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Developments of Chiral Metallocenes as Polymerization Catalysts

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Abstract. This review article describes developments in chiral metallocenes as polymerization catalysts focusing on C_2 symmetric *ansa*-zirconocene complexes. Selective synthesis of *rac*-isomers of *ansa*-zirconocenes are surveyed. Isospecific polymerizations of propylene catalyzed by chiral zirconocenes are summarized. Advanced series of polymerizations by chiral metallocenes such as asymmetric polymerization and polymerization of polar monomers are also introduced.
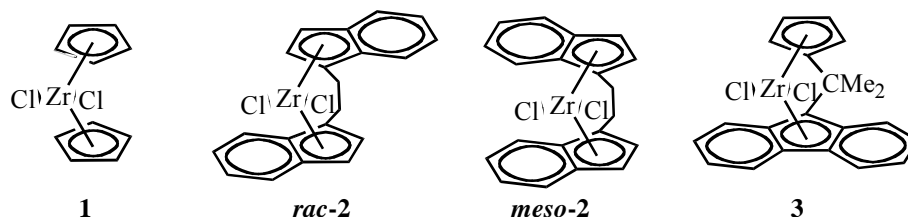
Keywords: Chiral Metallocene Catalysts, Polymerization Catalysts, Isotactic Polypropylene, Asymmetric Polymerization, Isotactic Poly(Methyl Methacrylate)

Introduction

Metallocenes of Group 4 metals have been attracted great attention as precursors of homogeneous olefin polymerization catalysts [1-3]. In comparison with heterogeneous Ziegler-Natta catalysts, the metallocene catalysts have many advantages based on their homogeneity. One of the most exciting features of the metallocene catalysts is the strong ligand effect on their catalytic behaviors such as activity, molecular weight control, and stereospecificity. Especially, tacticities of the resulting poly(α-olefin)s highly depend on the structures of the precatalysts: achiral simple metallocenes such as Cp_2ZrCl_2 (**1**, Cp = cyclopentadienyl) produce atactic polymers, while C_2-symmetric chiral metallocenes such as *rac*-$(C_2H_4)(Ind)_2ZrCl_2$ (***rac*-2**, Ind = 1-indenyl)) and C_s-symmetric complexes such as $Me_2C(C_5H_4)(Flu)ZrCl_2$ (**3**, Flu = fluorenyl) yield isotactic and syndiotactic poly(α-olefin)s, respectively (Scheme 1).

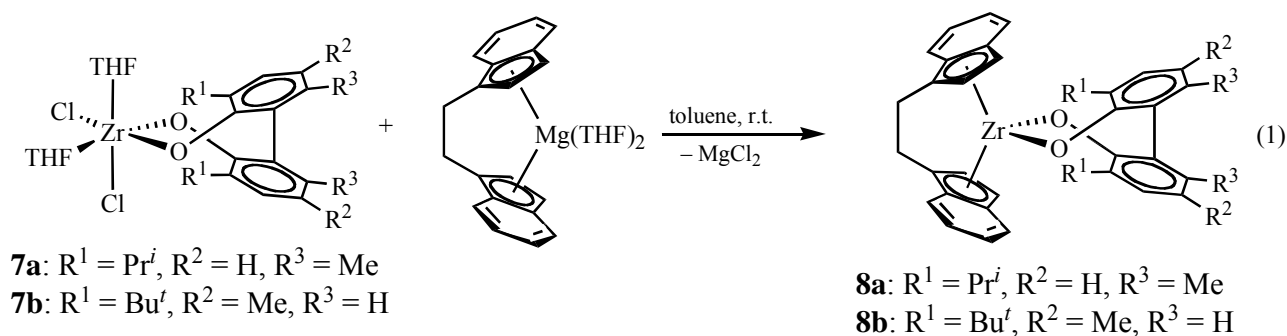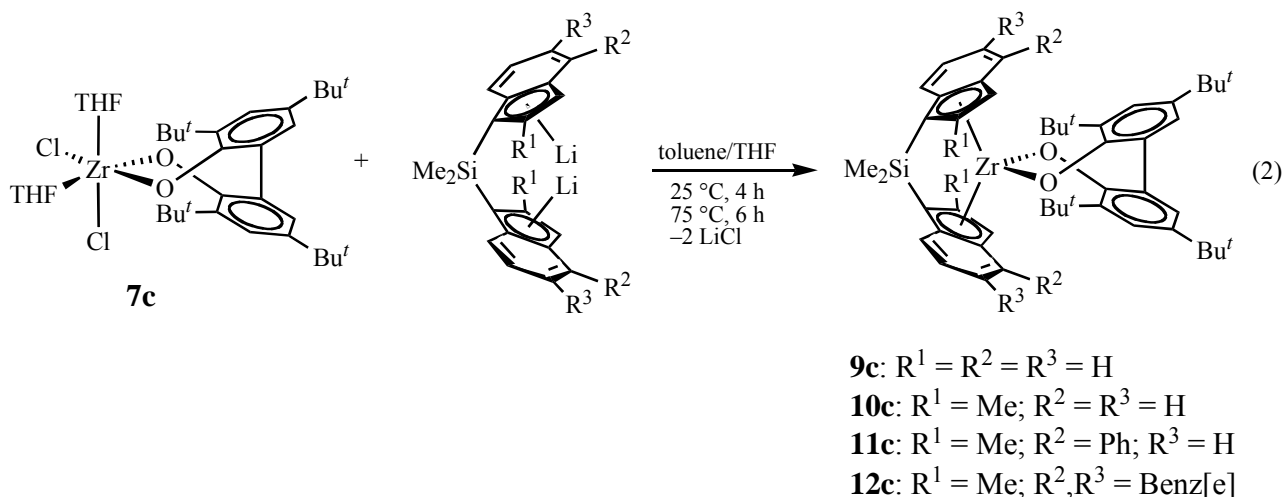**Scheme 1**

1   ***rac*-2**   ***meso*-2**   **3**

Among these three types of metallocene catalysts, C_2-symmetric chiral metallocenes are of great importance, because isotactic polypropylene is one of the most popular commodity resins. For the purpose of isospecific polymerization, contamination of achiral meso-isomers such as ***meso*-2**, which produce atactic polymers, should be avoided. In this review article, we survey developments of chiral metallocenes focusing on C_2 symmetric *ansa*-zirconocene catalysts, including their selective synthesis and their catalytic behavior for stereospecific polymerization of α-olefins and polar monomers.

Selective Synthesis of Chiral *ansa*-Metallocenes

For the purpose of isospecific polymerization of α-olefins, chiral metallocenes are not necessary to be optically active, but should be free from undesired impurities such as achiral *meso*-isomers. Chiral *ansa*-metallocenes such as *rac*-$(C_2H_4)(Ind)_2MCl_2$ (M = Ti (***rac*-4**), Zr (***rac*-2**), Hf (***rac*-5**)) had been synthesized by the reaction of $MCl_4(THF)_2$ and $Li_2\{(C_2H_4)(Ind)_2\}$ [4-7]. However, these reactions are always suffered by the formation of byproducts such as undesired achiral *meso*-isomers and polymeric complexes. Thus, *rac*-selective syntheses of *ansa*-metallocenes have been studied.
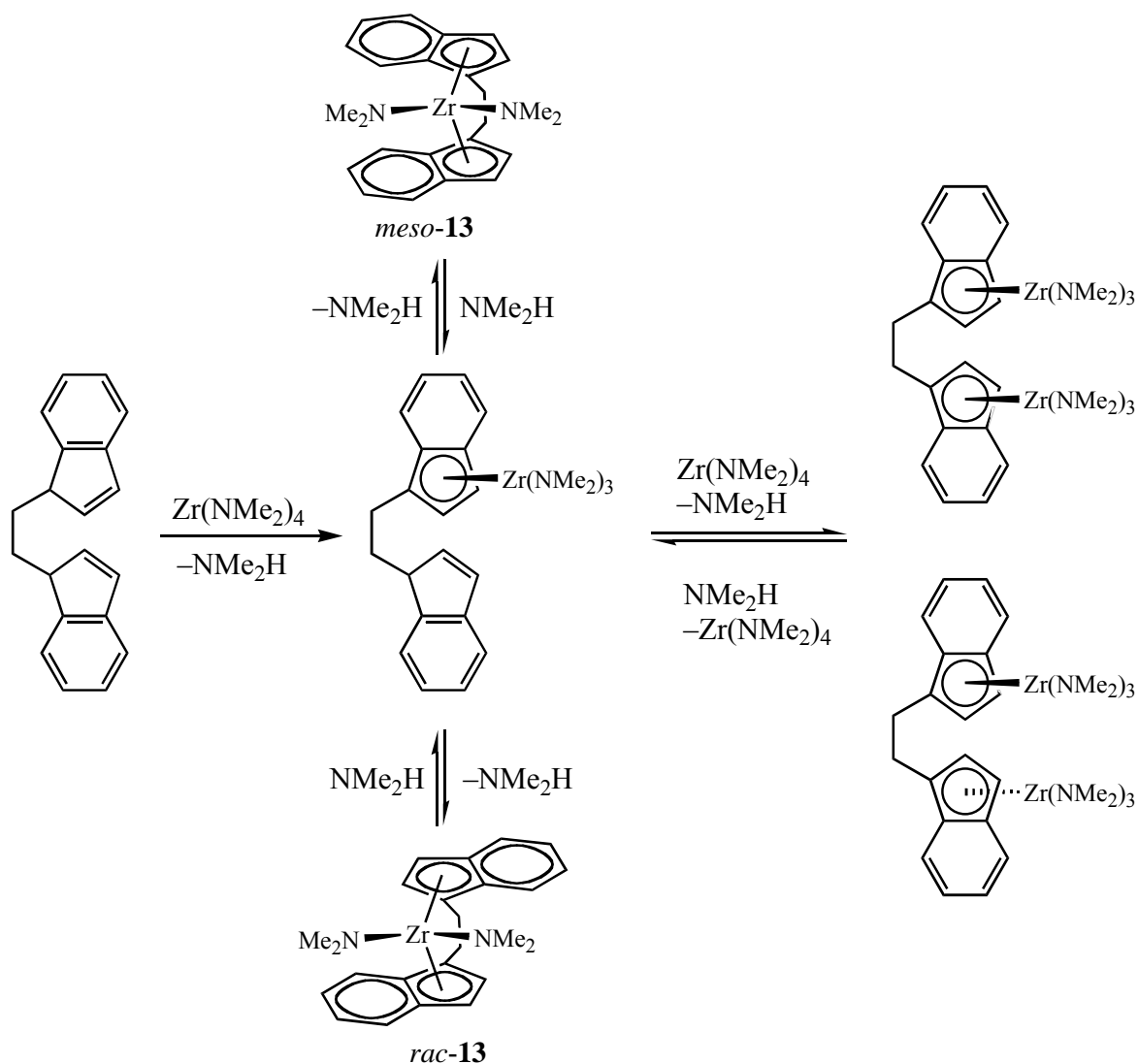
A reaction of binaphtholate complex $Cl_2Ti(BIN)$ (BIN = 1,1'-bi-2-naphtholate) with $C_2Me_4(C_5H_3Bu^t-3)_2Li_2$ was reported to give a *rac*-isomer, *rac*-$C_2Me_4(C_5H_3Bu^t-3)_2Ti(BIN)$ (**6**), selectively [8], although the yield was rather low (~15%), probably due to the aggregation of $Cl_2Ti(BIN)$. The use of bulky biphenolate (BIP) ligands instead of binaphtholate substantially improved the yields [9]. Mononuclear zirconium biphenolates, $Cl_2Zr(BIP)(THF)_2$ (BIP = 3,3'-Pr^i_2-6,6'-Me_2-1,1'-bi-2-phenolate (**7a**), and 3,3'-Bu^t_2-5,5'-Me_2-1,1'-bi-2-phenolate (**7b**) react with $(C_2H_4)(Ind)_2Mg(THF)_2$ to give *rac*-isomers **8a** and **8b** directly in good yields (equation 1). The reaction of 3,3',5,5'-Bu^t_4-1,1'-bi-2-phenolate complex (**7c**) with $(Me_2Si)(Ind)_2Li_2$ also directly affords a *rac*-complex **9c**, while the reactions of **7c** with bulkier substituted *ansa*-bis(indenyl) ligands such as $Me_2Si(2\text{-}MeInd)_2$, $Me_2Si(2\text{-}Me\text{-}4\text{-}PhInd)_2$, and $Me_2Si(2\text{-}Me\text{-}benz[e]Ind)_2$ initially give kinetic mixtures of *meso*- and *rac*-isomers. Heating the reaction mixtures to 75 °C for 5—7 h affords pure thermodynamically-favored *rac*-derivatives **10c**—**12c** (Equation 2).

7a: $R^1 = Pr^i$, $R^2 = H$, $R^3 = Me$
7b: $R^1 = Bu^t$, $R^2 = Me$, $R^3 = H$

8a: $R^1 = Pr^i$, $R^2 = H$, $R^3 = Me$
8b: $R^1 = Bu^t$, $R^2 = Me$, $R^3 = H$

(1)

$$\text{(2)}$$

9c: $R^1 = R^2 = R^3 = H$
10c: $R^1 = Me; R^2 = R^3 = H$
11c: $R^1 = Me; R^2 = Ph; R^3 = H$
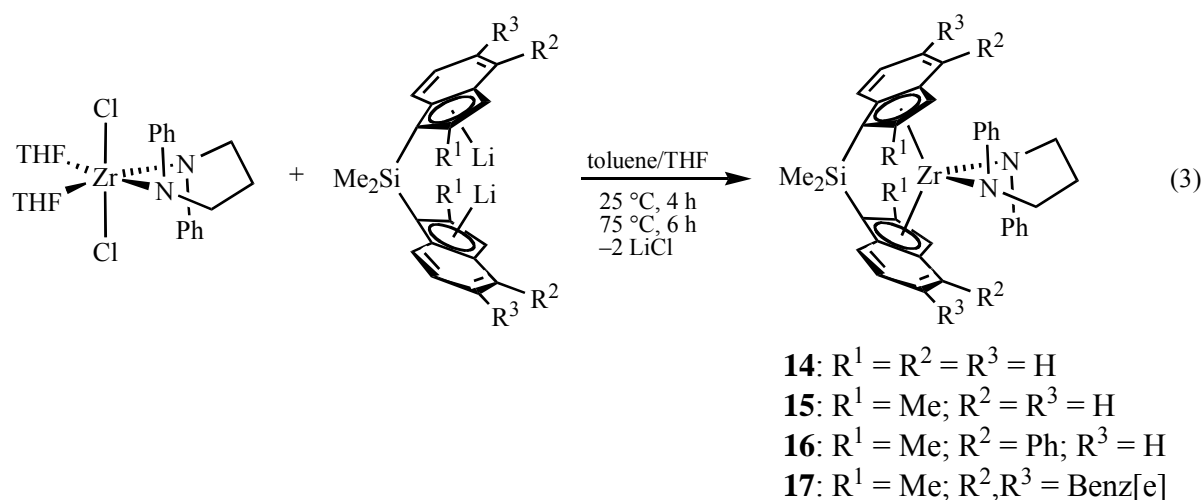**12c**: $R^1 = Me; R^2, R^3 = Benz[e]$

Jordan *et al*. developed amine-elimination approach for the selective synthesis of chiral *rac*-metallocenes (Scheme 2) [10-13]. The key features for high *rac*-selectivity is reversibility of the amine elimination reaction and thermodynamically higher stability of *rac*-isomers than *meso*-isomers..
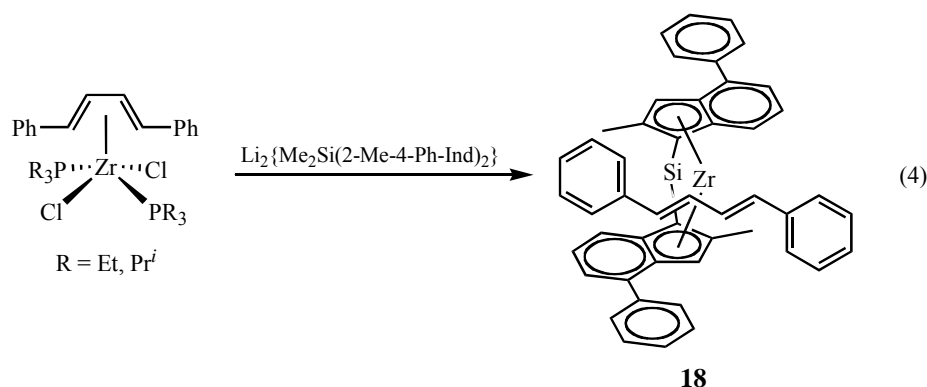
Scheme 2

The reaction of $Zr(NMe_2)_4$ with $(C_2H_4)(Ind)_2H_2$ under continuous N_2 flow gives a 1:1 mixture of *rac*- and *meso*-$(C_2H_4)(Ind)_2Zr(NMe_2)_2$. In sharp contrast, the same reaction under static N_2 atmosphere affords $(C_2H_4)(Ind)_2Zr(NMe_2)_2$ in a 13/1 *rac/meso* ratio, from which pure *rac*-$(C_2H_4)(Ind)_2Zr(NMe_2)_2$ (**rac**-**13**) can be isolated in ~70% yield by a single crystallization. Treatment of the resulting chiral *ansa*-metallocene bis(amide) with Me_3SiCl or $AlMe_3$ affords the corresponding dichloride or dimethyl complex, respectively. The *rac*-selectivity is dependent on both the *ansa*-cyclopentadienyl ligand and amide ligand, e.g., the use of $Zr(NEt_2)_4$, $Zr(NPr^i_2)_2(NMe_2)_2$, and $Zr(NC_4H_8)_4$, result in lower *rac*-selectivity than the case of $Zr(NMe_2)_4$ in the synthesis of $(C_2H_4)(Ind)_2Zr(NR_2)_2$. This strategy is also effective for the *rac*-selective synthesis of silylene bridged metallocene complexes, when appropriate amide complexes are chosen depending on the *ansa*-cyclopentadienyl ligand used.

The amine elimination reaction is quite useful for the preparation of rather simple chiral *ansa*-metallocenes, but not so effective for bulky substituted bridged-indenyl derivatives. A chelating diamide complex, $Zr\{PhN(CH_2)_3NPh\}Cl_2(THF)_2$ was found to be an effective precursor for *rac*-selective synthesis of bulky *ansa*-metallocenes (**14**—**17**) (equation 3) [14]. Treatment of these complexes with Me_3SiCl or HCl converts to the corresponding dichloride complexes

$$\text{(3)}$$

14: $R^1 = R^2 = R^3 = H$
15: $R^1 = Me$; $R^2 = R^3 = H$
16: $R^1 = Me$; $R^2 = Ph$; $R^3 = H$
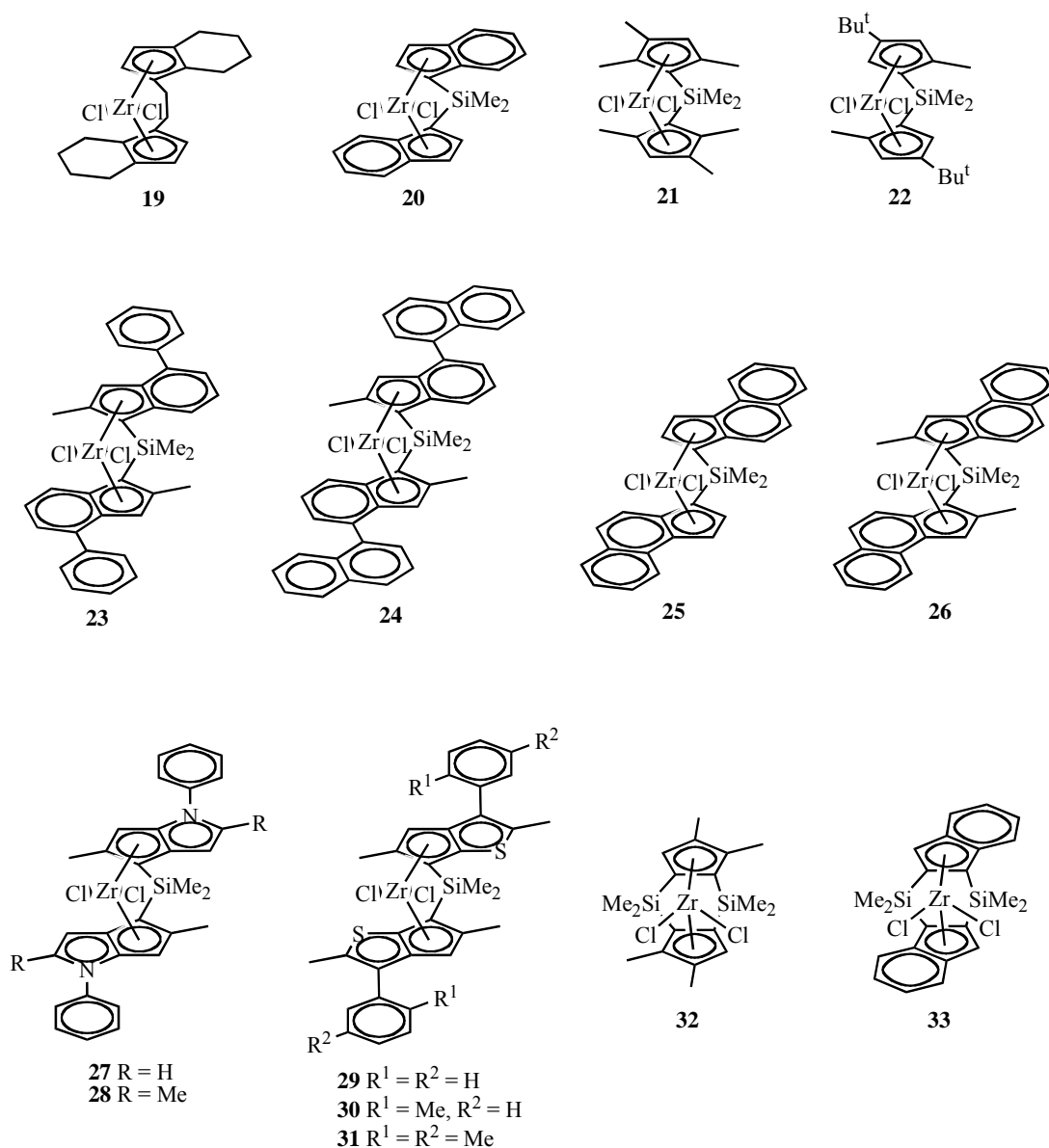**17**: $R^1 = Me$; $R^2,R^3 = Benz[e]$

A 1,4-diphenyl-1,3-butadiene complex is also effective for *rac*-selective synthesis of bulky *ansa*-metallocenes (Scheme 4) [15]. The diphenylbutadiene complex, $ZrCl_2(PR_3)_2(DPBD)$ (R = Et, Pr^i; DPBD = 1,4-diphenyl-1,3-butadiene), can be prepared by the reduction of $ZrCl_4(PR_3)_2$ with Li metal in the presence of diphenylbutadiene in 90-93% yields. The treatment of $ZrCl_2(PR_3)_2(DPBD)$ with $Li_2\{Me_2Si(2-Me-4-Ph-Ind)_2\}$ in toluene produces quantitatively the desired racemic, divalent *ansa*-zirconocene (**18**). The DPBD complex **18** can be used as highly active isospecific propylene polymerization catalyst in combination with MAO without the conversion to the corresponding dichloride or dimethyl complexes.

$$(4)$$

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Isospecific Polymerization of Propylene by Chiral *ansa*-Type (Bridged) Metallocenes

In 1984, Ewen found that chiral *ansa*-metallocene catalysts promote isospecific polymerization of propylene [16]. A mixture of *meso*- and *rac*-isomers of (C$_2$H$_4$)(Ind)$_2$TiCl$_2$ (**4**) upon activation with MAO afforded a mixture of isotactic PP and atactic PP [16], this opened a new era of mtallocene catalyst. Examples of chiral metallocenes as precursors of olefin polymerization catalysts are illustrated in Scheme 3, and the representative results of isospecific polymerization of propylene are shown in Table 1.

Scheme 3

19   **20**   **21**   **22**

23   **24**   **25**   **26**

27 R = H
28 R = Me

29 R^1 = R^2 = H
30 R^1 = Me, R^2 = H
31 R^1 = R^2 = Me

32   **33**

Table 1. Isospecific Polymerization of Propylene by Chiral Metallocenes upon Activation with MAO.

Catalyst	Temp (°C)	Activity[a]	M_n /10^3	M_w/M_n	*mmmm* (%)	T_m (°C)	ref.
ansa-Metallocenes							
(C$_2$H$_4$)(Ind)$_2$ZrCl$_2$ (**2**)	60	1.375	6.3	1.9	63	—	[58]
	30	7.0	35.9[b]	2.40	85.2	142.3	[22]
rac-(C$_2$H$_4$)(IndH$_4$)$_2$ZrCl$_2$ (**19**)	20	4.75	45[b]	1.9	95[c]	—	[18]
rac-Me$_2$Si(Ind)$_2$ZrCl$_2$ (**20**)	65	11.0[d]	44[b]	2.2	96.2[c]	—	[21]
rac-Me$_2$Si(2,3,5-Me$_3$Cp)$_2$ZrCl$_2$ (**21**)	30	5.3	134[b]	1.99	97.7	162.0	[22]
rac-Me$_2$Si(3-Bu^t-5-MeCp)$_2$ZrCl$_2$ (**22**)	50	0.505	9.19[b]	2.5	94	149	[23]
rac-Me$_2$Si(2-Me-4-PhInd)$_2$ZrCl$_2$ (**23**)	70	755	729	—	95.2	157	[24]
rac-Me$_2$Si(2-Me-4-NaphInd) $_2$ZrCl$_2$ (**24**)	70	875	920	—	99.1	161	[24]
rac-Me$_2$Si(Benz[e]Ind)$_2$ ZrCl$_2$ (**25**)	40	37.5	28	1.7	93.9	146.6	[26]
rac-Me$_2$Si(2-Me-Benz[e]Ind)$_2$ZrCl$_2$ (**26**)	40	45.0	248	2.2	96.2	164.1	[26]
rac-Me$_2$Si(5-Me-1-Ph-4-Pyr[b]Cp)$_2$ZrCl$_2$ (**27**)	70	443[d]	145[b]	—	—	146	[27]
rac-Me$_2$Si(2,5-Me$_2$-1-Ph-4-Pyr[b]Cp)$_2$ZrCl$_2$ (**28**)	70	324[d]	198[b]	—	—	155	[27]
rac-Me$_2$Si(2,5-Me$_2$-3-Ph-6-Tp[b]Cp)$_2$ZrCl$_2$ (**29**)	70	1953[d]	445[b]	—	—	156	[27]
rac-Me$_2$Si{2,5-Me$_2$-3-(2-MeC$_6$H$_4$)-6-Tp[b]-Cp}$_2$ZrCl$_2$ (**30**)	70	850[d]	604[b]	—	—	160	[27]
rac-Me$_2$Si{2,5-Me$_2$-3-(2,5-Me$_2$C$_6$H$_3$)-6-Tp[b] Cp}$_2$ZrCl$_2$ (**31**)	70	479[d]	795[b]	—	—	160	[27]
rac-(C$_2$H$_4$)(Ind)$_2$HfCl$_2$ (**5**)	50	43.6	304[b]	2.3	95–99[e]	136	[29]
rac-(C$_2$H$_4$)(IndH$_4$)$_2$HfCl$_2$ (**34**)	50	9.1	150[b]	2.2	95–99[e]	142	[29]
rac-Me$_2$Si(2,3,5-Me$_3$Cp)$_2$HfCl$_2$	30	0.10	256	2.38	98.7	162.8	[22]
(C$_2$H$_4$)(Ind)$_2$TiCl$_2$ (**4**) (56% *rac* 44% *meso*)	–60	0.018[d]	96.6	1.59	54[c]	—	[16]
MeCH(Ind)(C$_5$Me$_4$)TiCl$_2$ (**35**)	50	0.167	66.6	1.9	40	51.2 66.0	[32]
Unbridged Metallocenes							
Cp$_2$TiPh$_2$ (**37**)	–60	0.055[d]	195	1.8	53	—	[16]
rac-(PhMeCHCp)$_2$ZrCl$_2$ (**38**)	–50	0.026[d]	310[f]	—	43	—	[36]
rac-(CyMeCHCy)$_2$ZrCl$_2$ (**39**)	–50	0.003[d]	86[f]	—	51	—	[36]
rac-{(9-BBN)CH$_2$CH(Ph)Cp}$_2$ZrCl$_2$ (**40**)	–50	0.012[d]	11[f]	—	54	—	[36]
rac-{(9-BBN)CH$_2$CH(Cy)Cp}$_2$ZrCl$_2$ (**41**)	–50	0.005[d]	10[f]	—	75	—	[36]
{2-(1-neoisomenthyl)Ind}$_2$ZrCl$_2$ (**42**)	–30	0.032[d]	260[f]	—	77	—	[37]
{2-(3'-α-cholestanyl)Ind}$_2$ZrCl$_2$ (**43**)	–30	0.041[d]	470[f]	—	80	—	[38]
(1-MeFlu)$_2$ZrCl$_2$ (**44**)	60	0.035[d]	65[b]	—	83	145	[40]

[a] Kg mmol^{-1}h^{-1}atm^{-1}.   [d] Kg mmol^{-1}h^{-1}.

[b] M_w value.   [e] mole % of units with the same relative configuration.

[c] *mm* value.   [f] M_η value.

The isospecificity of $(C_2H_4)(Ind)_2ZrCl_2$ (**2**)/MAO in the polymerization of propylene tends to decrease with raising polymerization temperature and decreasing [Al]/[Zr] ratio [17]. Brintzinger found that a pure *rac* isomer of *ansa*-zirconocene, *rac*-$(C_2H_4)(IndH_4)_2ZrCl_2$ (**19**, $IndH_4$ = tetrahydroindenyl), polymerized propylene to produce isotactic polypropylene [18]. The investigation on the stereo- and regioirregularity of the polypropylenes obtained by ***rac*-2** and **19** concluded that the isospecific polymerizations by the chiral *ansa*-metallocene catalysts proceed with the enantiomorphic site control mechanism [19]. This is in sharp contrast to the fact that stereospecific polymerizations by achiral titanocenes proceed with chain end control [20].

C_2-Symmetric silylene bridged metallocenes are also catalyst precursors for isospecific polymerization of propylene. Actually, a silylene bridged derivative, *rac*-$Me_2Si(Ind)_2ZrCl_2$ (**20**) [21], shows higher activity and isospesificity than the ethylene-bridged complex **2**. A C_2-symmetric silylene-bridged bis(trimethylcyclopentadienyl)zirconium complex, *rac*-$Me_2Si(2,3,5-Me_3Cp)_2ZrCl_2$ (**21**) [22], exhibits quite high isospecificity to give polymers with high molecular weight and high melting point. A *tert*-butyl substituted complex, *rac*-$Me_2Si(3-Bu^t-5-MeCp)_2ZrCl_2$ (**22**) [23], is less stereospecific than **21**. Silylenebis(indenyl)complexes having aromatic group at 4-position of the indenyl rings, *rac*-$Me_2Si(2-Me-4-PhInd)_2ZrCl_2$ (**23**) and *rac*-$Me_2Si(2-Me-4-NaphInd)_2ZrCl_2$ (**24**), show high activity and high isospecificity to produce high molecular weight polymers. The isospecificity of the **24**/MAO system seems to be highest among those of the metallocene catalysts.

Complexes having extended fused aromatic rings, *rac*-$Me_2Si(Benz[e]Ind)_2ZrCl_2$ (**25**) and *rac*-$Me_2Si(2-Me-Benz[e]Ind)_2ZrCl_2$ (**26**), are also effective for isospecific polymerization of propylene [24-26]. In comparison between **25** and **26**, the Me-substituent at 2-position of the indenyl group in **26** was found to be effective for suppression of chain transfer to produce high molecular weight polymers [26]. The fused pyrrol complexes **27** and **28** are slightly less active and less isoselective but more regioselective in comparison with the similar indenyl complex **23** under the same conditions [27]. The fused thiophene complexes **29**—**31** are notable for the highest activity among the reported propylene polymerization catalysts [27]. Their isospecificity is only slightly lower and their regioselectivity is higher than those of **23**.

Chiral C_2-symmetric doubly bridged zirconocene complexes, $(Me_2Si)_2\{1,2-(3,4-Me_2Cp)\}_2ZrCl_2$ (**32**) and $(Me_2Si)_2(1,2-IndH_4)_2ZrCl_2$ (**33**), produced polypropylene in the presence of MAO, but their isospecificities (mmmm = 38 and 80%, respectively) are lower than the similar singly bridged metallocenes [28].

The ethylene-bridged hafnocenes, *rac*-$(C_2H_4)(Ind)_2HfCl_2$ (**5**) and *rac*-$(C_2H_4)(IndH_4)_2HfCl_2$ (**34**), also catalyze isospecific polymerization of propylene upon the activation by MAO [29]. The hafnium catalysts produce polypropylenes with similar isotacticities and higher molecular weights in comparison with zirconium catalysts, however, their activities are significantly lower than the zirconium catalysts.

Stereospecificities of chiral C_1-symmetric complexes depend on their steric hindrances. For example, a 3-methyl substitutedcomplex, $Me_2C(3-MeCp)(Flu)ZrCl_2$, provides hemiisotactic polypropylene [30], while the similar *tert*-butyl substituted complex, $Me_2C(3-Bu^tCp)(Flu)ZrCl_2$, affords isotactic polypropylene [31].

Chiral titanocene complexes such as **4** also produce isotactic polypropylene, however, their activities and isospecificities tend to be lower than the similar zirconium catalysts [32]. Chiral C_1-symmetric ethylidene-bridged titanium complexes, $MeCH(Ind)(C_5Me_4)TiX_2$/MAO (X = Cl (**35**),

Me (**36**)) polymerize propylene to give a stereoblock polymer comprising alternating sequences of stereoregular and stereoirregular polypropylene, which is a thermoplastic elastomer [32-34].
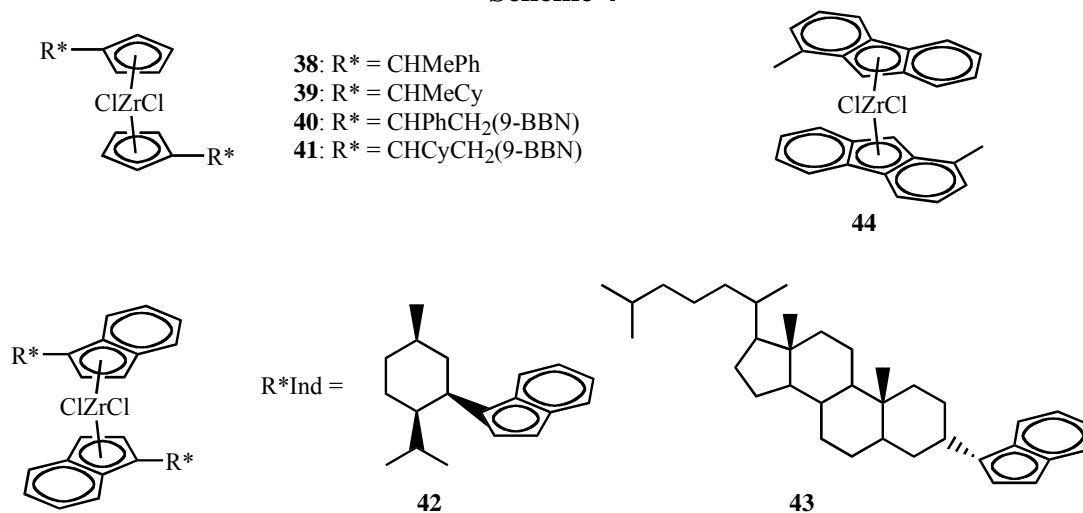
Isospecific Polymerization of Propylene by Unbridged Metallocenes

Some unbridged metallocenes having chiral substituents on Cp rings catalyze isospecific polymerization of propylene. Examples of such complexes are illustrated in Scheme 4, and the representative results are included in Table 1. A simple achiral metallocene catalyst, Cp_2TiPh_2 (**37**)/MAO, promotes isospecific polymerization of propylene (mmmm ~ 50%) at low temperature by chain-end control mechanism [16]. Zirconocene complexes having chiral substituents on Cp rings, *rac*-$(R*Cp)_2ZrCl_2$ (**38—41**), produces partially isotactic polypropylene (mmmm ~75%) at low temperature upon activation with MAO [35,36]. Bis(indenyl)zirconium complexes having bulky chiral substituents on indenyl rings, $(R*Ind)_2ZrCl_2$ (R* = neoisomenthy (**42**), 3-α-cholestanyl (**43**)), are more isospecific (mmmm = 77% for **42**, 80% for **43**) than **38—41** [37-39].
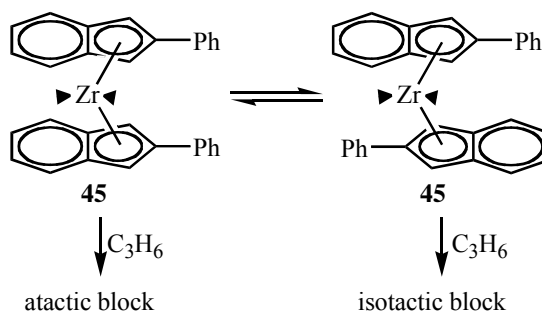
A reaction of $ZrCl_4$ with two equiv. of 1-methylfluorenyllithium selectively affords a stereorigid and chiral zirconocene, $(1\text{-MeFlu})_2ZrCl_2$ (**44**), because of steric effect of the ligand. The complex **44** together with MAO polymerized propylene to give polypropylene with relatively high isotacticity among the unbridged zirconocene systems even at 60 °C [40].

A unique unbridged bis(2-phenylindenyl)zirconium complex (**45**) gave elastic, isotactic-atactic stereoblock polypropylene controlled by rotation of the 2-phenylindenyl as shown in Scheme 5 [41].
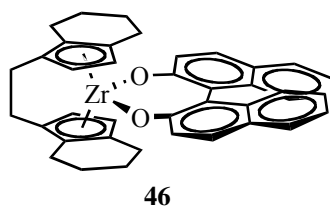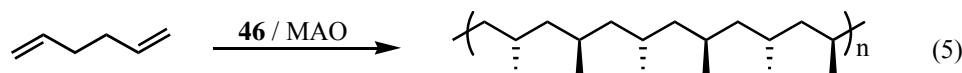
Scheme 4

38: R* = CHMePh
39: R* = CHMeCy
40: R* = CHPhCH₂(9-BBN)
41: R* = CHCyCH₂(9-BBN)

R*Ind =

Scheme 5

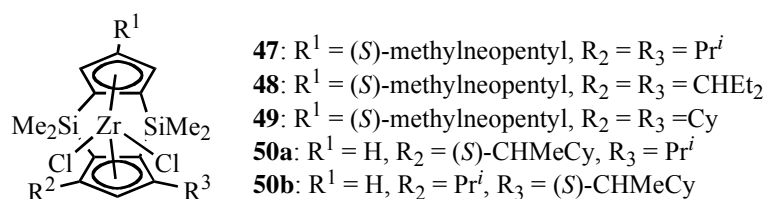atactic block   isotactic block

Asymmetric Polymerization by Enantiopure Chiral Metallocenes

Polymerization of 1,5-hexadiene by an enantiopure *ansa*-zirconocene (**46**)/MAO system proceeds with cyclization to give an main-chain optically active *trans*-diisotactic polymer (equation 5, 68% trans rings) [42-44]. The enantioselectivity for this cyclopolymerization can be explained by the fact that the same prochiral face of olefins was selected by the chiral zirconium center. Asymmetric hydrogenation as well as C-C bond formation catalyzed by **46** has recently been developed to achieve high enantioselectivity. This parallels to the high stereoselectivity in the polymerization.

(5)

46

Enantiopure doubly bridged metallocenes **47**—**50** (Scheme 6) are effective for kinetic resolution of racemic mixture of chiral α-olefins by enantio-selective polymerization [45]. The zirconocene dichlorides having an enantiopure methylneopentyl group on the "upper" cyclopentadienyl ligand **47**—**49** showed unprecedent activity for the polymerization of -olefins having bulky substituents at 3- and/or 4-positions. these complexes achieved partial kinetic resolution of 3-methyl-1-pentene, 3-methyl-1-hexene, and 3,5,5-trimethyl-1-hexene ($s = k_{faster}/k_{slower} \approx 2$), and in paricular, realized high resolution of 3,4-dimethyl-1-pentene ($s > 15$ for **47**). The zirconocene dichlorides having an enantiopure 1-cyclohexylethyl group on the "lower" cyclopentadienyl ligand **50a** and **50b** are less effective for kinetic resolution of those monomers than **47**—**49**.

Scheme 6

47: R^1 = (*S*)-methylneopentyl, R$_2$ = R$_3$ = Pr^i
48: R^1 = (*S*)-methylneopentyl, R$_2$ = R$_3$ = CHEt$_2$
49: R^1 = (*S*)-methylneopentyl, R$_2$ = R$_3$ =Cy
50a: R^1 = H, R$_2$ = (*S*)-CHMeCy, R$_3$ = Pr^i
50b: R^1 = H, R$_2$ = Pr^i, R$_3$ = (*S*)-CHMeCy

Isospecific Polymerization of Polar Monomers

Metallocene catalysts are also effective for the polymerization of polar monomers such as methyl methacrylate (MMA), and the representative results of the polymerization of MMA are listed in Table 2.

Table 2. Isospecific Polymerization of MMA by Chiral Metallocenes.

Catalyst (Initiator)	Temp (°C)	$[MMA]_0$ /[cat.]	Time (h)	Yield (%)	M_n /10^3	M_w /M_n	*mm* (%)	*mr* (%)	*rr* (%)	ref.
rac-$(C_2H_4)(Ind)_2ZrMe_2$ (**54**) /[Ph_3C][$B(C_6F_5)_4$] /$Zn(CH_2CH_2CH=CH_2)_2$	0	1870	24	48	599	1.30	98.0	1.3	0.7	[50]
rac-$(C_2H_4)(IndH_4)_2ZrMe_2$ (**55**) /[Ph_3C][$B(C_6F_5)_4$] /$Zn(CH_2CH_2CH=CH_2)_2$	0	1870	24	64	339	1.25	95.5	3.3	1.2	[50]
rac-$Me_2Si(Ind)_2ZrMe_2$ (**56**) /[Ph_3C][$B(C_6F_5)_4$] /$Zn(CH_2CH_2CH=CH_2)_2$	0	1870	24	34	345	1.34	91.4	5.3	2.3	[50]
rac-$Me_2Si(Ind)_2ZrMe_2$ (**56**) /$B(C_6F_4$-2-$C_6F_5)_3$	0	935	5.5	100	—	—	93.0	4.8	2.2	[51]
rac-$(C_2H_4)(Ind)_2ZrMe_2$ (**54**)/$B(C_6F_5)_3$	r.t.	200	1	98	48.7	1.20	95	4	1	[52]
rac-$Me_2Si(Ind)_2ZrMe_2$ (**56**)/$Al(C_6F_5)_3$	0	200	4	100	73.9	1.32	4.6	34.6	60.8	[53]
rac-$(C_2H_4)(Ind)_2ZrMe\{OC(OPr^i)=$ $CMe_2\}$ (**57**)/$B(C_6F_5)_3$	r.t.	400	1/6	>99	48.6	1.03	96.7	2.2	1.1	[55]
[*rac*-$(C_2H_4)(Ind)_2Zr\{OC(OPr^i)=CMe_2$ $\}$]-[$MeB(C_6F_5)_3$] (**58**)	r.t.	600	1/6	>99	75.5	1.03	95.3	3.2	1.5	[55]
rac-$(C_2H_4)(Ind)_2Zr^+Me$-$OCPr^iOAl^-(C_6F_5)_3$ (**59**)	r.t.	400	20	90	51.9	1.93	6.6	34.2	59.2	[55]

A cationic achiral zirconocene, [$Cp_2ZrMe(THF)$][BPh_4] (**51**), polymerize MMA in the presence of neutral zirconocene, Cp_2ZrMe_2 (**52**), to give syndiotactic-rich poly(methyl methacrylate) (PMMA) by chain-end control mechanism [46]. A two component system composed of neutral zirconocene ester enolate complex, $Cp_2ZrMe\{OC(OBu^t)=CMe_2\}$ (**53**) as initiator and **51** as catalyst polymerize MMA in a living fashion, and also produces syndiotactic-rich PMMA [47,48].
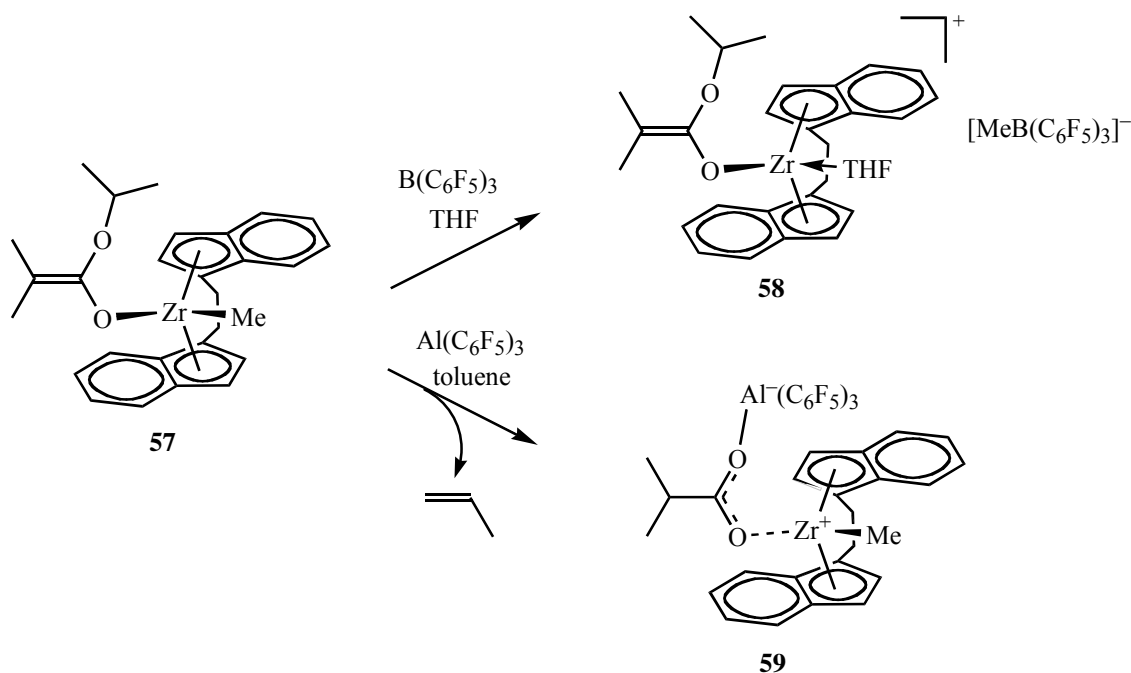
In contrast, chiral *ansa*-zirconocene catalysts produce highly isotactic PMMAs via enantiomorphic site-control mechanism. Chiral ethylene-bridged complexes, *rac*-$(C_2H_4)(Ind)_2ZrMe_2$ (**54**), *rac*-$(C_2H_4)(IndH_4)_2ZrMe_2$ (**55**) and *rac*-$Me_2Si(Ind)_2ZrMe_2$ (**56**), catalyze polymerization of MMA in the presence of [Ph_3C][$B(C_6F_5)_4$] and ZnR_2 (R = Me, Et, *n*-Bu, 1-buten-4-yl) to give highly isotactic PMMA (mm ~98%) at 0 °C [49,50].

Although the **54-56**/[Ph_3C][$B(C_6F_5)_4$] systems are inactive for MMA polymerization without ZnR_2, the use of $B(C_6F_4$-2-$C_6F_5)_3$ (PBB) as a cocatalyst for zirconocene dimethyl complexes develops catalytic activity for MMA polymerization without ZnR_2 [51]. Thus, **56**/$B(C_6F_4$-2-$C_6F_5)_3$ shows higher activity and higher isospecificity than the three-component **56**/[Ph_3C][$B(C_6F_5)_4$]/ZnR_2 system. The **54**/$B(C_6F_5)_3$ system rapidly polymerizes MMA in CH_2Cl_2 to give highly isotactic PMMA with narrow molecular weight distribution [52].

In a sharp contrast to the case of boron-containing cocatalysts, the use of an aluminum-based cocatalyst $Al(C_6F_5)_3$ yields syndiotactic-rich PMMA even in a combination of chiral metallocene **56** [53]. The polymerization by the $Al(C_6F_5)_3$ system is proposed to proceed via enolaluminate. A unique combination of the isospecific metallocene catalyst and syndiospecific aluminum catalyst realize isotactic-*b*-syndiotactic stereoblock copolymerization of MMA ([mm]/[mr]/[rr] = 46.4/7.9/45.7) (Scheme 7) [54].

The active species in these MMA polymerization by zirconocene systems had been suggested to be metal enolates, therefore chiral *ansa*-zirconocene ester enolates were isolated to reveal the polymerization mechanism [55]. The chiral *ansa*-zirconocene diamide complex ***rac*-13** can be derived to a ester enolate complex, *rac*-$(C_2H_4)(Ind)_2ZrMe\{OC(OPr^i)=CMe_2\}$ (**57**). The complex **57** reacts with $B(C_6F_5)_3$ in THF to give a cationic complex $[rac$-$(C_2H_4)(Ind)_2Zr(THF)\{OC(OPr^i)=CMe_2\}][MeB(C_6F_5)_3]$ (**58**) as expected, while the reaction of **57** with $Al(C_6F_5)_3$ yields a tight ion pair *rac*-$(C_2H_4)(Ind)_2Zr^+MeOCPr^iOAl^-(C_6F_5)_3$ (**59**) with liberating propylene (Scheme 8). Both the **57**/$B(C_6F_5)_3$ and **58** systems show high activity for the polymerization of MMA to afford highly isotactic PMMA with extremely narrow molecular weight distribution. In contrast, the ion pair **59** produces syndiotactic-rich PMMA.

Scheme 7

Scheme 8

Cationic chiral C_1-symmetric *ansa*-zirconocene methyl complexes such as [Me$_2$Si(C$_5$H$_4$)(3-R-C$_5$H$_3$)ZrMe][MeB(C$_6$F$_5$)$_3$] (R = H, Me, Cy, Pr^i, Bu^t) and butadiene derivatives show moderate activity for MMA polymerization . These two series of catalysts have substantial difference in stereoselectivity in MMA polymerization probably due to an influence of the respective counteranions [56].

The cationic complex **58** also achieved highly isospecific and controlled polymerization of *N,N*-dimethylacrylamide (DMAA) for the first time [57]. The polymerizations of DMAA by cationic methyl complexes [*rac*-(C$_2$H$_4$)(Ind)$_2$ZrMe][MeM(C$_6$F$_5$)$_3$] (M = B and Al) produce isotactic-rich poly(*N,N*-dimethylacrylamide) (PDMAA, *mm* = 93% and 61%, respectively). Both complexes yielded highly isotactic PDMAA (*mm* = 98%) in the presence of radical-inhibitor (galvinoxyl), but their molecular weight distributions are broad. The cationic ester enolate complex **58** selectively promotes coordination polymerization of DMAA even without radical-inhibitor to afford almost perfectly isotactic (*mm* > 99%) PDMAA with narrow molecular weight distribution (M_n = 92.7 kg/mol, M_w/M_n = 1.07) and high melting point (T_m = 306 °C).

Conclusions

Because of their commercial importance, chiral zirconocenes developed at first as catalyst precursors for the isospecific polymerization of α-olefins, especially of propylene. Now, research interests seem to be moving onto the polymerization of functionalized monomers. Highly stereoregular polymerization of many technologically important polar monomers still remains challenging. Because both enantioselective polymerization of hydrocarbon monomers and isospecific polymerization of polar monomers had been achieved, asymmetric polymerization of polar monomers by enantiopure chiral metallocene catalysts could also be possible. Thus, polymerization of polar monomers by chiral metallocenes seems to be promising.

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