

Palladium Catalysts for the Synthesis of Carbon Monoxide-Alkene Copolymers

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Polyketones are a new class of polar polymers that have a desirable set of material properties. Though polyketones have been known for more than 60 years,¹ only recently have they received commercial interest as a viable replacement for currently used polymers such as polyamides, polyolefins, and polyacetals. Polyketones are useful in a number of industrial applications, such as joints for a medical breathing apparatus, lining for gasoline transportation tubes, and heavy-duty ties for undersea cable ducts. Furthermore, polymer production companies are attracted to the extremely low cost of the starting materials, and to the green nature of the synthesis. In order to design more effective catalysts, the mechanistic details of the catalytic cycle have been studied in depth since the discovery of highly active palladium(II) complexes in the late 1980s.²

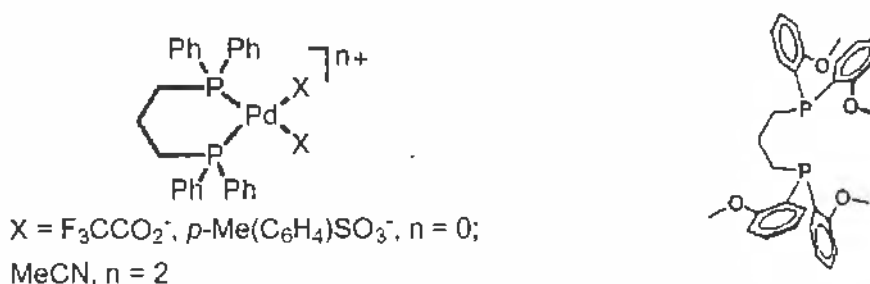


Figure 1. Active Catalytic Species and 1,3-bis(di-(*o*-methoxyphenyl)-phosphino Propane Ligand

Two catalytic cycles for polyketone synthesis operate simultaneously, one involving a Pd-OMe⁺ initiator, and the other involving a Pd-H⁺ initiator.³ Propagation involves perfect alternation of insertion steps by ethylene and carbon monoxide. Ethylene and carbonyl double insertions are thermodynamically⁴ and kinetically unfavorable; ethylene double insertions only occur once every 10⁶ propagation steps.⁵ An important part of the mechanism is the formation of keto chelates from the growing polymer chain, which must be opened by CO binding prior to ethylene insertion.⁶ The rate law for polymerization appears to be of the form rate = k[CO]^{0.63}[C₂H₄]^{0.72}, but is actually of the form k{([CO][C₂H₄)]/(1 + a[CO] + b[C₂H₄])}.⁷ Finally, termination takes place by protonolysis, methanolysis, β-hydrogen elimination, or hydrolysis. Termination mechanisms depend on solvent, and each mechanism forms a different end-group functionality, giving rise to ketone or ester groups in methanol, and aryl and vinyl groups in aprotic solvents.⁸ Deactivation occurs by means of several pathways, involving the creation of inactive dinuclear bis-chelated Pd(II) species or Pd⁰. Acids and oxidants increase polymer yields by generating active catalytic species, while acids additionally provide weakly coordinating anions for the metal center.⁹

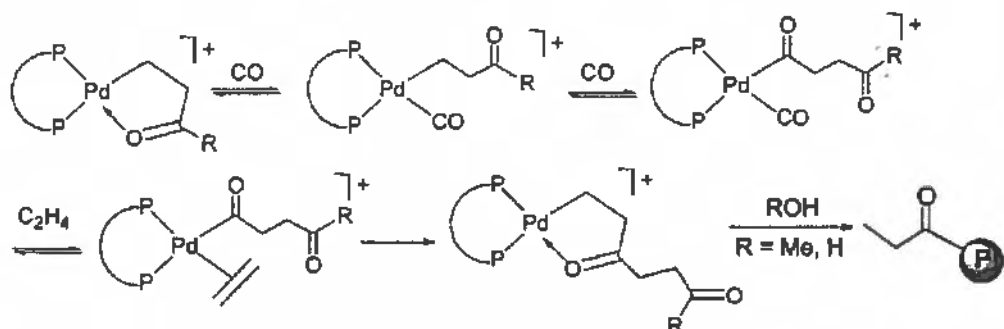


Figure 2. Propagation occurs with alternating C_2H_4 and CO insertion steps.

Copolymerization of higher α -olefins creates stereogenic centers. Enantioface selection is largely chain-end controlled, but control can be enhanced or opposed by using chiral chelating ligands. In addition, the mode of insertion into a Pd-acyl bond leads to regioselective diads. Regioregularity is controlled by electronic factors, and monomers show preferential insertion modes. Propene-based polyketones, which are in equilibrium with a polyspiroketal form,¹⁰ show a preference for 1,2-insertion, though regioregularity can be decreased by introducing electronically inequivalent phosphine ligands.¹¹ Regioregular, isotactic propene/CO copolymers can be easily made,⁹ but a synthesis for syndiotactic copolymers has not yet been discovered.¹² Styrene/CO copolymers, however, have more controllable enantioface selectivity, such that stereoblock styrene-based polyketones can be made through ancillary ligand exchange.¹³

Liquid crystalline polyketones, which are high performance engineering plastics used in electronic components and thermoplast reinforcement, can be synthesized using long chain allenes with living Rh or Pd catalysts. The first example of a non-perfectly alternating copolymerization has recently been documented.¹⁴ Greater control of polymer properties through ligand design and reaction conditions may give polyketones an edge in a competitive polymer market.

References

1. Drent, E.; Budzelaar, P. "Palladium-Catalyzed Alternating Copolymerization of Alkenes and Carbon Monoxide," *Chem. Rev.* **1996**, 96, 663-681.
2. Drent, E.; van Broekhoven, J. A. M.; Doyle, M. J. "Efficient Palladium Catalysts for the Copolymerization of Carbon Monoxide with Olefins to Produce Perfectly Alternating Polyketones," *J. Organomet. Chem.* **1991**, 417, 235-251.
3. Bianchini, C.; Meli, A.; Oberhauser, W. "Catalyst Design and Mechanistic Aspects of the Alternating Copolymerisation of Ethene and Carbon Monoxide by Diphosphine-modified Palladium Catalysis," *Dalton Trans.* **2003**, 13, 2627-2635.

4. Chen, J.; Sen, A. "Mechanism of Transition-Metal-Catalyzed 'Double Carbonylation' Reactions. Synthesis and Reactivity of Benzoylformyl Complexes of Palladium(II) and Platinum(II)," *J. Am. Chem. Soc.* **1984**, *106*, 1506-1507.
5. Shultz, C. S.; Ledford, J.; DeSimone, J.; Brookhart, M. "Kinetic Studies of Migratory Insertion Reactions at the (1,3-Bis(diphenylphosphino)propane)Pd(II) Center and Their Relationship to the Alternating Copolymerization of Ethylene and Carbon Monoxide," *J. Am. Chem. Soc.* **2000**, *122*, 6351-6356.
6. Mul, W. P.; Oosterbeek, H.; Beitel, G. A.; Kramer, G.; Drent, E. "In Situ Monitoring of a Heterogeneous Palladium-Based Polyketone Catalyst," *Angew. Chem. Int. Ed.* **2000**, *39*, 1848-1851.
7. Tomiolo, L.; Kulkarni, S. M.; Fatutto, D.; Chaudhari, R. V. "Kinetic Modeling of Copolymerization of Ethylene with Carbon Monoxide Using Pd Complex Catalyst," *Ind. Eng. Chem. Res.* **2001**, *40*, 2037-2045.
8. Barlow, G. K.; Boyle, J. D.; Cooley, N. A.; Ghaffar, T.; Wass, D. F. "Mechanistic Studies of Alkene/CO Polymerization with Palladium Complexes Promoted by B(C₆F₅)₃," *Organometallics* **2000**, *19*, 1470-1476.
9. Bianchini, C.; Meli, A. "Alternating Copolymerization of Carbon Monoxide and Olefins by Single-site Metal Catalysis," *Coord. Chem. Rev.* **2002**, *225*, 35-66.
10. Jiang, Z.; Sen, A. "Palladium(II)-Catalyzed Isospecific Alternating Copolymerization of Aliphatic α -Olefins with Carbon Monoxide and Isospecific Alternating Isomerization Cooligomerization of a 1,2-Disubstituted Olefin with Carbon Monoxide. Synthesis of Novel, Optically Active, Isotactic 1,4- and 1,5-Polyketones," *J. Am. Chem. Soc.* **1995**, *117*, 4455-4467.
11. Meier, U. W.; Hollmann, F.; Thewalt, U.; Klinga, M.; Leskelä, M.; Rieger, B. "Nonsymmetric Palladium Complexes of Partly Fluorinated Bisphosphine Ligands: Efficient Catalysis for Flexible Propene/CO Copolymer Materials of Ultrahigh Molecular Weight," *Organometallics* **2003**, ASAP.
12. Sesto, B.; Consiglio, G. "Regioselectivity of the Insertion of Propene with Achiral Pd(II) Catalysts to Highly Isotactic Poly[1-oxo-2-methylpropane-1,3-diyl]. Is the Syndiotactic Structure Accessible?" *Chem. Commun.* **2000**, *12*, 1011-1012.
13. Brookhart, M.; Wagner, M. I. "Synthesis of a Stereoblock Polyketone through Ancillary Ligand Exchange," *J. Am. Chem. Soc.* **1996**, *118*, 7219-7220.
14. Drent, E.; van Dijk, R.; van Ginkel, R.; van Oort, B.; Pugh, R. I. "The First Example of Palladium Catalysed Non-perfectly Alternating Copolymerisation of Ethene and Carbon Monoxide," *Chem. Commun.* **2002**, *9*, 964-965.

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