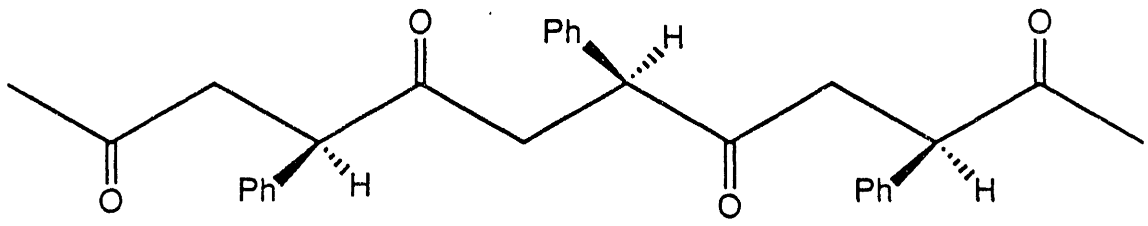
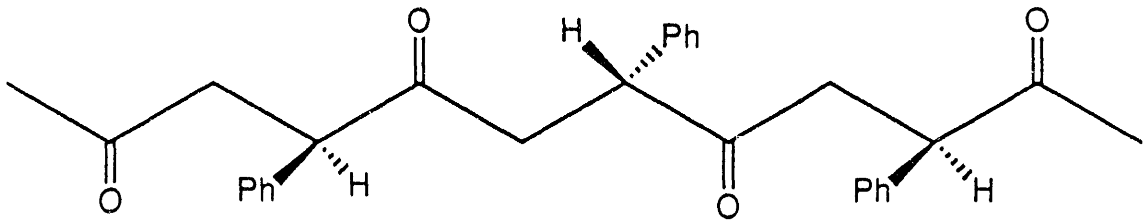


Fig. 1. View of the inner coordination sphere of $[Pd(PPh_3)_2(C_7H_{10}COCH_3)]BF_4$, including the entire chelating 2-acetylnorborn-1-yl ligand.

One of the stated goals in the previous proposal was the achievement of metal catalyzed alternating copolymerization of *α-olefins* with carbon monoxide (previously, only ethylene and strained olefins were observed to participate in the reaction). We have now achieved the alternating copolymerization of propylene and other α-olefins, as well styrene derivatives, with carbon monoxide to form high molecular weight polymers[5,6,7]. The new catalysts fall into two classes. The first was derived from our original system by substituting Ph_3P in $[Pd(PPh_3)_2(solv)_2](BF_4)_2$ by either Me_3P or $Ph_2P(CH_2)_3PPh_2$, and was effective for the copolymerization and terpolymerization of alkyl-substituted α-olefins with carbon monoxide.[5,6] The second system involved 1,10-phenanthroline derivatives as ligands and were also effective for the copolymerization of styrene derivatives.[7] This latter system was modeled after a Shell patent. Although our understanding of the new catalytic systems is in its infancy, it is very clear that the new systems differ mechanistically from the Ph_3P-based system in several remarkable ways. First, while the new systems were also effective in aprotic solvents, they were most active in the presence of lower alcohols, such as methanol. On the other hand, because of the termination of Pd(II)-acyl intermediates by alcohols, only oligomeric polyketoesters were formed when the Ph_3P-based system was employed. Second, the copolymerization rates were much higher (for example, C_2H_4-CO copolymerization rate of 3.6 Kg/g.Pd-h for the $Ph_2P(CH_2)_3PPh_2$-based system versus 160 g/g.Pd-h for the Ph_3P-based system). Third, for the copolymerization of propylene, the ratio of head-to-tail to head-to-head repeating units in the copolymer increased in the order: $Ph_2P(CH_2)_3PPh_2 <$ 1,10-phenanthroline $< Me_3P$. For the Me_3P-based system, complete regiospecificity in propylene incorporation was observed. This trend clearly cannot be explained on the basis of steric arguments. Finally, and most significantly, the 1,10-phenanthroline-based system gave copolymers of styrene derivatives with carbon monoxide that were not only regiospecific, but also stereospecific, with respect to styrene incorporation, i. e., the polymers were tactic.[7] Although it is not clear at this point whether the copolymers are syndio- or isotactic (Fig. 2), the presence of high tacticity was verified by both NMR and X-ray powder diffraction. A unique feature of these polymers is that the two tactic forms are, in principle, interconvertible through keto-enol tautomerization. Indeed, in the presence of bases, the tactic polymers converted to the atactic form.



SYNDIOTACTIC

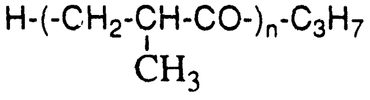


ISOTACTIC

Fig. 2. Possible structures for the tactic alternating styrene-CO copolymers.

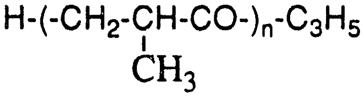
In addition to copolymers of a single olefin with carbon monoxide, the new catalyst systems allowed the synthesis of terpolymers incorporating two different olefins. Interesting solvent effects were observed for the latter process. For example, using the $Ph_2P(CH_2)_3PPh_2$-based system,[6] terpolymers of ethylene, propylene and carbon monoxide were formed in CH_3NO_2-THF mixture when all three monomers were present. On the other hand, in CH_3NO_2-CH_3OH mixture, *only* the C_2H_4-CO copolymer formed until all the C_2H_4 present was used up, whereupon the formation of C_3H_6-CO copolymer began.

Finally, the tractability of the alternating C_3H_6-CO copolymer (compared to C_2H_4-CO copolymer) allowed us to investigate the initiation and termination steps through an examination of polymer end-groups.[5,6] The following oligomers (along with their relative amounts) were observed when a low molecular-weight C_3H_6-CO copolymer synthesized in CH_3NO_2-CH_3OH was analyzed. Clearly, most of the polymer chains (90%) were initiated by a palladium-hydride while



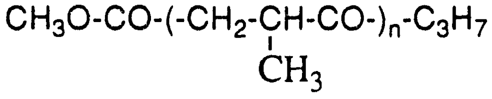
$\mathrm{H\text{-}(\text{-}CH_2\text{-}\underset{\displaystyle CH_3}{CH}\text{-}CO\text{-})_n\text{-}C_3H_7}$

(61.4%)



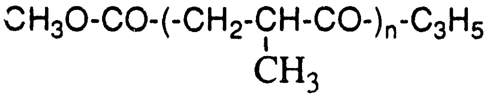
$\mathrm{H\text{-}(\text{-}CH_2\text{-}\underset{\displaystyle CH_3}{CH}\text{-}CO\text{-})_n\text{-}C_3H_5}$

(26.9%)



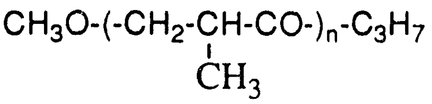
$\mathrm{CH_3O\text{-}CO\text{-}(\text{-}CH_2\text{-}\underset{\displaystyle CH_3}{CH}\text{-}CO\text{-})_n\text{-}C_3H_7}$

(6.0%)



$\mathrm{CH_3O\text{-}CO\text{-}(\text{-}CH_2\text{-}\underset{\displaystyle CH_3}{CH}\text{-}CO\text{-})_n\text{-}C_3H_5}$

(3.4%)



$\mathrm{CH_3O\text{-}(\text{-}CH_2\text{-}\underset{\displaystyle CH_3}{CH}\text{-}CO\text{-})_n\text{-}C_3H_7}$

(2.3%)

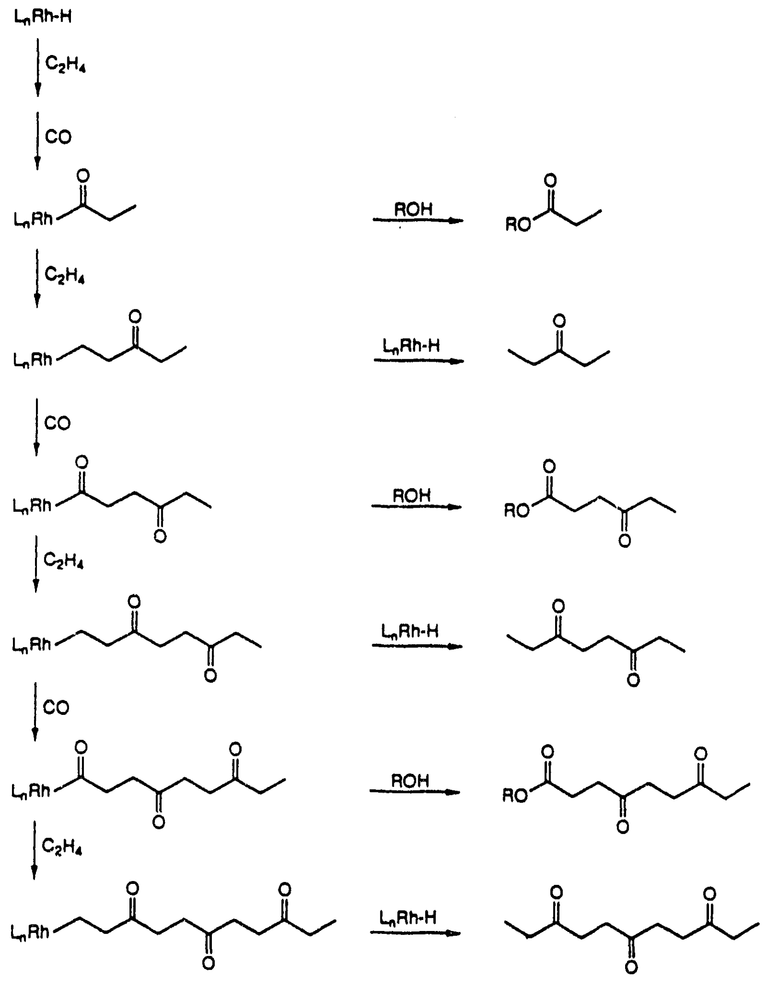
palladium-methoxide initiated the rest. Protonation was the major termination step while termination by β-hydrogen abstraction was also observed. In an aprotic solvent, such as CH_3NO_2-THF, an long induction period was observed before the onset of the copolymerization reaction. However, the induction period was eliminated upon the addition of a hydride source, such as H_2 or H_2O. The initiation by a palladium-hydride in this system was confirmed by the observation of deuterated terminal alkyl groups in the presence of D_2 or D_2O.

We have also explored the role of transition metal ions other than Pd(II) in the catalytic alternating copolymerization of olefins with carbon monoxide. In a detailed paper, we have reported on the Rh(I) catalyzed cooligomerization of ethylene, propylene, and butenes with carbon monoxide.[8] In the presence of either $Rh(PPh_3)_4(H)$, $Rh(PPh_3)_3(CO)(H)$, or $Rh(PPh_3)_2(CO)(Cl)(H)$, the cooligomerization of ethylene and carbon monoxide was observed with a typical rate of 1500 combined turnovers (C_2H_4 plus CO) per mole of catalyst per day. In a combination of alcohol and acetic acid, a mixture of oligomeric polyketones and polyketoesters was formed (eq. 3). The polyketone to polyketoester ratio increased with increasing bulk of the alcohol. The polyketones were formed almost exclusively when a combination of water and either alcohol, acetone or acetonitrile was used as the reaction medium. The reaction did not proceed in pure water or acetic acid. A combination of

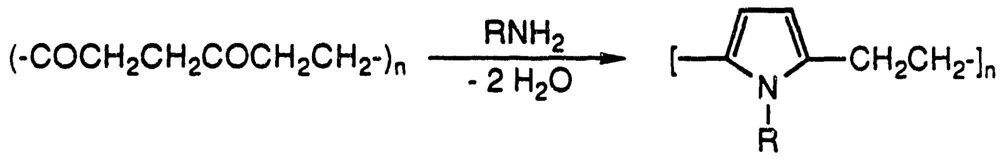
$$\begin{aligned} CO + CH_2{=}CH_2 \xrightarrow[HOAc/ROH]{Rh(I)} \; & H\text{-}(\text{-}CH_2CH_2\text{-}CO\text{-})_n\text{-}CH_2CH_3 \; + \\ & H\text{-}(\text{-}CH_2CH_2\text{-}CO\text{-})_n\text{-}OR \quad (n=1\text{-}4) \end{aligned} \tag{3}$$

mechanistic studies and mathematical modeling of the chain growth sequence led to the following conclusions.[8] The reactions were initiated by a rhodium-hydride species formed through the water-gas shift reaction. The chain-growth involved the alternate insertions of ethylene and carbon monoxide into the initial rhodium-hydride bond. The oligomeric polyketoesters were formed by the alcoholysis of the intermediate rhodium-acyl species, whereas the oligomeric polyketones were generated through a bimolecular reductive elimination from the intermediate rhodium-alkyls and a rhodium-hydride. Overall mechanism is shown in Scheme 3.

Scheme 3



In addition to our studies on the copolymerization process, we have also examined the reactivity of the copolymers themselves. We had earlier reported the one-step synthesis of poly(ethylenepyrrolediyl) derivatives starting with the alternating C_2H_4-CO copolymer (eq. 4). Depending on the primary amine employed, 92-99% of the carbonyl groups in the original polymer was found to react. We have now discovered that the poly(ethylenepyrrolediyl) derivatives exhibited electronic conductivity upon doping with iodine.[9] The conductivity of the iodine-doped polymers was in the range of 5×10^{-5} to 2×10^{-3} Ω^{-1} cm^{-1}. Remarkably, the doped polymers were stable to moisture and air for at least one year. Finally, the strength and flexibility of the polymers could be improved by cross-linking using a diamine. It should be noted that these polymers constitute only the second known class of nonconjugated conducting polymers.



(4)

A second stated goal in the previous proposal was the catalytic synthesis of polyureas and polyoxamides directly from carbon monoxide and diamines. The synthesis of polyoxamides currently involves reactions of oxalic acid and oxalic esters with diamines. Polyureas are made through the reaction of diisocyanates with diamines. All of the above procedures employ relatively expensive organic compounds as the source for the carbonyl functionality. In principle, it should be possible to replace these simply with carbon monoxide under oxidative conditions, (eqs. 5 and 6). We have now discovered that PPh_3-coordinated Pd(II) ion, in basic THF, catalyzes the carbonylation of α,ω-diamines to form polymers with *both*

$$H_2N\text{-}R\text{-}NH_2 \ + \ CO \longrightarrow (\text{-}HN\text{-}R\text{-}NH\text{-}CO\text{-})_n \ + \ 2\,H^+ \ + \ 2\,e^- \qquad (5)$$

$$H_2N\text{-}R\text{-}NH_2 \ + \ 2\,CO \longrightarrow (\text{-}HN\text{-}R\text{-}NH\text{-}CO\text{-}CO\text{-})_n \ + \ 2\,H^+ \ + \ 2\,e^- \qquad (6)$$

oxamide and urea linkages in the backbone.[10] The reaction was promoted by iodine. As Table 1 indicates, the ratio of oxamide to urea linkages in the resultant polymers was a sensitive function of the added iodine with the ratio decreasing from 1.5 to 0 with increasing iodine concentration. Unreacted amines constituted the end-groups and, thus, further reactions of the polymers through reactions of the termini should be possible.

TABLE 1[a]

I_2 mol/Pd mol	% Oxamide[b]	M_n[b]	DP[b]	% Yield[c]
1	58	3480	21.2	79.9
2	43	2520	15.6	74.2
4	30	3040	19.4	79.1
30	0	1886	13.5	89.7

[a] Typical reaction conditions: $Pd(OAc)_2$ (0.1 mmol); Ph_3P (0.2 mmol); K_2CO_3 (0.2 mmol); CO (1000 psi); 1,6-hexanediamine (3 mmol); THF (50 ml)

[b] Calculated from ^1H-NMR spectra.

[c] Yields based on initial amount of diamine (diamine: catalyst = 30).

A new research area that we have initiated under the current grant involves the development of novel approaches to low temperature oxidation of organic substrates where the active catalyst is a metal surface. To date we have made two interesting discoveries. The first is that metallic Pt was capable of activating C-H bonds that were α to an oxygen or nitrogen and in aqueous medium it was possible to directly oxidize ethers, esters and amines to the corresponding acids by O_2 using metallic Pt as catalyst (e. g., eq. 7).[11,12] An interesting application of the oxidation

$$\mathrm{CH_3CH_2OCH_2CH_3} \xrightarrow[\mathrm{D_2O,\ 95^{o}C}]{\mathrm{Pt/O_2}} \mathrm{CH_3COOCH_2CH_3} \xrightarrow[\mathrm{D_2O,\ 95^{o}C}]{\mathrm{Pt/O_2}} [\mathrm{CH_3COOCOCH_3}]$$

$$\xrightarrow{\mathrm{D_2O}} 2\ \mathrm{CH_3COOD} \qquad (7)$$

procedure that may have some practical value involves the oxidative degradation of polymers (to be published). For example, a sample of poly(ethylene oxide) was oxidized stepwise to glycolic acid, oxalic acid, and eventually to carbon dioxide using the above procedure (eq. 8). Starting with a polymer sample of molecular weight 3 million and a polymer repeating unit to Pt ratio of 100, complete degradation of the polymer was observed in a few hours.

$$[\mathrm{-CH_2\text{-}CH_2\text{-}O\text{-}}]_n \xrightarrow[\mathrm{D_2O,\ 85^{\circ}C}]{\mathrm{Pt\ /O_2\ (1\ atm)}} \mathrm{DO\text{-}CH_2\text{-}COOD}$$

$$\mathrm{MW} = 3{,}000{,}000$$

$$\longrightarrow \mathrm{DOOC\text{-}COOD}$$

$$\longrightarrow \mathrm{CO_2}$$

$$(8)$$

Publications 11 and 12 also describe stoichiometric hydrocarbon oxidations by Pt(II) in solution, in addition to catalysis by metallic Pt. The former work was supported by an NSF grant.

More recently, we have discovered that metallic Pt and Pd will catalyze the direct oxidation of olefins to 1,2-diols by O_2 (Table 2) (to be published). 1,2-Diols, such as ethylene glycol and propylene glycol, have a number of important industrial applications and are currently made primarily through a two-step procedure involving, first, the synthesis of the corresponding epoxide, and, second, the hydrolysis of the epoxide to the 1,2-diol. Additionally, organic hydroperoxides rather than O_2 are used as oxidants in the case of propylene. In our system, a control experiment indicated that the corresponding alcohol was *not* an intermediate in the conversion of the olefin to the diol. The effect of CO on the reaction was remarkable. In its presence, the formation of acetic acid from ethylene was suppressed while the rate of glycol formation was enhanced.

The final project in the area of oxidation chemistry involved the examination of the chemistry Mo(VI)-oxoalkyl complexes as a possible model for the heterogeneous oxidation of alkanes and olefins on MoO_3 surfaces. The general features of the latter oxidations indicate that an intermediate alkyl (or allyl) species is formed initially and that this is followed by oxygen transfer from either O_2 or a metal-oxo species. In order to gain a detailed understanding of this step involving the the conversion of the metal-bound hydrocarbyl group to the corresponding oxidized organic product, we have studied the mechanism of anaerobic and aerobic decomposition of Mo(VI) compounds of the type, (4,4'-dimethyl-2,2'-dipyridyl)$Mo(O)_2R_2$.[13] The anaerobic decomposition mode followed by a given complex was a sensitive function of the hydrocarbyl group, R. If accessible β-hydrogens were present on R, equal amounts

Table 2. Oxidation of Ethylene[a]

				Turnovers[b]	
CO	100°C	180°C	Time (h)	Ethylene Glycol	Acetic Acid
		X	9	130	580
		X	22	830	710
		X	51.5	4040	2600
		X	53	3940	1900
		X	93	2020	720
	X		70	14	65
X	X		49	271	--
X		X	43.5	413	--

[a] Reaction conditions: 0.011 g of 5% Pt on carbon; 10 ml of H_2O; C_2H_4, 300 psi; O_2, 35 psi; Ar, 615 psi. CO (100 psi) was added for the last two runs.

[b] Turnover numbers were calculated assuming that only the surface metal atoms (approx. 10% of the total) are active (the relative proportion of these was determined from H_2 chemisorption studies)

of alkane and alkene were formed through β-hydrogen abstraction followed by reductive elimination. When β-hydrogens were absent from R, the free radical, R•, formed by Mo-R bond homolysis was the predominant product. However, in every case, there was an additional minor pathway for the formation of the alkane, RH, that involved α-hydrogen abstraction from the neighboring hydrocarbyl group. In the presence of O_2, however, the decomposition of (4,4'-dimethyl-2,2'-dipyridyl)$Mo(O)_2R_2$ proceeded almost exclusively through the intermediacy of the free radical, R•. In inert solvents, the principal organic product was the aldehyde and the role of O_2 in its formation from the Mo(VI) complex was two-fold: (a) O_2 promoted the homolysis of the Mo-R bond to form R•, and (b) O_2 trapped the resultant radical to yield the aldehyde. Labeling studies indicated that O_2, rather than the Mo=O group, was the predominant source of oxygen for the aldehydes. Our observation of the dual role of O_2[13] has important implications for the heterogeneous oxidation of alkanes and olefins by Mo(VI)-oxo species. For example, in this system, it is possible that an alkyl (or allyl) radical is formed by O_2-promoted homolysis of the initially formed metal-alkyl (or allyl) bond. Indeed, while the allyl radical has been detected in heterogeneous propylene oxidations, the oxidation-induced homolysis of metal-carbon bond has never been invoked as a step in these catalytic reactions.

Lastly, in addition to our studies in organometallic chemistry, homogeneous, and heterogeneous catalysis, we have a small ongoing effort directed toward the synthesis of polymer-trapped metal, metal oxide, and metal sulfide nanoclusters (size <1-10 nm).[14-17] The long term goal in this area is the development of novel materials that will exhibit size-dependent catalytic properties. The synthetic approach that we have taken encompasses the concept of "site isolation". The basic idea is to synthesize and maintain the clusters in isolated pockets within the polymeric matrix, and we achieve this by (a) prebinding the discrete precursor compound to specific sites on the polymer backbone and, sometimes, (b) chemically relating the formation of the nanocluster from the precursor with the final curing of the polymer. By using this approach, we have obtained flexible, free-standing, films incorporating a fairly high loading of nanoclusters of metallic Pd (to be published), Cr_2O_3,[14,16] α-Fe(O)(OH),[14,16] SiO_2,[15,16] TiO_2,[15,16] CuS,[17] and CdS.[17]

PUBLICATIONS BASED ON CURRENT DOE GRANT.

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2. "Tailored Cationic Palladium(II) Compounds as Catalysts for Highly Selective Linear Dimerization of Styrene and Linear Polymerization of p-Divinylbenzene,"
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