The Insertion Copolymerization of Carbon Monoxide with Olefins

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Aliphatic polyketones are made from the insertion copolymerization of olefins and carbon monoxide,\(^1\)-\(^4\) both of which are inexpensive and abundant. The copolymer of carbon monoxide with ethylene (Figure 1) has highly desirable properties: it is strong without being brittle, it is resistant to organic solvents, acids and bases, and heat, and it is impermeable to gases. It has potential applications as a metal-replacement plastic, as hoses for automotive fluids, and as packaging material in the form of a film.\(^6\)

Early forms of this material were prepared by unselective free radical reactions that gave poorer properties.\(^6\),\(^7\) In 1983, Drent and coworkers from Shell described a highly active, high-yielding (dppp)Pd(II) catalyst that produced high molecular weight, perfectly alternating copolymer with parts-per-million defects. This final material was commercialized as Carilon in 1996.\(^1\)-\(^4\)

In the same year, Brookhart and co-workers studied the catalytic cycle leading to the perfectly alternating copolymerization of ethylene with carbon monoxide using a palladium-phenanthroline model catalyst (Figure 3). Using \(^1\)H NMR spectroscopy, the palladium center was found to have a much greater binding affinity for carbon monoxide than ethylene (Figure 4). This alkyl-ethylene complex is a prerequisite for the migratory insertion of the growing alkyl polymer chain onto ethylene, giving the double insertion defect. The migratory insertion of a methyl group onto an ethylene ligand had a higher activation barrier of 3 kcal/mol than the same reaction with a carbonyl ligand.\(^8\) Sen and co-workers had previously determined that double carboxylations had very high activation barriers of 25-27 kcal/mol.\(^9\) These three reasons explain why polyethylene defects are rare and polycarbonyl defects do not exist, leading to perfect copolymers.
While perfect alternation imparted many desirable properties to the polymer, the melting point of the pure copolymer (257 °C) was too high, making this material difficult to process. The high temperature also induced undesirable cross-links via aldol reactions between chains. In Carilon, Shell solved the problem by incorporating 6 wt. % of propylene in the polymer, reducing the melting point to 220 °C.

In 2002, Drent found an alternative solution to this problem: by replacing the dppp ligand with a phosphine-sulfonate (Figure 5), he was able to introduce significant double, triple, and more polyethylene defects. Seven years later, using a well-defined version of Drent’s catalyst, Sen and co-workers demonstrated the ability to produce an alternating copolymer containing 0-50 mol % of carbon monoxide by adjusting its partial pressure in the feed, in contrast with the (dppp)Pd(II) catalyst that gave perfect alternation until carbon monoxide was exhausted.

Unlike dppp, the phosphine-sulfonate coordinates to the metal center via two different donor atoms. Rieger and co-workers modeled a simplified \{P,SO_3\}Pd(II) system, and found that cis/trans isomerization would provide a lower energy barrier for the migration of an alkyl ligand onto ethylene. This cis/trans isomerization has been proposed to occur by a pseudorotation, aided by the coordination of another oxygen atom at the sulfonate group (Figure 6).

Experimentally, the activation barrier to the migration of an alkyl group onto an ethylene ligand was 8 kcal/mol higher than migration onto a carbonyl ligand for the \{P,SO_3\}Pd(II) system. The binding affinities of \{P,SO_3\}Pd(II) for ethylene and carbon monoxide were approximately 10^5 greater than the case for the phenanthroline complex (Figure 4). Despite the higher barrier to alkyl migration onto ethylene, the higher concentration of the alkyl-ethylene complex makes such polyethylene linkages more probable than when the dppp ligand was used.

This \{P,SO_3\}Pd(II) catalyst has since been found to work with many other highly electron-poor systems, including some containing potentially interfering ligands like esters. In particular, Nozaki and coworkers reported the copolymerization of vinyl acetate and methyl acrylate with carbon monoxide in 2007 and 2008 respectively. For the methyl acrylate process, they compared (dppp)Pd(II) and \{P,SO_3\}Pd(II) systems. The latter

![Figure 4. The equilibrium between the [Pd(alkyl)(CO)] and [Pd(alkyl)(olefin)] species for (phen)Pd(II) and \{P,SO_3\}Pd(II) catalysts.](image)

![Figure 5. An example of the \{P,SO_3\}Pd(II) catalyst used by Nozaki. Here, it has inserted methyl acrylate into a metal acyl bond.](image)

![Figure 6. A pseudorotation provides a non-dissociative mechanism for cis/trans isomerization.](image)
system had a lower energy barrier (14 vs. 18 kcal/mol) for the migration of the growing acyl polymer chain onto methyl acrylate (Figure 7).\textsuperscript{16} Like Rieger,\textsuperscript{13} this lower reaction path was attributed to the ability of the phosphine-sulfonate complex to undergo cis/trans isomerization.\textsuperscript{16}

![Activation barriers for the migration of the growing acyl polymer chain onto methyl acrylate.](image)

Other than affording aliphatic polyketones from olefins and carbon monoxide, this “second generation catalyst” incorporated vinyl fluoride units in the homopolymerization of ethylene.\textsuperscript{17,18} The scope of this second generation catalyst is being explored.\textsuperscript{4,19-22}

References