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polymer papers

Stereochemical control in propylene polymerization with non-bridged metallocene dichloride/methylaluminoxane

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Propylene polymerization was carried out with non-bridged *bis*(substituted-cyclopentadienyl)zirconium dichloride ((RCp)$_2$ZrCl$_2$)/methylaluminoxane (MAO) and *bis*(substituted indenyl)zirconium dichloride ((RInd)$_2$ZrCl$_2$)/MAO catalyst at various polymerization temperature. In the case of (RCp)$_2$ZrCl$_2$, the pentad *meso* sequence ([mmmm]) increased with lowering polymerization temperature. The isotactic sequence of polypropylene increased with an increase of formula weight of substituents in the case of mono-alkyl substituted *bis*(cyclopentadienyl)zirconium dichloride. The number of methyl (Me) substituents in [(CH$_3$)$_n$–(C$_5$H$_{5-n}$)]$_2$ZrCl$_2$ effected the stereo control of polymerization of propylene, and one or two Me substitution resulted in higher isotacticity than the usage of non- or full substituted ligands. Lowering polymerization temperature gave higher isotacticity as observed in Cp$_2$TiCl$_2$. The (RInd)$_2$ZrCl$_2$ (R = non or 2-Me) showed minimum *meso* sequence ([mmmm]) at 0°C. Chain-end control was predominant for producing the isotactic portion. The stereoregulation energies were evaluated from the stereochemical dyad composition of the obtained polypropylenes by the Arrhenius plot of ln ([m]/[r]) *versus* 1/T (T = polymerization temperature (K)). © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: stereochemical control; propylene polymerization; non-bridged metallocene dichloride)

INTRODUCTION

Since the discovery of metallocene/MAO catalysts and their development by Kaminsky and Sinn[1], polymerization of olefins has been carried out from both scientific and industrial points of view. Ewen and Zambelli reported the mechanisms of stereochemical control in propylene polymerization with Cp$_2$TiPh$_2$ (Ph = phenyl) and isospecific polymerization following chain-end stereochemical control mechanisms at low polymerization temperatures[2,3]. Erker *et al.* synthesized various *bis*-cyclopentadienyl metallocenes substituted by steric-bulky group and investigated the isospecific polymerization of propylene at low polymerization temperature[4–14]. The steric distribution of obtained polypropylenes with *bis*(substituted cyclopentadienyl) metallocenes obeyed the Bernoullian statistical model and the isotactic sequence was derived from chain-end stereochemical control. Waymouth *et al.* developed a theory that ligand rotation occurs during propylene polymerization with (2-Ph Ind)$_2$ZrCl$_2$ to give stereoblock polypropylene[15,16]. They applied the two-site model (Bernoullian and enantiomorphic-site control model) analysis for the resulting polypropylene. Much effort has been expended in the development of elastomeric polypropene with non-bridged metallocenes for both mechanism and material interests[17–21].

Resconi *et al.* reported on the effect of polymerization temperature on syndiospecific chain-end control in 1-butene polymerization with some metallocene catalysts, and discussed the effect of ligand on stereochemical control[22]. Such a ligand effect was not observed in case of propylene polymerization, because the change of microstructure was expected to be very small.

In this paper, we have studied the effect of polymerization temperature, substitution of the ligand and identity of metals of non-bridged metallocenes (and a bridged metallocene for reference) on microstructure of polypropylene, and considered its stereoregulation energies.

EXPERIMENTAL

Materials

All metallocene were purchased from Witco Co. and Nippon Fine Chemical Co., and used without further purification. The list of metallocenes is shown in *Scheme 1*. MAO was commercially obtained from Tosoh Akzo Co, Ltd. and used without further purification.

Polymerization of propylene

Polymerization of propylene was carried out in a 1-litre autoclave and 280 g of liquid propylene was introduced to the autoclave. Toluene (10 ml), MAO and catalyst were mixed in a 100-ml glass flask at 25°C for 5 min in advance. The Al/M (M = Ti, Zr, Hf) molar ratio was adjusted to 1000. Polymerization was started by adding the catalyst solution to the autoclave. Temperature was kept at a fixed temperature during the polymerization. Polymerization was terminated by adding isobutyl alcohol. The obtained polymer was precipitated in excess methanol and dried under vacuum at 60°C for 6 h.
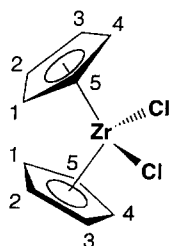
Analytical procedures

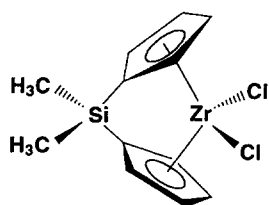^{13}C n.m.r. spectra were recorded at 135°C on a JEOL EX-270 NMR spectrometer operating at 67.8 MHz.
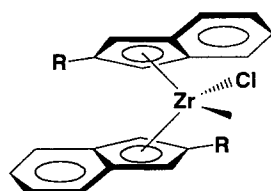
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*To whom correspondence should be addressed
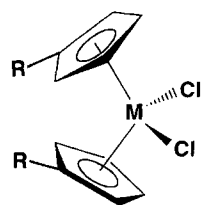
1: M = Zr, R = H
2: M = Zr, R = methyl
3: M = Zr, R = *n*-butyl
4: M = Zr, R = *i*-butyl
5: M = Zr, R = cyclopentyl
6: M = Zr, R = benzyl
10: M = Ti, R = H
11: M = Hf, R = H

7: 1,2-dimethyl
8: 1,3-dimethyl
9: pentamethyl

12:

13: R = H
14: R = methyl

Scheme 1

Polymers were dissolved in *o*-dichlorobenzene/benzene-d$_6$ (vol. ratio = 9/1) up to 5 wt%. Pentad assignment was determined according to the previous research[23-26]. Molecular weight and molecular weight distribution of the polymers were measured at 145°C by means of gel-permeation chromatography (Waters 150CV) using *o*-dichlorobenzene as solvent, calibrating with standard polystyrene samples. Weight-average molecular weight (M_w) was determined by the following equation: M_w = $A w \cdot Q$ (A_w and Q are, respectively, weight-average molecular size (Å) and Q-factor (26.4 for polypropene))[27].

RESULTS AND DISCUSSION

Propylene polymerization with (RC$_5$H$_4$)$_2$ZrCl$_2$

Propylene polymerizations with *bis*(mono-alkyl substituted cyclopentadienyl)zirconium dichloride ((RC$_5$H$_4$)$_2$ZrCl$_2$) (2-6)/MAO were carried out at 40, 0 and − 20°C in liquid propylene and the results are summarized in *Table 1* (containing *Scheme 1*). Microstructures of the resulting polypropylenes are shown in *Table 2*. In all catalysts, [mmmm] value increased with lowering of the polymerization temperature, even in the case of non-substituted Cp$_2$ZrCl$_2$. The [mmmm] value increased in the order R: benzyl > *i*-butyl > *n*-butyl > methyl > cyclopentyl > H. It is likely that higher [mmmm] value observed for *i*-butyl substituted complex as compared with

n-butyl substituted complex may originate from the steric difference existing between *i*-butyl and *n*-butyl group. Judging from the triad sequence, chain-end control is predominant for producing the isotactic portion (2[rr]/[mr] = 1 for site control and 4[mm][rr]/[mr]^2 = 1 for chain-end control)[2].

Propylene polymerization with [((CH$_3$)$_n$-C$_5$H$_{5-n}$)]$_2$ZrCl$_2$

Propylene polymerizations with *bis*(methyl substituted cyclopentadienyl)zirconium dichloride ([(CH$_3$)$_n$-(C$_5$H$_{5-n}$)]$_2$ZrCl$_2$) (7-9)/MAO were conducted and the results are shown in *Table 1*. Generally, the molecular weight of polymer increases with lowering the polymerization temperature due to significant decrease of chain transfer rate. However, the lower molecular weight polypropylenes were obtained at − 20°C rather than at 0°C for 1,3-Me$_2$ (8) and Me$_5$ (9) substituted zirconocenes. This tendency could be explained by the more effective decrease of propagation rate at −20°C. The microstructures of obtained polypropylenes are shown in *Table 2*. The content of [mmmm] increased with Me substitution in the order n: 2(1,2) > 2(1,3) > 1 > 0 > 5. The position of two methyl groups (1,2- or 1,3-) does not greatly effect the stereo sequence of the polymer. Metallocenes with non- or full substituted cyclopentadienyl ligand (n = 0, 5) produced lower isotactic polypropylenes than the complexes with one or two Me substituted ligands. Especially, [(CH$_3$)$_5$-C$_5$]$_2$ZrCl$_2$ produced syndiotactic-rich polypropylene. This result is the same as the result of 1-butene polymerization[22].

Comparison of polypropylenes obtained with Cp$_2$MCL$_2$ (M = Ti, Hf) and Me$_2$SiCp$_2$ZrCl$_2$

Results of propylene polymerization with Cp$_2$MCl$_2$ (M = Ti (10), Hf (11)), and their microstructures are shown in *Tables 3* and *4*, respectively. The [mmmm] value varies depending on the polymerization temperature. In the case of titanocene, fitting the triad tests resulted in changes from site-control to chain end control with lowering of the polymerization temperature (T_p), 2[rr]/[mr] = 1.11 at T_p = 40°C and 4[mm][rr]/[mr]^2 = 0.97 and 1.09 at T_p = 0 and −20°C, respectively. At any polymerization temperature, the hafnocene series gave higher isotacticity than the zirconocene series. The comparison of polypropylenes with dimethylsilylene-bridged zirconocene (Me$_2$SiCp$_2$ZrCl$_2$) (12) and Cp$_2$ZrCl$_2$ was investigated (*Tables 3 and 4*). In the case of Me$_2$SiCp$_2$ZrCl$_2$, by lowering the polymerization temperature the extent of [mmmm] value was lower than that observed for Cp$_2$ZrCl$_2$. These differences may be derived from the difference of mobility between ligands (non-bridged or bridged). Furthermore, triad tests of polypropylene obtained with Me$_2$SiCp$_2$ZrCl$_2$, if anything, conform to the enantiomorphic site control.

Propylene polymerization with (RIND)$_2$ZrCl$_2$

Propylene polymerizations with non-bridged *bis*(indenyl) and *bis*(2-methyl indenyl)zirconium dichloride ((Ind)$_2$ZrCl$_2$ (13) and (2-Me Ind)$_2$ZrCl$_2$ (14)) were carried out at 40, 0 and −20°C in liquid propylene and the polymerization results and microstructure of obtained polymers are summarized in *Tables 3 and 4*, respectively. These (RInd)$_2$ZrCl$_2$ (R = non, 2-Me) produced higher molecular-weight polypropylenes than the (RCp)$_2$ZrCl$_2$ catalyst, especially (2-Me Ind)$_2$ZrCl$_2$. The same tendencies were observed in the case of *ansa*-metallocene[29]. (RInd)$_2$ZrCl$_2$ showed a different effect with polymerization temperature

Table 1 Results of propylene polymerization with $(RCp)_2ZrCl_2^a$

Run no.	Cat.[a]	μmol	$T_p\,^\circ C$[b]	t[c] h	Yield in g	Activity kg PP/mol Zr·h	$M_n \cdot 10^{-4}$	M_W/M_n
1	**1**	11.6	40	1.0	75.8	6500	0.20	2.1
2		11.6	0	2.0	5.8	250	0.36	2.9
3		17.2	−20	4.0	31.8	460	3.41	2.0
4	**2**	10.3	40	1.0	105	10200	0.30	2.1
5		11.9	0	2.0	48.5	2000	2.82	2.1
6		14.1	−20	4.0	6.0	110	1.93	2.1
7	**3**	7.7	40	1.0	41.6	5400	0.35	2.2
8		8.7	0	2.0	14.7	850	1.88	2.2
9		8.9	−20	4.0	5.9	170	3.70	2.0
10	**4**	6.2	40	1.0	26.3	4300	0.47	3.4
11		7.4	0	2.0	14.1	980	2.59	2.0
12		13.1	−20	3.0	8.2	1800	4.75	1.9
13	**5**	7.0	40	1.0	73.6	10500	0.49	2.1
14		3.7	0	2.0	18.7	2500	2.96	2.1
15		14.3	−20	4.0	89.7	1600	16.2	1.9
16	**6**	4.9	40	1.0	20.2	4100	0.31	2.3
17		5.5	0	2.0	28.2	2600	3.17	2.4
18		13.6	−20	4.0	11.3	210	4.46	2.7
19	**7**	6.6	40	1.0	60.5	9200	1.13	2.1
20		8.7	0	2.0	2.6	150	2.55	2.4
21		12.1	−20	4.0	9.3	190	16.2	1.9
22	**8**	5.5	40	1.0	110	19900	1.98	2.0
23		9.7	0	2.0	22.1	1100	6.78	1.9
24		11.8	−20	3.0	1.6	45	5.04	1.9
25	**9**	9.0	40	1.0	48.4	5400		
26		12.3	0	1.0	22.5	1800	0.46	2.5
27		12.3	−20	2.0	0.9	37	0.34	2.2

Conditions: 1 L autoclave, liquid propylene = 280 g, (MAO)Al/Metal = 1000 (mol/mol)

[a] See *Scheme 1*

[b] Polymerization temperature

[c] Polymerization time

on [mmmm] value as compared with $(RCp)_2ZrCl_2$, and the minimum [mmmm] value was observed at $T_p = 0°C$. Triad *meso* sequence ([mm]) and dyad *meso* sequence ([m]) increased with lowering polymerization temperature. According to a previous report[15], $(2\text{-Ph Ind})_2ZrCl_2$ produced isotactic–atactic stereoblock polypropylene, and an increase of [mmmm] value was observed with a decrease in polymerization temperature. The proposed mechanism is that the rotation of ligands result in equilibrium of *rac-meso* conformation, which leads to isotactic and atactic sequences, respectively. In the case of $(RInd)_2ZrCl_2$ (R = H, 2-Me), triad tests of polypropylenes fit to the chain-end control, and one can conclude that the isospecific polymerization mechanism is different from that of $(2\text{-Ph Ind})_2ZrCl_2$. The substituent of 2-position in the indenyl ligand is essential in determining the stereochemistry of polymers.

Stereoregulation energy in propylene polymerization

Stereoregulation energies were determined on the basis of an Arrhenius plot according to the equation

$$[m]/[r] = P_m/P_r$$

$$\ln([m]/[r]) = \ln a_m/a_r + (E_r - E_m)/RT$$

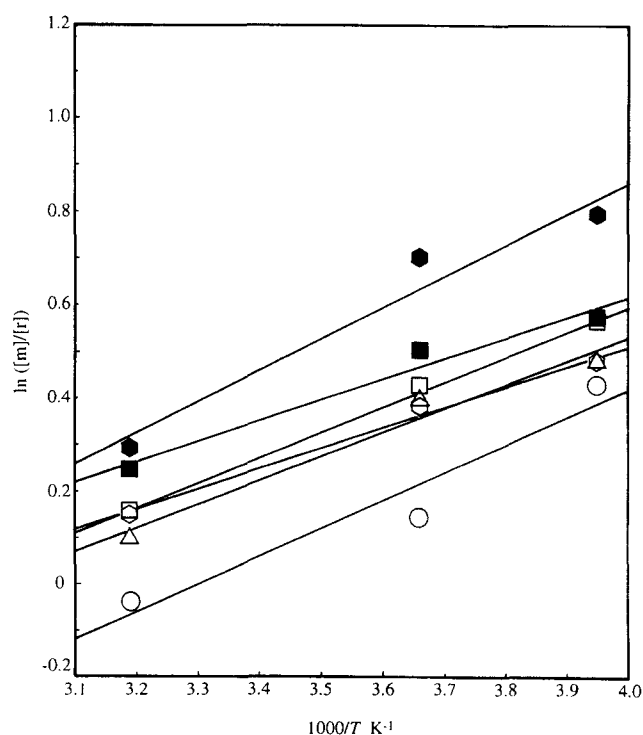where P_m and P_r are the probability of isotactic and

Figure 1 Arrhenius plots of $\ln([m]/[r])$ versus $1/T$ for polypropylene: (○) 1; (△) 2; (□) 3; (■) 4; (◯) 5; (●) 6

Table 2 Microstructure and statistical analysis of polypropylenes obtained with $(RCp)_2ZrCl_2^a$

Run no.	Cat.[a]	$T_p°C$[b]	[mmmm]%	[mm]%	[mr]%	[rr]%	[m]%	[r]%	Triad tests 2[rr]/[mr]	4[mm][rr]/[mr]²	E_r-E_m kcal/mol
1	1	40	5.1	23.3	51.5	25.2	49.1	50.9	0.98	0.86	
2		0	7.8	28.6	50.2	21.3	53.7	46.3	0.85	0.97	1.19
3		−20	10.2	34.9	51.5	13.6	60.7	39.3	0.53	0.72	
4	2	40	6.6	27.3	50.4	22.2	52.5	47.5	0.88	0.95	
5		0	10.6	35.3	49.1	15.6	59.9	40.1	0.64	0.91	1.03
6		−20	12.6	37.0	49.7	13.2	61.9	38.1	0.53	0.79	
7	3	40	7.9	28.9	50.2	20.8	54.0	46.0	0.83	0.95	
8		0	11.3	35.8	49.5	14.7	60.6	39.4	0.59	0.86	1.07
9		−20	14.0	39.7	48.2	12.3	63.8	36.2	0.51	0.84	
10	4	40	9.3	30.8	50.7	18.6	56.2	43.8	0.73	0.89	
11		0	13.2	37.7	49.3	13.1	62.4	37.6	0.53	0.81	0.89
12		−20	15.1	40.5	47.1	12.4	64.1	35.9	0.53	0.91	
13	5	40	7.1	27.8	52.0	20.2	53.8	46.2	0.78	0.83	
14		0	10.1	33.6	51.9	14.4	59.6	40.4	0.55	0.72	0.88
15		−20	11.5	36.0	51.7	12.3	61.9	38.1	0.48	0.66	
16	6	40	10.3	32.4	49.8	17.9	57.3	42.7	0.72	0.94	
17		0	19.4	43.9	46.0	10.0	66.9	33.1	0.43	0.83	1.35
18		−20	21.4	47.3	43.3	9.2	69.0	31.0	0.42	0.93	
19	7	40	9.0	30.7	49.9	19.4	55.7	44.3	0.78	0.96	
20		0	12.9	36.9	48.1	15.0	61.0	39.0	0.62	0.96	0.79
21		−20	14.1	39.5	46.5	14.0	62.8	37.2	0.60	1.02	
22	8	40	9.4	31.6	50.2	18.2	56.7	43.3	0.73	0.91	
23		0	12.2	37.0	49.9	13.2	62.0	38.0	0.53	0.78	0.76
24		−20	14.4	39.2	48.5	12.4	63.5	36.5	0.51	0.83	
25	9	40	2.0	13.7	47.0	39.2	37.2	62.8	1.67	0.97	
26		0	4.0	19.5	47.7	32.8	43.4	56.6	1.38	1.12	0.79
27		−20	4.3	20.3	47.7	32.0	44.2	55.8	1.34	1.14	

[a] See *Scheme 1*

Table 3 Results of propylene polymerization with Cp_2MCl_2 (M = Ti, Hf), $Me_2SiCp_2ZrCl_2$ and $(RInd)_2ZrCl_2$[a]

Run no.	Cat.[a]	μmol	$T_p°C$[b]	t[c] h	Yeild in g	Activity kg PP/ mol M·h	$M_W·10^{-4}$	M_W/M_n
28	10	13.3	40	1.0	2.9	220	0.95	2.4
29		16.1	0	2.0	12.4	390	2.85	2.3
30		18.9	-20	3.0	19.0	340	13.3	1.8
31	11	7.1	40	1.0	6.3	890	1.68	2.2
32		11.3	0	2.0	1.6	71	7.55	1.6
33		11.1	-20	2.0	0.6	29	8.50	1.4
34	12	7.2	40	1.0	20.1	2800	0.21	2.5
35		10.9	0	2.0	7.5	340	1.01	3.6
36		13.5	-20	4.0	9.1	170	4.12	5.1
37	13	6.6	40	1.0	35.5	5400	1.66	2.8
38		9.2	0	2.0	9.1	500	16.7	1.9
39		16.3	-20	4.0	20.2	310	49.6	2.1
40	14	7.2	40	1.0	13.0	1800	6.56	3.6
41		8.1	0	2.0	74.4	4600	99.3	2.1
42		9.8	-20	1.5	42.5	2900	409	2.1

Conditions: 1 L autoclave, liquid propylene = 280 g, (MAO)Al/Metal = 1000 (mol/mol)
[a] See *Scheme 1*
[b] Polymerization temperature
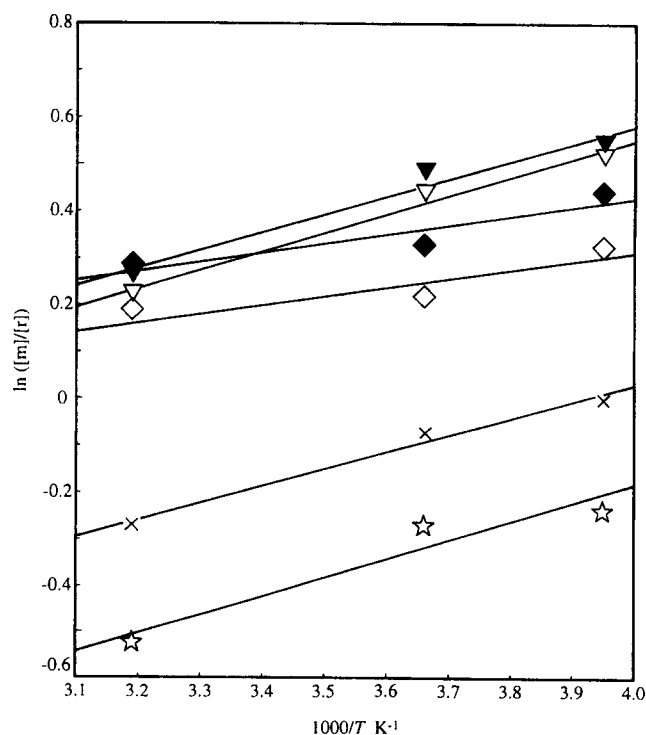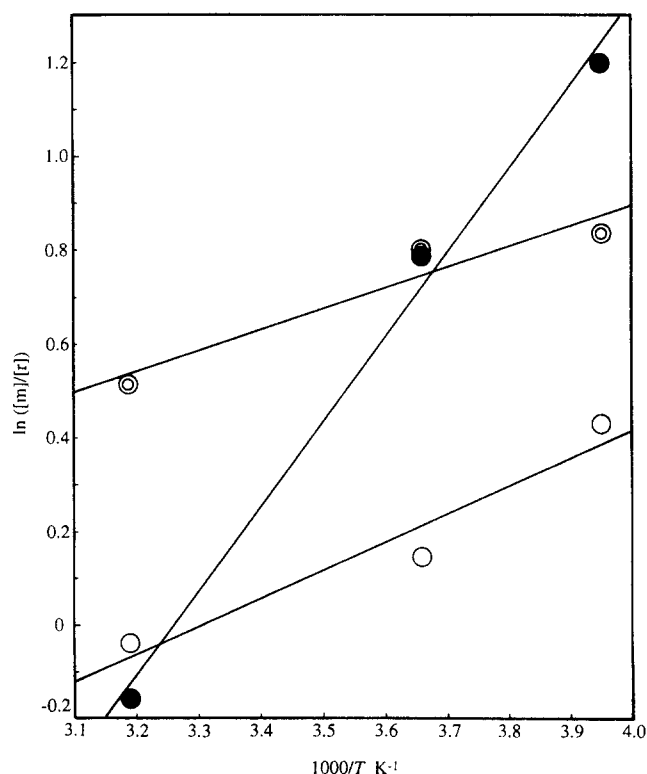[c] Polymerization time

Table 4 Microstructure and statistical analysis of polypropylenes obtained with Cp_2MCl_2 (M = Ti, Hf) $Me_2SiCp_2ZrCl_2$ and $(RInd)_2ZrCl_2$ [a]

Run no.	Cat.[a]	$T_p°C$[b]	[mmmm] %	[mm] %	[mr] %	[rr] %	[m] %	[r] %	2[rr]/[mr]	4[mm][rr]/[mr]²	E_r-E_m kcal/mol
28	**10**	40	3.9	20.6	51.0	28.3	46.1	53.9	1.11	0.22	
29		0	21.4	47.0	43.4	9.7	68.7	31.3	0.45	0.97	3.60
30		−20	34.4	59.4	35.0	5.6	76.9	23.1	0.32	1.09	
31	**11**	40	13.0	38.5	48.3	13.1	62.7	37.3	0.54	0.86	
32		0	19.3	46.3	45.5	8.2	69.1	30.9	0.36	0.72	0.87
33		−20	20.8	47.6	44.4	8.1	69.8	30.2	0.36	0.78	
34	**12**	40	4.0	18.6	49.4	32.0	43.4	56.6	1.30	0.98	
35		0	5.3	22.5	51.5	26.1	48.3	51.7	1.01	0.86	0.72
36		−20	5.9	24.3	51.4	24.3	50.0	50.0	0.95	0.89	
37	**13**	40	9.0	30.3	49.0	20.8	54.8	45.2	0.85	1.05	
38		0	8.4	30.5	50.0	19.5	55.5	44.5	0.78	0.95	0.33
39		−20	10.7	33.7	48.8	17.5	58.1	41.9	0.72	0.99	
40	**14**	40	11.2	33.1	48.1	18.8	57.2	42.8	0.78	1.08	
41		0	8.5	35.6	45.1	19.4	58.2	41.8	0.86	1.36	0.38
42		−20	14.4	37.8	46.2	15.8	60.9	39.1	0.68	1.12	

[a] See *Scheme 1*
[b] Polymerization temperature

syndiotactic placement, a_m and a_r are the Arrhenius pre-exponential coefficients, and E_m and E_r are the activation energies for the formation of isotactic and syndiotactic dyads in propagation process[10,22,28]. Arrhenius plot and stereoregulation energies are shown in *Figures 1–3* and *Tables 2 and 4*, respectively. In the case of $(RC_5H_4)_2ZrCl_2$, the value of $E_r - E_m$ decreases in the order R: benzyl > H > n-butyl > methyl > i-butyl > cyclopentyl. This order is not consistent with the order of [mmmm] values. In the case of $[(CH_3)_n-(C_5H_{5-n})]ZrCl_2$, the value of $E_r - E_m$ is smaller than non-substituted Cp (n = 0). Further more, existence of

a bridge (Me_2Si) decreased the value of $E_r - E_m$. The effect of metal in Cp_2MCl_2 (M = Ti, Zr, Hf) was observed and Cp_2TiCl_2 showed the highest value of $E_r - E_m = 3.60$ kcal/mol. In the case of $(RInd)_2ZrCl_2$ (R = non, 2-Me), the value of $E_r - E_m$ was smaller than *bis*-cyclopentadienyl metallocenes ($E_r - E_m = 0.3–0.4$ kcal/mol). The clear relationship between the value of $E_r - E_m$ and ligand structure did not account for the difference in stereoregulation energies.

Figure 2 Arrhenius plots of $\ln([m]/[r])$ versus $1/T$ for polyporpylene: (▽) 7; (▼) 8; (☆) 9; (×) 12; (◇) 13; (◆) 14

Figure 3 Arrhenius plots of $\ln([m]/[r])$ versus $1/T$ for polyporpylene with C_pMCl_2: M = (●) Ti 10; (○) Zr 1; (◎) Hf 11

CONCLUSION

Stereochemical control in propylene polymerization with non-bridged metallocene dichloride was studied. In the case of $(RC_5H_4)_2ZrCl_2$, the isotactic portion of resulting polypropylenes increased with an increase in formula weight of the substituents, except for the cyclopentyl substituent. The one or two methyl substituted zirconocenes in $[(CH_3)_n-(C_5H_{5-n})]_2ZrCl_2$ produced a higher isotactic portion than non-or all substituted catalysts. No difference was observed between 1,2-dimethyl and 1,3-dimethyl substituted metallocene on the stereochemistry of the resulting polypropylene. The marked increase of the isotactic sequence by lowering the polymerization temperature was observed for Cp_2TiCl_2. For $(RInd)_2ZrCl_2$, the *meso* dyad [m] increased with the decrease in polymerization temperature, while the minimum [mmmm] value was observed at the polymerization temperature of 0°C. The stereoregulation energies were evaluated from the stereochemical dyad composition by Arrhenius plot. No melting temperature of the resulting polypropylene was detected because of lower isotactic portion. These polypropylenes were elastomeric materials (high-molecular weight) or oily products (low-molecular weight).

Further studies are necessary to discuss the effect of polymerization temperature and ligands on the polymerization mechanism with non-bridged metallocene species.

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