

学 位 論 文 概 要

題目 Chain-walking polymerization of terminal and internal alkenes catalyzed by group 10 α -diimine complexes
(第 10 族 α ジイミン金属錯体触媒による末端および内部アルケンの Chain-walking 重合)

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Polymerization of alkenes such as ethylene and propylene plays pivotal roles in today's polymer industry, because polyolefins are tremendously important in everyday life. Over the past two decades, nickel and palladium complexes ligated by α -diimine have attracted considerable attentions as a catalyst for alkene polymerization because the metal-alkyl species move on the polymer backbone before the next monomer insertion, i.e., chain-walking, via rapid β -hydride elimination and re-insertion. In this thesis, the chain-walking polymerization of internal alkenes and alkenylcyclohexanes with nickel and palladium catalysts, which have been reported only in a limited number of cases, were investigated in detail to synthesize novel polymers which can be obtained only by chain-walking polymerization.

The thesis consists of 9 chapters including "General introduction" and "Summary".

Chapter 1 "General introduction" describes the motivation and detailed background of this work, which contains the chain-walking alkene polymerization by group 10 complexes and the recent advances in catalyst design.

In Chapter 2, a series of phenyl substituted α -diimine nickel complexes were applied for ethylene polymerization and found to produce highly-branched polyethylene with high activities upon activation with Et_2AlCl or MMAO. The catalysts were also active for 1-alkene polymerization to produce branched polymers with high molecular weight. In Chapter 3, a series of α -diimine nickel and palladium complexes containing 2,6-diphenyl groups were synthesized. The nickel complexes exhibited high catalytic activity for ethylene polymerization and produced highly-branched polyethylene upon activation with Et_2AlCl . Interestingly, 4-fluorine substituted complex conducted polymerization of methyl methacrylate to produce syndiotactic-rich polymers at 0°C (up to 77.2% of *rr* triads). Chapter 4 reports the chain-walking polymerization of linear internal alkenes using the α -diimine nickel catalysts activated with MMAO in comparison with the corresponding terminal alkenes polymerization. In Chapter 5, the precision chain-walking polymerization of *trans*-4-octene was achieved by α -diimine nickel catalysts bearing *ortho-sec*-phenethyl groups. In Chapter 6, the living/controlled polymerization of branched 1-alkenes, i.e., 4-methyl-1-hexene (4MH) and 4-methyl-1-pentene (4MP), was achieved by the α -diimine nickel catalysts containing phenyl groups upon activation with MMAO. Chapter 7 describes controlled polymerization of alkenylcyclohexanes by α -diimine nickel and palladium catalysts. In Chapter 8, copolymerization of propylene and 1-alkene was conducted by a 4-phenyl substituted α -diimine nickel complex in combination with MMAO. Additionally, propylene-based block copolymers containing poly(propylene-*co*-1-alkene) were successfully fabricated in high yields.

Chapter 9 is "Summary", several important conclusions of this study are given in detail and suggestions are provided for further study.