

## **Abstracts for Whitby Lecture Series presentations by Dr. Kyoko Nozaki**

### **Synthesis and Properties of Linear Ethylene/Polar Monomer Copolymers**

Polar vinyl monomers such as methyl acrylate, vinyl acetate, and acrylonitrile are inexpensive and widely used monomers in radical, anionic and cationic polymerization. Incorporation of these monomers into polyolefins would change their physical properties such as adhesion, dyeability, printability and compatibility. Radical copolymerization of olefins with polar monomers affords copolymers with high incorporation of polar monomers with branched structures. Until recently, however, the metal-catalyzed coordination–insertion polymerization of the basic polar vinyl monomers remained unsolved. A major challenge to incorporating polar vinyl monomers in coordination–insertion polymerization is the strong coordination of functional group of the monomers to the Lewis acidic metal center. The catalysts that are most often utilized for coordination–insertion polymerization, especially for polyolefin production, are based on early transition metals such as group 4–6 metals.

Due to the highly Lewis-acidic nature of these early transition metals, however, they tend to form stable  $\sigma$ -complexes with the functional groups of polar monomers, thus preventing the formation of  $\pi$ -complex needed for activation of the C=C double bond. In this talk, synthesis of linear poly(ethylene-co-polar vinyl monomers) using palladium complexes of phosphine–sulfonate ligands will be presented. Before the use of phosphine–sulfonate catalysts, the ethylene/polar monomer copolymers were produced either by a radical polymerization or a late-transition metal catalyzed coordination polymerization and thus the products had branched structures rather than linear ones. The word “polar vinyl monomers” here represents common commercially available ones such as acrylates, acrylonitrile, vinyl acetate, etc.

### **Synthesis of Sterecontrolled Polymers Made of Carbon Monoxide or Carbon Dioxide**

Carbon monoxide and carbon dioxide are promising candidates as a C1 carbon resource.

Utilization of these monomers for polymer synthesis has long been examined.

As one example, copolymerization of carbon monoxide with olefins has been long known to proceed either under radical conditions or in the presence of transitionmetal catalysts. Here in this presentation, effect of stereocontrol will be discussed for the alternating copolymerization of mono-substituted ethenes with carbon monoxide using a chiral catalyst.

Carbon dioxide, the most oxidized and stable form of carbon, is an abundant and inexpensive carbon source, and catalytic reduction of carbon dioxide with hydrogen or hydrides is one of the attractive ways of its utilization. The copolymerization of carbon dioxide with epoxides is one of the most promising processes for CO<sub>2</sub> utilization. Since the first report by Inoue and co-workers with Et<sub>2</sub>Zn/H<sub>2</sub>O as a catalyst in the late 1960s, a variety of combinations of metal centers and ligands have been investigated to improve the catalyst performance. In this lecture, our catalyst development aiming at stereoregularity-control will be discussed.