博士論文

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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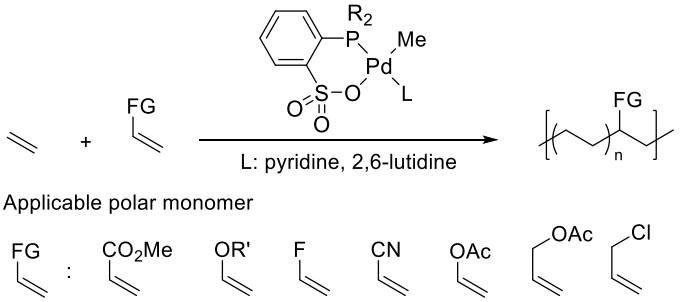
1. General Introduction

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 fivers. 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 (Scheme 1).[1]

Scheme 1. Copolymerization by Pd complexes



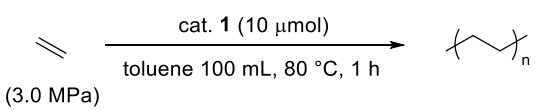
Palladium/phosphine–sulfonate catalyst, however, has two limitations; first, most of the reported molecular weights of copolymers were limited to 10^3 order.[2] For practical applications, there is a need to improve the molecular weights of copolymers. Although the steric and electronic effects of the palladium catalysts have been investigated to improve the polymer molecular weight[3], 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.

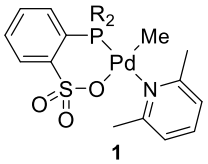
In this thesis, the author focused on the steric effect in palladium complexes bearing an alkylphosphine-sulfonate ligand to improve the molecular weight of copolymer and found that the catalyst bearing bulky alkyl groups, menthyl groups in particular, on the phosphorus atom can provide high molecular weight copolymers of ethylene and polar monomers. Furthermore, homo- and copolymerization of propylene and polar monomers by palladium/phosphine-sulfonate complexes were investigated.

2. Polymerization of ethylene by a variety of palladium/phosphine-sulfonate complexes

Initially, palladium complexes bearing a series of alkylphosphine-sulfonate ligands were synthesized and utilized for the homopolymerization of ethylene (Table 1). The molecular weights of polyethylenes obtained by reported catalyst **1a**-**c** were less than 10×10^3 (entries 1–3 in Table 1). When newly synthesized ligands, **1d** (3-Pen; pentan-3-yl), **1e** (Dmhep; 2,6-dimethylheptan-4-yl), and **1f** (Men; menthyl), were used, the molecular weight of the polyethylenes increased to 34, 72, and 169×10^3 g/mol, respectively, albeit with lower catalytic activity than **1a**–**c**. The highest molecular weight 169×10^3 observed in the case of catalyst **1f** is noteworthy, because synthesis of polyethylene with molecular weight over 100×10^3 g/mol by palladium catalyst was quite limited.[1]

Table 1. Polymerization of ethylene by Pd complexes **1a**–**1f**





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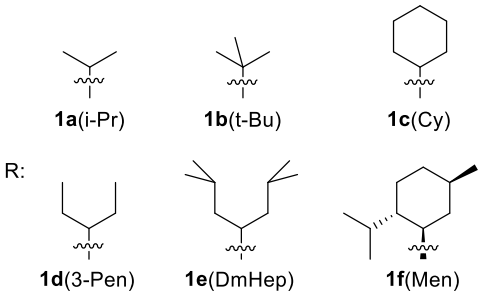


entry	catalyst	Activity (g mmol^{-1} h^{-1})	Mn (10^3)	Mw/Mn
1	**1a**	640	6.7	2.7
2	**1b**	1860	6.2	4.1
3	**1c**	1150	9.9	2.4
4	**1d**	130	33	2.3
5	**1e**	200	72	1.8
6	**1f**	210	169	1.5

A plausible explanation for the increase in molecular weights could be the steric congestion in the axial positions of the palladium plane, which led to suppression of chain transfer reactions.[3b] In order to determine the steric bulk around the palladium center, steric maps were drawn. As shown in Figure 2, steric congestion in the axial positions of the palladium center (y-axis) increased as a result of the increased steric demand of the alkyl substituents from **1a** to **1f**.[5]

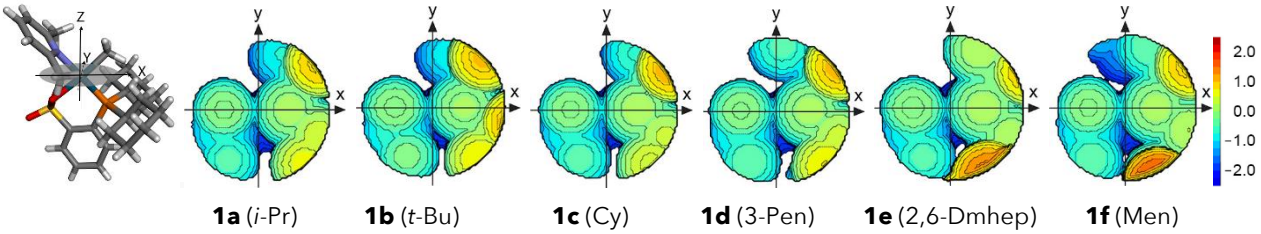


Figure 2. Steric map of palladium complex **1a**-**f**. The *y*-axis represents the axial position of the *xz*-plane containing the palladium center.

3. Quantification of steric effects of the substituents on the phosphorus atom

In order to obtain deeper understanding, the steric effects of the substituents were quantified by 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.[4] 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).

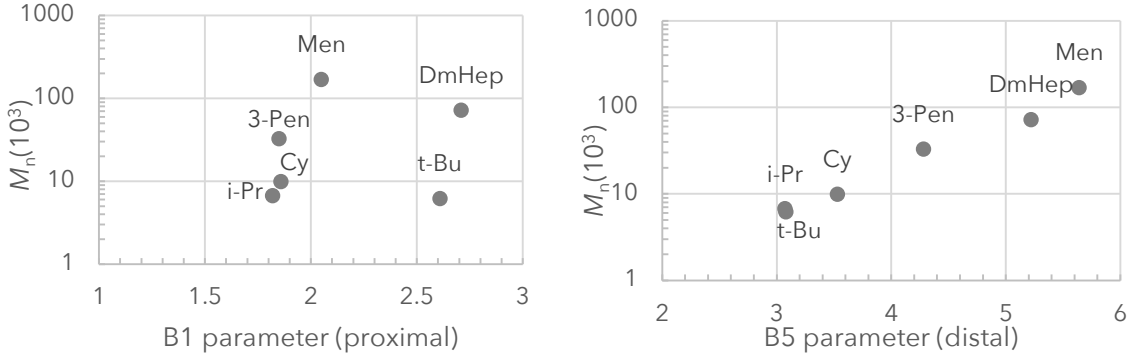
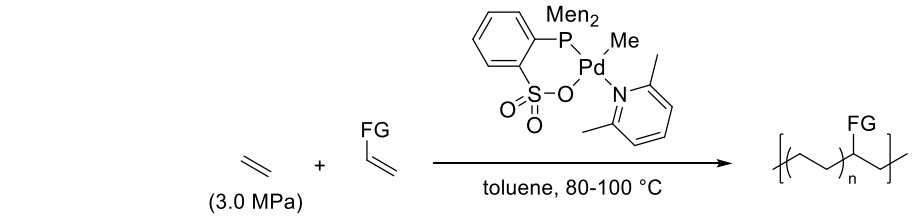


Figure 1. Correlation analysis between polymer molecular weights and the Sterimol parameters

4. Synthesis of high molecular weight ethylene/polar monomer copolymer

Copolymerization of ethylene and a variety of polar vinyl and allyl monomers was performed to investigate the scope and versatility of complex **1f** (Figure 3). Catalyst **1f** exhibited high activities and produced high-molecular-weight copolymers especially in copolymerization of ethylene and methyl acrylate and allyl acetate.



FG	CO_2Me	OBu	CN	OAc	OAc	Cl	CN
Activity (g $mmol^{-1}$ h^{-1})	67.3	54.0	2.0	2.3	55.0	2.2	9.1
M_n (10^3)	72	15	14	5.7	177	33	44
M_w/M_n	2.5	4.1	1.9	2.5	2.0	2.3	2.3
Incorp.(%)	1.3	1.1	0.7	1.3	0.6	0.6	0.4

Figure 3. Copolymerization of ethylene and polar monomers by complex **1f**

In order to improve the incorporation ratio of allyl acetate, different reaction conditions were examined. As the results, increase in the incorporation ratio of polar monomers up to 7.8% was achieved by changing reaction conditions including higher reaction temperatures and decreased ethylene pressures, although the molecular weights of copolymers decreased concomitantly. These results are indicative of a trade-off relationship between the molecular weight and the incorporation ratio of polar monomers (Figure 4). The solid black line shows that the values for number-average molecular weight (M_n) and the incorporation ratio of allyl acetate obtained from **1f** substantially exceed those of previously reported catalytic system **1c** (dotted black line).[6] Copolymerization of ethylene and methyl acrylate were also performed under various conditions to afforded copolymers with molecular weights (M_n = 6.1–72 × 10^3 g/mol) and its incorporation ratios of 1.4–11%. The ratios between M_n and the comonomer incorporation ratio for the ethylene/methyl acrylate copolymers obtained in this study (solid grey line in Figure 4) were higher than the ratios of previously reported catalyst systems (dotted grey line).[1]

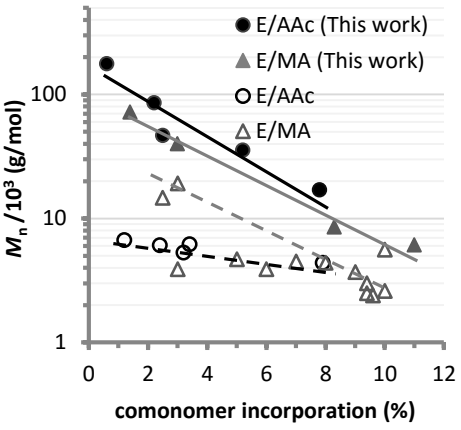


Figure 4. Comparison of M_n vs. incorporation ratio

5. Propylene polymerization by palladium/phosphine-sulfonate catalysts

In polymerization of propylene, regio- and stereoregularity need to be controlled because they are closely related to thermal and physical properties of the resultant polypropylene (Figure 5). However, the polymerization of propylene by late transition metals suffered from low regio- and stereoselectivity. To overcome the problems, the polymerization of propylene were performed at low temperatures of −20 °C to −78 °C.[7] At such low temperature, however, these catalysts cannot copolymerize polar

monomers with propylene due to the lack of thermal energy to promote a reaction of the metal center chelated by heteroatom after polar monomer insertion (Scheme 2).

In this thesis, the author envisioned that the introduction of bulky substituents on the phosphorus atom would, not only suppress the chain-transfer reaction to increase polymer molecular weight, but also control the regio- and stereoregularity in propylene polymerization.

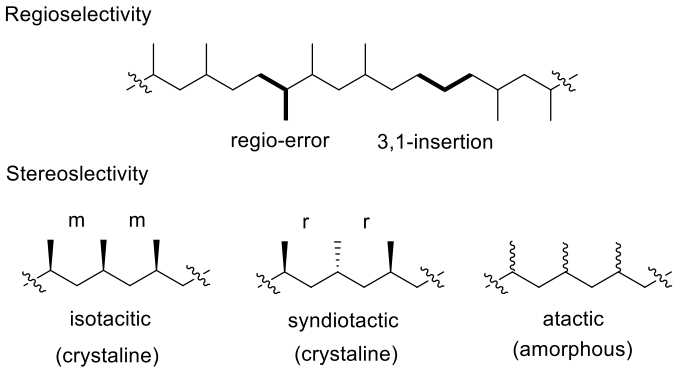
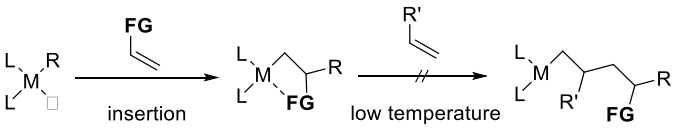


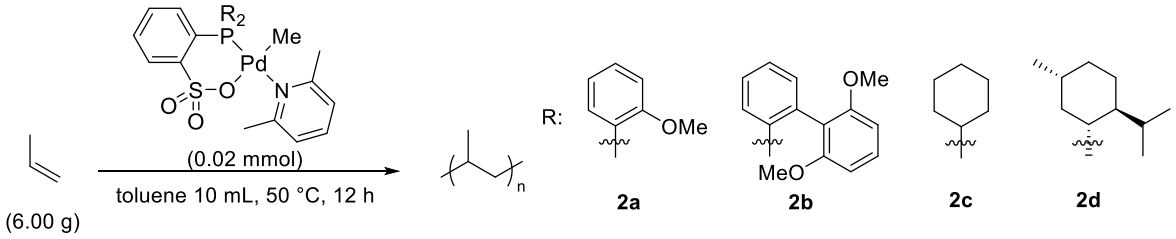
Figure 5. Microstructures in polypropylene

Scheme 2.



Initially, homopolymerization of propylene by palladium/phosphine–sulfonate catalysts **2a**–**2d** was performed to investigate the effect of the substituent on the phosphorus atom (Table 2). Palladium catalyst **2a**, widely used in the copolymerization of ethylene with polar monomers, yielded atactic oligopropylene (entry 1). Employing catalyst **2b**, bearing bulky biaryl groups on the phosphorus atom, resulted in the formation of oligomer and no improvement in molecular weight (entry 2). Replacing the substituents to alkyl groups, catalyst **2c**, led to an little increase in molecular weight (entry 3). Finally, the use of catalyst **2d**, bearing bulky 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 (entry 4). ^{13}C NMR analysis of the obtained polymer revealed that regioregularity was almost perfectly controlled and stereoregularity was much improved to a *mm* triad ratio of 49%.

Table 2. Homopolymerization of propylene by palladium complex **2a**-**2d**

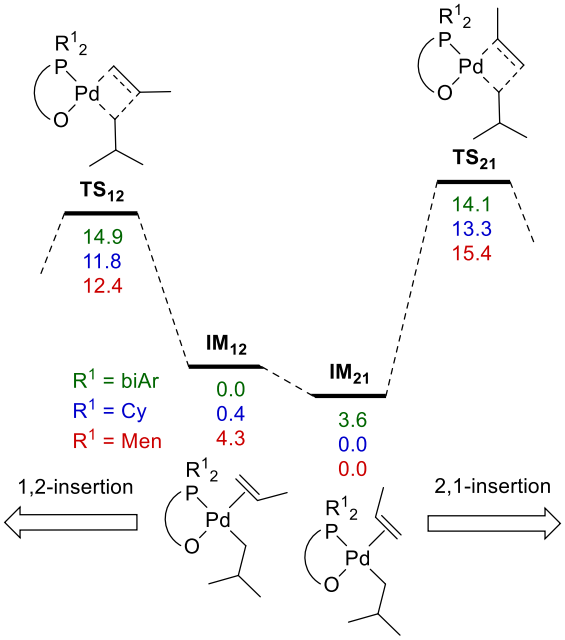


entry	catalyst	Activity (g mmol^{-1} h^{-1})	Mw (10^3)	Mw/ Mn	[mm] (%)
1	**2a**	0.1	0.9	1.2	23
2	**2b**	1.7	0.7	1.2	n.d.
3	**2c**	2.3	1.8	1.8	27
4	**2d**	7.5	28	2.1	49

Theoretical study - insertion mode of propylene

In order to study the high regioregularity of polypropylene, the mechanisms of propylene insertion for palladium/phosphine–sulfonate complexes bearing aryl and alkyl substituents were investigated by DFT calculations. The energy diagram is shown in Figure 6, in which the propylene-coordinated

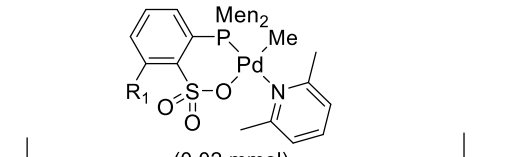
complexes (**IM**) and transition states (**TS**) for propylene insertion were calculated with isobutyl complexes. For the biaryl complex, the activation energy of 2,1-insertion (14.1 kcal/mol) is slightly lower than that of 1,2-insertion (14.9 kcal/mol). On the other hand, alkyl substituents such as cylohexyl and menthyl groups favored 1,2-insertion. In the case of the menthyl-substituted ligand, the energy difference between **TS_{12}** (12.4 kcal/mol) and **TS_{21}** (15.4 kcal/mol) became as large as 3.0 kcal/mol, which was consistent with high regio-regularity of the polypropylene obtained by **2d**.



6. Ligand-controlled stereospecific polymerization of propylene

Further optimization of the phosphine–sulfonate ligand was performed to improve the molecular weight of polymers and stereoregularity of polypropylene. 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 catalytic activity.[8] Encouraged by the reports, catalysts bearing various substituents at the *ortho* position of the sulfonate group were synthesized (Table 3). When catalyst **2e** having a trimethylsilyl group on the ligand was used, the molecular weight and *mm* triad ratio were improved (entry 2), compared with **2d** (entry 1). Introduction of the bulkier diphenylmethylsilyl group did not further improve the molecular weight and tacticity (entry 3). The highest *mm* triad ratio of 59% was then observed by introducing phenyl group (entry 4), although the molecular weight and catalytic activity was lower than those of **2e** in entry 5. Replacing the phenyl group with pentafluorophenyl group resulted in a significant decrease in molecular weight and *mm* triad ratio (entry 5).

Table 3. Homopolymerization of proyplene by palladium complex **2d**-**f**

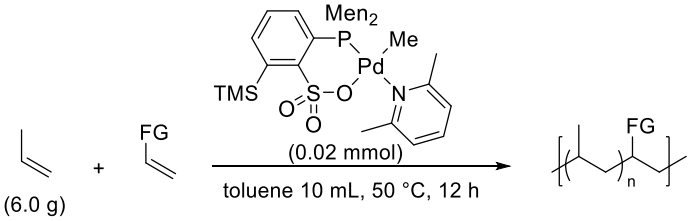


entry	catalyst (R_1)	Activity (g mmol^{-1} h^{-1})	M_w (10^3)	M_w/M_n	[*mm*] (%)	Regio-defects(%)
1	**2d** (H)	7.5	28	2.1	49	0.8
2	**2e** (Me_3Si)	9.9	47	2.0	57	0.9
3	**2f** (Ph_2MeSi)	7.6	38	2.0	55	1.3
4	**2g** (Ph)	5.9	39	1.9	59	0.9
5	**2h** (C_6F_5)	6.1	15	2.2	51	1.3

7. Copolymerization of propylene and polar monomer

Copolymerization of propylene and polar monomers was then performed (Table 4). Since the highest molecular weight and catalytic activity were observed in the case of **2e**, catalyst **2e** 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. In all the copolymerizations, the observed catalytic activities were under 1 g/mmol h^{-1} and *mm* triad ratios remained moderately isotactic, compared with that in the homopolymerization of propylene (Compare entry 2 of Table 3 with entries of Table 4).

Table 4. Copolymerization of propylene and polar monomer by catalyst **2e**



entry	FG	comonomer (mL)	activity ($g \cdot mmol^{-1} \cdot h^{-1}$)	M_w (10^3)	M_w/M_n	incorp. (%)	[*mm*] (%)	Regio-defects(%)
1	CH_2OAc	0.5	0.75	23	2.7	1.7	55	1.0
2	CH_2CN	1.0	0.79	14	1.9	1.5	55	1.1
3	CH_2Cl	0.25	0.58	24	2.2	1.7	56	1.1
4	CO_2Me	0.25	0.83	9.7	2.2	1.6	56	1.1

8. Summary

In this dissertation, the author investigated the steric effect of substituents on the phosphorus atom in alkylphosphine-sulfonate ligands to control the molecular weight of ethylene/polar monomer copolymer and the microstructure of polypropylene.

First, novel alkylphosphine-sulfonate ligands were synthesized and utilized for homopolymerization of ethylene. Encouraged by the polymerization results, steric effects of the substituents on the phosphorus atom were quantified showing strong correlation between obtained molecular weights and the Sterimol B5 parameters. Thus, ligands with bulkier alkyl substituents provided higher-molecular-weight polyethylenes. With the homopolymerization results in hand, the copolymerization of ethylene and polar monomers was also performed using bulky alkylphosphine-sulfonate ligands to afford higher-molecular-weight functionalized polyethylenes than the copolymers obtained by any other catalytic systems in literature.

Then propylene polymerization by palladium/phosphine-sulfonate catalysts was investigated. The optimization of the substituents on the phosphorus atom of the ligand revealed that the presence of bulky alkyl groups, e.g. menthyl group, is crucial for the generation of high-molecular-weight regioregular polypropylenes. The introduction of substituents at the *ortho*-position of the sulfonate group resulted in the improvement in polymer molecular weight and tacticity. Finally, copolymerization of propylene and polar monomers was examined. A variety of functional groups could be incorporated in ~1–3 mol% into the polymer main chain to afford moderately isotactic polar polypropylenes.

References

[1] Nakamura, A.; Ito, S.; Nozaki, K. *Chem. Rev.* **2009**, *109*, 5215–5244 and references cited therein.[2] Reports of copolymer with the molecular weight of 10^4 order, see (a) Skupov, K. M.; Marella, P. R.; Simard, M.; Yap, G. P. A.; Allen, N.; Conner, D.; Goodall, B. L.; Claverie, J. P. *Macromol. Rapid Commun.* **2007**, *28*, 2033–2038. (b) Allen, N. T.; Goodall, B. L.; McIntosh, L. H. EP1760086 A2, **2007** [3](a) Piche, L.; Daigle, J.-C.; Rehse, G.; Claverie, J. P. *Chem. Eur. J.* **2012**, *18*, 3277–3285. (b) Neuwald, B.; Falivene, L.; Caporaso, L.; Cavallo, L.; Mecking, S. *Chem. Eur. J.* **2013**, *19*, 17773–17788. [4](a) Hansch, C.; Leo, A. Exploring *QSAR: Fundamentals and Applications in Chemistry and Biology*; American Chemical Society: Washington, DC, 1995. (b) Harper, K. C.; Bess, E. N.; Sigman, M. S. *Nat. Chem.* **2012**, *4*, 366. [5]https://www.molnac.unisa.it/OM-2.0/2.0/ [6] Ito, S.; Kanazawa, M.; Munakata, K.; Kuroda, J.-i.; Okumura, Y.; Nozaki, K. *J. Am. Chem. Soc.* **2011**, *133*, 1232. [7] (a) Pellecchia, C.; Mazzeo, M.; Pappalmdo, D. *Macromol. Rapid Commun.* **1998**, *19*, 651−655 (b) Small, B. L.; Brookhart, M. *Macromolecules* **1999**, *32*, 2120−2130. (c) Cherian, A. E.; Rose, J. M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2005**, *127*, 13770–13771. (d) Rose, J. M.; Deplace, F.; Lynd, N. A.; Wang, Z.; Hotta, A.; Lobkovsky, E. B.; Kramer, E. J.; Coates, G. W. *Macromolecules* **2008**, *41*, 9548−9555. [8] (a) Kobayashi, M.; Uchino, H.; Yamamoto, K. JP2011-256167, **2011**. (b) Kobayashi, M.; Iwama, T.; Uchino, H.; Yamamoto, K. JP2011-201673, **2011**. (c) Kobayashi, M.; Uchino, H.; Yamamoto, K. JP2012-229190, **2012**.

List of publications

[Publications related to this thesis]

1. Ota, Y.; Ito, S.; Kuroda, J.; Okumura, Y.; Nozaki, K. *J. Am. Chem. Soc.,* **2014***, 136,* 11898-11901.
2. Ota, Y.; Ito, S.; Kobayashi, M.; Tayano, T.; Nozaki, K. *manuscript in preparation.*

[Other publications]

1. Ito, S.; Ota, Y.; Nozaki, K. *Dalton Trans.*, **2012**, *41*, 13807-13809.
2. Ota, Y.; Murayama, T.; Nozaki, K. *manuscript in preparation.*