

**Catalysis
by
Metal
Complexes**

***Catalytic
Synthesis of
Alkene-Carbon
Monoxide Copolymers
and Cooligomers***

***edited by
Ayusman Sen***

Kluwer Academic Publishers

CATALYTIC SYNTHESIS OF ALKENE-CARBON MONOXIDE COPOLYMERS AND COOLIGOMERS

edited by

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CATALYTIC SYNTHESIS OF ALKENE-CARBON MONOXIDE
COPOLYMERS AND COOLIGOMERS

Catalysis by Metal Complexes

Volume 27

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Chapter 1

INTRODUCTION AND FUTURE DIRECTIONS

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Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania, 16802

1. INTRODUCTION

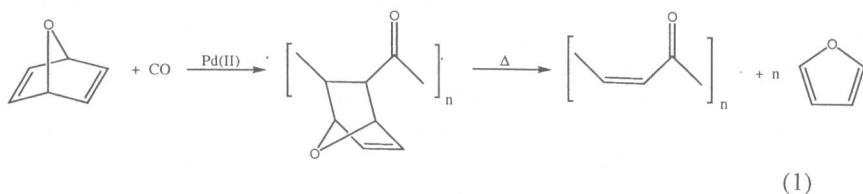
The discovery of facile catalytic alternating olefin/carbon monoxide copolymerization (Chapter 4) [1] has significantly impacted the fields of polymer science, organometallic chemistry, and catalysis. Below we discuss some of the highlights and unsolved problems.

One of the most significant advantage that the olefin/carbon monoxide copolymers have over other functional polymers is the cost of monomers: both carbon monoxide and simple olefins are plentiful and inexpensive. This can be compared, for example, with nylons which have physical and mechanical properties comparable to the alternating ethylene/carbon monoxide copolymer [1c,d,f]. The diamines, diacids, and lactams that are the nylon precursors are typically synthesized through multistep processes and are much more expensive [2].

The alternating olefin/carbon monoxide copolymerization procedure allows the synthesis of a host of new functional materials because of the ability to incorporate functionalized olefins. The resultant materials are likely to be of considerable practical importance given the varied applications of the presently known functional polymers [3]. Examples of functional groups present on olefins that have been successfully used as monomers in the copolymerization reaction include alcohol, ether, epoxide, carboxylic acid, amide, carbamate, perfluoro alkyl and aryl [1c,e,f,g, 4]. The one class of olefins that does not undergo ready copolymerization with carbon monoxide are those that have the functionality directly adjacent to the C=C bond, e. g. acrylates, methacrylates, and vinyl carboxylates. In this

sense, olefin/carbon monoxide copolymerization fills a gap between Ziegler-Natta type and radical polymerizations. The former typically uses early transition metals that do not tolerate oxygen or nitrogen functionalities [5]. On the other hand, radical polymerization of olefins do not proceed well unless a stabilizing functionality is present next to the C=C bond. Thus, the discovery of olefin/carbon monoxide copolymerization allows access to a new group of monomers.

One particularly interesting example of a new material synthesized through alternating olefin/CO copolymerization is illustrated in eq. 1 and involves the two-step synthesis of poly(ketovinylene) [6]. The synthesis of optically active, isotactic, α -olefin/CO copolymers through the use of chiral ligands is another noteworthy achievement (Chapters 6 and 7). The resultant materials are very rare examples of optically active, chiral main-chain polymers synthesized from achiral monomers. These materials exhibit the unusual phenomenon of solid-state steric recognition, forming stereo complexes with properties that are markedly different from those of the chiral components [7]. Other examples of new materials synthesized include polymeric liquid crystals [8], polymeric crown ethers [9], and thermoplastic elastomers [1f].



Apart from the ability to use functionalized olefins in the copolymerization reaction, the presence of the reactive carbonyl group in the polymer backbone provides avenues for further functionalizations. Indeed, about two dozen polymers incorporating a variety of functional groups have been previously synthesized from the *random* ethylene-carbon monoxide copolymer ($\text{C}_2\text{H}_4:\text{CO} > 1$) made through radical-initiated polymerization [1a]. Since carbon monoxide does not homopolymerize, the *alternating* olefin-carbon monoxide copolymers (olefin: $\text{CO} = 1$) 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 (e.g., Figure 1-1) [10]. Indeed, a cross-linking technology leading to thermoset and thermoreversible resins has been developed based on the reaction with primary amines (see Chapter 4) [11].

One remarkable feature of the olefin/carbon monoxide copolymerization catalysts is their tolerance for a wide range of solvents. Thus, apart from the usual organic solvents, the polymerization has been carried out in water [12], ionic liquids [13], and supercritical carbon dioxide [14]. Also successful has been emulsion polymerization in water, leading to stable latices [15].

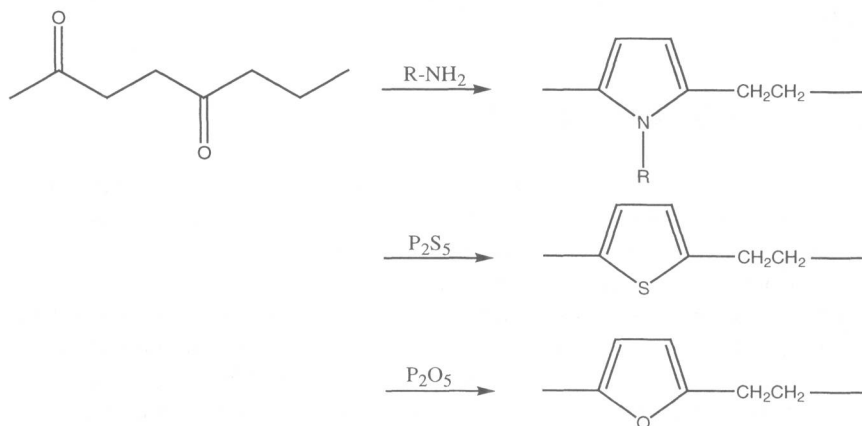


Figure 1-1. Examples of functionalizations involving 1,4-keto groups in olefin/CO copolymers [10].

The catalytic copolymerization of olefins with carbon monoxide has also had a significant impact on organometallic chemistry and catalysis. It has led to a blossoming of the area of catalysis by electrophilic, cationic, late transition metal compounds. Studies on ligand effects have resulted in the discovery of new highly active systems that allow the directed synthesis of compounds ranging from low molecular weight esters, ketones, and aldehydes (Chapters 2 and 3) to high molecular weight copolymers (Chapter 4). Additionally, copolymerizations with high regio, stereo, and enantioselectivity have been achieved (Chapters 6 and 7).

Fundamental studies on the copolymerization reaction has led to the discovery of novel chain initiation and termination processes (Chapter 5). The chain-propagation mechanism has been shown to consist of two alternating steps [1b]: the insertion of carbon monoxide into a metal-alkyl bond and the insertion of olefin into a metal-acyl bond (leading to the formation of a β -chelate because of carbonyl group coordination) (Chapters 8 and 9). The perfectly alternating structure of the copolymer arises from a combination of thermodynamic and kinetic constraints [1b,16]. The double insertion of carbon monoxide (i.e., carbon monoxide insertion into the metal-

acyl bond) is thermodynamically uphill. On the other hand, the double insertion of olefin (i.e., olefin insertion into metal-alkyl bond) is kinetically disfavored due to (a) the stronger binding ability of carbon monoxide and (b) its faster rate of insertion. Finally, a number of systems have been discovered that effect the living polymerization of olefins, as well as allenes, with carbon monoxide, thereby making it possible to form block copolymers [17].

2. FUTURE DIRECTIONS

What are some of the unsolved problems in the copolymerization reaction? First, one of the consequences of the special chain-growth mechanism is that, with one exception, it has not been possible to vary the ratio of olefin to carbon monoxide units in the polymer backbone. While the successive insertions of two carbon monoxide molecules is precluded on thermodynamic grounds, there is no such bar for the successive insertions of olefin units. However, as described above and in Chapters 8 and 9, a combination of factors prevents this from occurring. Very recently, Drent has reported *neutral* palladium(II)-based compounds containing specific P-O chelating ligands that catalyze the formation of ethylene/carbon monoxide copolymers with a $C_2H_4: CO > 1$ [18]. Polyolefins with a few carbonyl units in the backbone are expected to provide properties (e.g., better adhesion) that are currently difficult to obtain with pure polyolefins.

One class of olefins that does not undergo ready copolymerization with carbon monoxide are those that have the functionality directly adjacent to the C=C bond, e. g. acrylates, methacrylates, and vinyl carboxylates. The problem is not the failure of these olefins to undergo migratory insertions: methyl acrylate and vinyl acetate have been shown to undergo facile 2,1-insertion into Pd-acyl bonds (e.g., Figure 1-2) [19]. Following insertion, it is the carbonyl of the former acyl group rather than that of the olefin that coordinates to the metal. This is in contrast to the observed coordination of the acrylate carbonyl following insertion in the palladium(II) catalyzed copolymerization of olefins with acrylates, a phenomenon that is responsible for significant rate attenuation in the acrylate/olefin copolymerization [20] (see Chapter 9). Thus, the stumbling block in the alternating copolymerization of acrylates, methacrylates, and vinyl carboxylates with carbon monoxide is *not* olefin insertion but rather the insertion of carbon monoxide *following* olefin insertion.

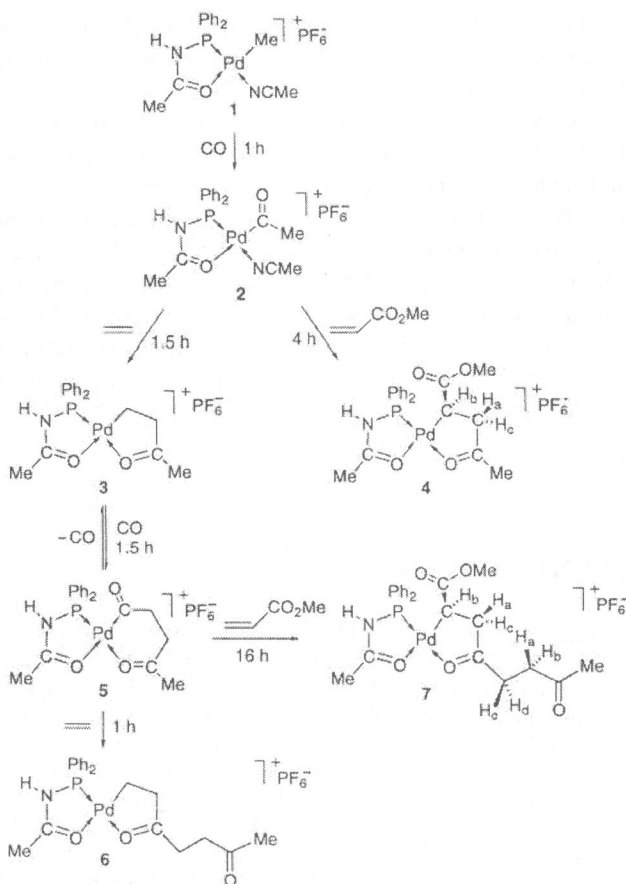


Figure 1-2. Model study involving acrylate insertion into palladium-acyl bonds [19d].

A final area of alternating olefin/carbon monoxide copolymerization that does not appear to have been adequately investigated involves catalysts based on metals other than palladium. Nickel(II) complexes have been investigated but have found little success in olefin/carbon monoxide copolymerization since they exhibit significantly lower activity when compared to their palladium(II) analogs (Chapter 4) [21]. Rhodium (I) complexes have also been shown to be active in alternating cooligomerization of ethylene, as well as norbornadiene, with carbon monoxide [22]. In addition, π -allylrhodium complexes serve as catalysts for the alternating copolymerization of arylallenes with carbon monoxide [23]. Lastly, there is a report on copper(II)-catalyzed copolymerization of styrene

with carbon monoxide [24]. The above reports strongly suggest that active olefin/carbon monoxide catalysts based on a variety of late transition metals may be waiting to be discovered.

A possible starting point in the hunt for new olefin/carbon monoxide copolymerization catalysts involves the known hydroformylation catalysts. 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 [25]. The final step in hydroformylation is the conversion of this metal-acyl species to the aldehyde by hydrogenolysis. 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 [22a,b].

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