Palladium Catalysts for the Synthesis of Carbon Monoxide-Alkene Copolymers

Richard L. Jew

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, 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.

![Figure 1. Active Catalytic Species and 1,3-bis(di-(o-methoxyphenyl)-phosphino Propane Ligand](image)

Two catalytic cycles for polyketone synthesis operate simultaneously, one involving a Pd-OMe$^+$ initiator, and the other involving a Pd-H$^+$ initiator. Propagation involves perfect alternation of insertion steps by ethylene and carbon monoxide. Ethylene and carbonyl double insertions are thermodynamically and kinetically unfavorable; ethylene double insertions only occur once every $10^6$ propagation steps. 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. The rate law for polymerization appears to be of the form $\kappa[CO]^{0.63}[C_2H_4]^{0.72}$, but is actually of the form $\kappa\{[CO][C_2H_4]/(1 + a[CO] + b[C_2H_4])\}$. 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. Deactivation occurs by means of several pathways, involving the creation of inactive dinuclear bis-chelated Pd(II) species or Pd$^0$. Acids and oxidants increase polymer yields by generating active catalytic species, while acids additionally provide weakly coordinating anions for the metal center.
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 regiospecific 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 thermoplastic 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


