

論文の内容の要旨

論文題目 Polymerization by Palladium/Phosphine–Sulfonate Catalysts:
Toward Control of Molecular Weight and Microstructure of Functional Polyolefins
(パラジウム/ホスフィン-スルホナート触媒による重合反応：
官能基化ポリオレフィンの分子量および微細構造の制御に向けて)

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General Introduction

Polyolefins such as polyethylene and polypropylene are the most widely used synthetic polymers and have a broad range of applications such as films, packages, and fibers. However, their low polarity causes surface properties, such as low adhesion, printability, and compatibility, that restrict their efficacy. Incorporation of functional groups into the main chains of polyolefins can improve such surface properties and expand the range of applications.

Recently, late-transition-metal-catalyzed coordination–insertion copolymerization of olefins with polar monomers has emerged as a powerful method to synthesize structurally-defined functional polyolefins. To date, the most successful catalysts for such copolymerization have been palladium complexes ligated by a phosphine-sulfonate, which are applicable to a variety of polar monomers. Palladium/phosphine-sulfonate catalyst, however, has two limitations; first, most of the reported molecular weights of copolymers were limited to 10^3 order. For practical applications, there is a need to improve the molecular weights of copolymers. Although the steric and electronic effects of the palladium catalysts have been investigated to improve the polymer molecular weight, it is still challenging to increase copolymer molecular weights in ethylene/polar monomer copolymerization. Second, all the reported catalytic systems have been utilized for ethylene (co)polymerization, and homo- and copolymerization of propylene with polar monomer have never been achieved.

In this thesis, the author focused on the substituent effect in palladium complexes bearing an alkylphosphine-sulfonate ligand to improve the molecular weight of copolymer and to perform regio- and stereo-controlled homo- and copolymerization of propylene and polar monomers.

Quantification of steric influence of alkylphosphine-sulfonate ligand in ethylene polymerization

Initially, palladium complexes bearing a series of alkylphosphine-sulfonate ligands were

synthesized and utilized for the homopolymerization of ethylene. Catalysts bearing pentan-3-yl, 2,6-dimethylheptan-4-yl, and menthyl group on the phosphorus atom produced polyethylene with the molecular weight of 34, 72, and 169×10^3 g/mol, respectively. Based on the experimental data, we analyzed correlation between the steric effects of the substituents and steric parameters. Here, the Sterimol B1 and B5 parameters were employed to represent the steric bulkiness of the substituents, which evaluated proximal and distal steric bulkiness respectively. As a consequence, a strong correlation was observed between the polymer molecular weights and the Sterimol B5 parameters of the substituents, which suggests that distal steric bulkiness of the substituents has a stronger influence on molecular weights than proximal steric effect (Figure 1).

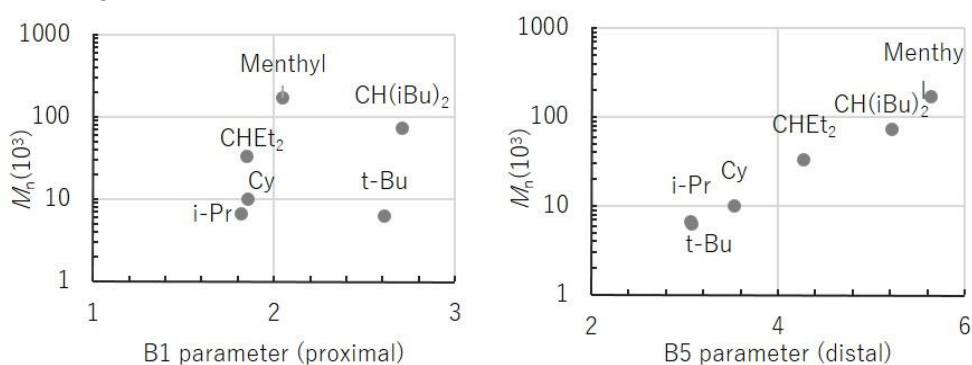


Figure 1. Correlation analysis between polymer molecular weights and the Sterimol parameters

Synthesis of high-molecular-weight copolymer of ethylene and polar monomer

With the quantitative analysis in hand, we performed copolymerization of with various polar monomers by menthyl-substituted phosphine-sulfonate catalyst. The Catalyst exhibited high activities and produced high-molecular-weight copolymers especially in copolymerization of ethylene and methyl acrylate and allyl acetate. Molecular weights of the copolymers were higher than those obtained by previously reported systems (Figure 2).

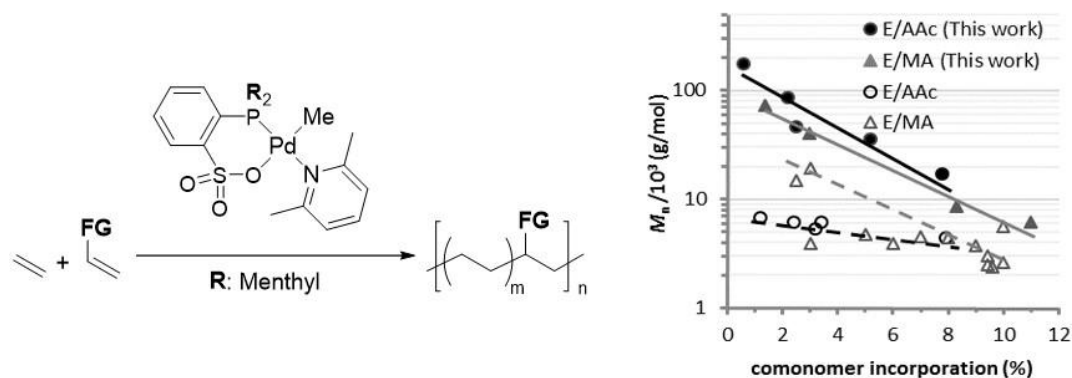


Figure 2. Copolymerization of ethylene and polar monomer

Effect of the substituents on phosphorus atom in propylene polymerization

Homopolymerization of propylene by palladium/phosphine–sulfonate catalysts was performed to investigate the effect of the substituent on the phosphorus atom. As the results, the use of catalyst bearing menthyl groups, was found to be effective to improve the molecular weight to afford the polypropylene with molecular weight of the order of 10^4 . ^{13}C NMR analysis of the obtained polymer revealed that regioregularity was almost perfectly controlled and stereoregularity was moderately controlled to a *mm* triad ratio of 49%.

Effect of the substituents at the *ortho* position of sulfonate in propylene polymerization

Further optimization of the phosphine–sulfonate ligand was performed to improve the molecular weight of polymers. Previous studies on the substituent effects on the phenylene linker of phosphine–sulfonate ligands revealed that the substituent at the *ortho* position of the sulfonate has strong influence on the polymer molecular weight and catalytic activity. Encouraged by the reports, catalysts bearing various substituents at the *ortho* position of the sulfonate group were synthesized and utilized for propylene polymerization. When catalyst having a trimethylsilyl group on the ligand was used, the molecular weight and *mm* triad ratio were improved. On the other hand, the highest *mm* triad ratio of 59% was then observed by introducing phenyl group.

Copolymerization of propylene and polar monomer by phosphine-sulfonate ligand

Copolymerization of propylene and polar monomers was then performed. Since the highest molecular weight and catalytic activity were observed in **2**, catalyst **2** was used for the copolymerization. A variety of functional groups, including acetoxy, cyano, chloro, and alkoxycarbonyl groups could be incorporated into the main chain of polypropylene to afford crystalline polar polypropylene (Figure 3).

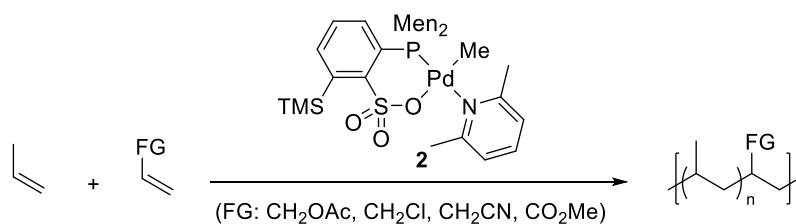


Figure 3, Copolymerization of propylene and polar monomers