

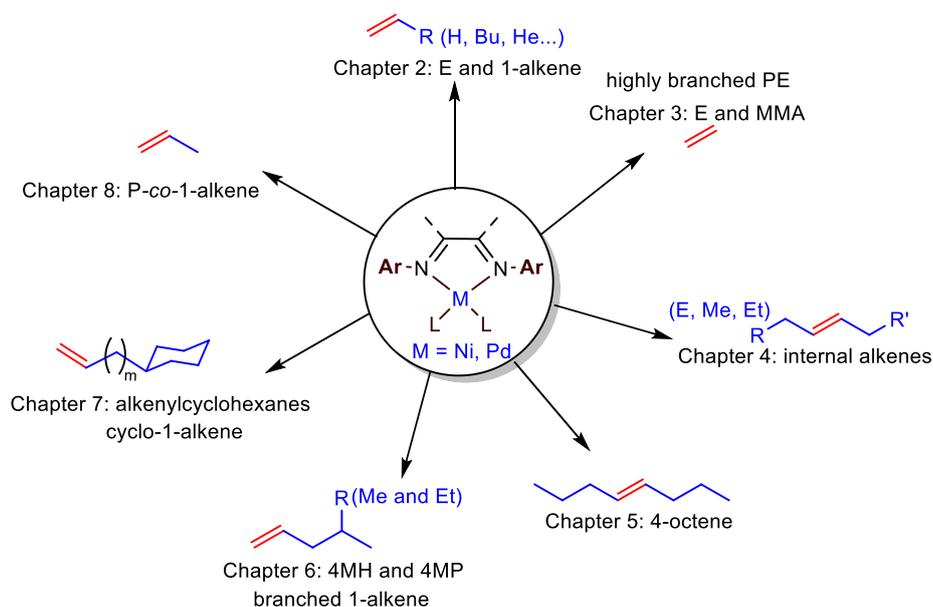
論文の要旨

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", each of which is summarized as follows.



Chapter 1. General introduction

The previous studies on the chain-walking alkene polymerization by nickel and palladium catalysts, and the recent advances in catalyst design were summarized. This chain-walking alkene polymerization indicated the possibility of precise control of branched structure, depending on the polymerization conditions (temperature, concentration and types of monomers) and the catalyst structures, which in turn strongly affects the physical properties of polymers. The importance of internal alkenes polymerization by nickel and palladium catalysts were described, which can give the novel polymers obtained only by chain-walking polymerization.

Chapter 2. Synthesis of highly branched polyolefins using phenyl substituted α -diimine nickel catalysts

A series of α -diimine nickel complexes containing bulky phenyl groups, $[\text{ArN}=\text{C}(\text{Naphth})\text{C}=\text{NAr}]\text{NiBr}_2$ (Naphth: 1,8-naphthdiyl, Ar = 2,6-Me₂-4-PhC₆H₂ (**1**); Ar = 2,4-Me₂-6-PhC₆H₂ (**2**); Ar = 2-Me-4,6-Ph₂C₆H₂ (**3**); Ar = 4-Me-2,6-Ph₂C₆H₂ (**4**); Ar = 4-Me-2-PhC₆H₃ (**5**); Ar = 2,4,6-Ph₃C₆H₂ (**6**)), were synthesized. Upon activation with either Et₂AlCl or MMAO, all nickel complexes showed high activities in ethylene polymerization and produced highly branched amorphous polyethylene (up to 145 branches/1000 carbons). Interestingly, the *sec*-butyl branches were observed in polyethylene depending on polymerization temperature. Polymerization of 1-alkene (1-hexene, 1-octene, 1-decene and 1-hexadecene) with **1**-MMAO at room temperature resulted in branched polyolefins with narrow M_w/M_n values (*ca.* 1.2), which suggested a living polymerization. The polymerization results indicated the possibility of precise microstructure control depending on the polymerization temperature and types of monomers.

Chapter 3. Synthesis and application of α -diimine nickel and palladium complexes with 2,6-diphenyl groups for polymerization of ethylene and methyl methacrylate

A series of α -diimine nickel and palladium complexes containing 2,6-diphenyl groups, $\{[(4\text{-R-}2,6\text{-Ph}_2\text{C}_6\text{H}_2\text{N}=\text{C})_2\text{Nap}]\text{MX}_2\}$ (Nap: 1,8-naphthdiyl, MX₂ = NiBr₂, R = F (**8**); R = Cl (**9**); R = Me (**4**); R = *n*-Bu (**10**) and MX₂ = PdCl₂, R = F (**Pd2**); R = Cl, (**Pd3**); R = Me (**Pd4**); R = *n*-Bu (**Pd5**)), $\{[4\text{-F-}2,6\text{-Ph}_2\text{C}_6\text{H}_2\text{N}=\text{C}(\text{Me})_2\text{PdCl}_2\}$ (**Pd6**), were synthesized. These complexes, when activated with Et₂AlCl, catalyzed polymerization of ethylene and MMA under mild conditions. The introduction of an electron-withdrawing group to the ligand improved the catalytic activity significantly. The nickel catalysts **4** and **8–10** exhibited high catalytic activity in ethylene polymerization (up to 10⁶ g PE (mol Ni h bar)⁻¹) and produced highly branched polyethylenes at high temperature. Interestingly, complex **8** produced syndiotactic-rich PMMAs at low temperature (0 °C, up to 77.2% of *rr* triads).

Chapter 4. Living/controlled polymerization of linear internal alkenes catalyzed by α -diimine nickel catalysts

The chain-walking polymerization of linear internal alkenes, i.e., 2-pentene, 2-hexene, 2-, 3- and 4-octene, using the α -diimine nickel catalysts activated with MMAO were studied in comparison with the corresponding terminal alkenes polymerization. At 0 °C, these 2-alkenes and 4-octene polymerized in a living/controlled manner to produce amorphous elastomers with glass transition temperature of at -70 ~ -65 °C. The NMR analyses of the polymers showed that 4-octene gave periodically branched polymers with the constant branching density by chain-walking polymerization, while the total branching degree of the obtained poly(2-alkene)s are less than the expected value due to monomer-isomerization. The branching analysis shows the obtained polymer was amorphous with various types of branches including C_{n+1}, C_{n+2}, C_{m+1} and C_{m+2} branches, which were correlated with the chain-walking mechanism of $[\text{CH}_3(\text{CH}_2)_n\text{CH}=\text{CH}(\text{CH}_2)_m\text{CH}_3]$.

Chapter 5. Precision chain-walking polymerization of *trans*-4-octene catalyzed by α -diimine nickel catalysts bearing *ortho-sec*-phenethyl groups

α -Diimine nickel complexes bearing bulky *ortho-sec*-phenethyl groups (bis{[*N,N'*-(4-methyl-2,6-di-*sec*-phenethylphenyl)imino]-1,2-dimethylethane}dibromonickel (**16**), bis{[*N,N'*-(4,6-dimethyl-2-*sec*-phenethylphenyl)imino]-1,2-dimethylethane}dibromonickel (**17**), bis{[*N,N'*-(4-methyl-2-*sec*-phenethylphenyl)imino]-1,2-dimethylethane}dibromonickel (**18**)) and {bis[*N,N'*-(2,4,6-trimethylphenyl)imino]-1,2-dimethylethane}dibromonickel (**19**) were used as a precatalyst for the polymerization of *trans*-4-octene upon activation with MMAO. These catalysts conducted chain-walking

polymerization of *trans*-4-octene to give polymers possessing propyl and butyl branches with high molecular weight and narrow molecular weight distribution ($M_w/M_n \approx 1.25$), and was amorphous with T_g of approximately -65 °C. The branching structure depended on the nickel complex as well as the polymerization temperature, and the ratio of propyl branch was increased with increasing the bulkiness of the ligand and decreasing the polymerization temperature. Consequently, the most bulky **16** among the complexes used was found to polymerize *trans*-4-octene with high 1,5-regioselectivity at -20 °C to give poly(1-propylpentan-1,5-diyl).

Chapter 6. Living/controlled polymerization of 4-methyl-1-hexene and 4-methyl-1-pentene with phenyl-substituted α -diimine nickel catalysts

Two branched 1-alkenes, i.e., 4-methyl-1-hexene (4MH) and 4-methyl-1-pentene (4MP) were polymerized with phenyl substituted α -diimine nickel complexes in the presence of MMAO to produce branched polymers with high molecular weight and narrow molecular weight distribution ($M_w/M_n < 2.0$). 4MH and 4MP polymerized in a living/controlled manner at 0 °C and 20 °C, respectively. The obtained poly(4MH) and poly(4MP) were amorphous with T_g of $-42 \sim -54$ °C and $-10 \sim -24$ °C, respectively. The microstructures of the produced polymers indicated the 2,1- and 1,2-insertion followed by chain-walking, and the latter was predominant. The ^{13}C NMR analyses of the polymers showed that the obtained poly(4MH) possessed various types of branches including methyl, ethyl, 3-methylalkyl, 3,5-dimethylalkyl and 3,6-dimethylalkyl groups and the obtained poly(4MP) possessed methyl, isobutyl, 2,4-dimethylpentyl and 2-methylhexyl groups.

Chapter 7. Controlled polymerization of alkenylcyclohexanes catalyzed by α -diimine nickel and palladium catalysts

Phenyl- and naphthyl- α -diimine nickel complexes, activated by MMAO, were tested in the polymerization of alkenylcyclohexanes under suitable conditions. These complexes catalyzed the isomerization polymerization of alkenylcyclohexanes to afford polymers which contained *trans*- and *cis*-1,4-cyclohexane groups. Interestingly, the *trans*- and *cis*-1,4-cyclohexane structures were controlled by the catalyst structure and reaction temperature. Complex **1** produced poly(allylcyclohexane) with *trans*-1,4-cyclohexane groups up to 91% at 100 °C. The naphthyl- α -diimine nickel complex **21** catalyzed the polymerization of butenylcyclohexane at 0 °C to afford polymer having 98% of *cis*-1,4-cyclohexane groups. The stereoregular polymers showed melting points, which were controlled by the ratio of *trans*- and *cis*-1,4-cyclohexane units.

Chapter 8. Living/controlled (block) copolymerization of propylene and 1-alkene by a phenyl substituted α -diimine nickel catalyst

Copolymerization of propylene and 1-alkene (1-hexene, 1-octene, 1-decene, 1-hexadecene and 4-methyl-1-pentene) was conducted by a 4-phenyl substituted α -diimine nickel complex **1** activated with MMAO at room temperature. The copolymerizations proceeded to give the copolymers with high molecular weight and narrow molecular weight distribution ($M_w/M_n \approx 1.2$), which indicated a living nature of copolymerization. Additionally, block copolymers composed of propylene and 1-alkene with high molecular weight ($M_n > 200$ kg/mol) and narrow M_w/M_n values were successfully fabricated in high yields by **1**-MMAO.

Chapter 9. Summary

Several important conclusions of this study are given in detail and suggestions are provided for further study.