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New half-sandwich metallocene catalysts for polyethylene and polystyrene

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Abstract

A new type of half-sandwich metallocene catalysts for the polymerization of ethylene and styrene, $Cp*MCl(DEA–R)$ $(DEA = (OCH_2CH_2)_2N$, $R = Me$, $M = Ti$ (**1**); $R = Me$, $M = Zr$ (**2**); $R = n$-Bu, $M = Ti$ (**3**)), was prepared by the reaction of corresponding N-alkyl-N,N-diethanolamine with $Cp*MCl_3$ in the presence of triethylamine. Compounds **1**–**3** are slightly air-sensitive and thermally unstable. All catalyst systems show moderate activities in ethylene polymerization and especially the **2**/MMAO system gives PE with broad molecular weight distribution at all polymerization temperatures. In addition, **1**/MMAO and **3**/MMAO show fairly good activities in sPS polymerization in the order **3**/MMAO > **1**/MMAO. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Olefin polymerization by homogeneous catalysis has been one of the most attractive subjects in the field of both organometallic chemistry and catalysis. There are many reports concerning this topic using metallocene compounds [1]. However, there are only few reports for the polymerization by non-bridged $CpTi(L)_nX_{n-3}$ complexes, which contain both one Cp ligand and one monodentate, bidentate, tridentate or tetradentate ligand, though the syntheses of these complexes were known several decades ago.

Recently, Nomura et al. [2] reported that $Cp-Ti(OAr)X_2$ (OAr = monodentate phenoxide ligand) complexes showed remarkable catalytic activities for ethylene and α-olefin polymerization in the presence of MAO or Al^iBu_3–$Ph_3CB(C_6F_5)_4$. They demonstrated that catalyst modification by changing the nature of spectator ligand could afford a new strategy for ethyl-

ene polymerization. In 1999, Stephan et al. [3] also showed that $Cp'TiCl_2(NPR_3)$ (NPR_3 = monodentate phospinimide ligand) complexes could act as highly active catalysts for ethylene polymerization. They insisted that phospinimide ligands could be sterically equivalent to cyclopentadienyl ligands. In 1998, Doherty et al. [4] developed the mixed-ligand complexes of the type $CpTi(NC_5H_4(CR_2O))Cl_2$ $(NC_5H_4(CR_2O) =$ bidentate pyridylalkoxide ligand) and $CpTi(ONO)Cl_2$ (ONO = tridentate N-alkoxy-β-ketoiminate ligand) as ethylene polymerization catalysts. They found that these systems, in the presence of MAO, catalyzed the polymerization of ethylene, generating high molecular weight polymers with narrow molecular weight distributions. In addition, Okuda et al. [5] reported that $Cp*TiCl(OSO)$ (OSO = tridentate sulfide-linked bis(phenol) ligand) complexes were used as catalysts for sPS and PE. The complexes could effectively polymerize ethylene, styrene and dienes as well as copolymerize ethylene with styrene. Furthermore, we [6] also reported that $Cp*Ti(TEA)$ (TEA = tetradentate tri-ethanolateamine ligand) showed very efficient catalytic behavior in the formation of syndiotactic polystyrene (sPS) [7] in the presence of MMAO as cocatalyst. We found that the introduction of an electron-rich tetra-

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dentate ligand could electronically modify the catalytic active site for sPS.

In this regard, we synthesized a new catalytic system containing one Cp* and one tridentate ligand. Reported herein, are the syntheses of Cp*MCl(DEA–Me) (M = Ti and Zr) and Cp*TiCl(DEA–Bu) as well as their efficient catalytic behavior in the formation of sPS and PE in the presence of MMAO as cocatalyst.

2. Experimental

2.1. General procedure

All reactions were carried out under an argon atmosphere using standard Schlenk and glove box techniques [8]. Argon was deoxygenated with activated Cu catalyst (regenerated by heating to 300 °C under H_2 gas) and dried with drierite (Aldrich). All solvents were dried under a nitrogen atmosphere and distilled from sodium–potassium alloy/benzophenone ketyl (toluene) or CaH_2 (methylene chloride) and stored over activated molecular sieves (3A) [9]. $CDCl_3$ was obtained from Aldrich and dried over activated molecular sieves (4A), and used after vacuum transfer to a Schlenk tube equipped with J. Young valve.

2.2. Measurements

^{1}H- and ^{13}C{^{1}H}-FT-NMR spectra were recorded using a Bruker AM 300 spectrometer. The chemical shifts are referenced to the residual peaks of the $CDCl_3$ (7.24 ppm in ^{1}H-NMR, 77.0 ppm in ^{13}C{^{1}H}-NMR). Electron impact mass spectra were obtained with a VG Auto Spectrometer. Elemental analyses were performed by the Korea Basic Science Center, Seoul, Korea. The thermal properties of the polymers were investigated by Thermal Analyst 200 DSC system under nitrogen atmosphere at a heating rate of 10 °C min^{-1} for polyethylene and of 20 °C min^{-1} for polystyrene. Molecular weights of polymers were determined at 140 °C in 1,2,4-trichlorobenzene by PL 220 + 220R GPC calibrated with standard polystyrenes.

2.3. Synthesis

All chemicals were purchased from Aldrich. Cp*MCl$_3$ [10] was synthesized by literature procedure. MMAO was purchased in Akzo (MMAO-3A type, Al content = 5.9 wt%, d = 0.89 g ml^{-1}, solvent = toluene).

2.3.1. Cp*TiCl((OCH$_2$CH$_2$)$_2$NMe) (1)

A reddish solution of Cp*TiCl$_3$ (1.45 g, 5.0 mmol) in 40 ml CH_2Cl_2 was added dropwise to a solution of N-methyldiethanolamine (0.596 g, 5.0 mmol) and triethylamine (2.1 ml, 15 mmol) in 40 ml CH_2Cl_2 at

−78 °C. The reaction mixture was allowed to warm to room temperature (r.t.) and stirred for 12 h before filtration. The residue, obtained by removing the solvent under vacuum, was redissolved in toluene and the resulting mixture was filtered through a Celite bed. The removal of solvent from the yellow filtrate gave the desired product 1 in 75% yield (1.26 g).

^{1}H-NMR (CDCl$_3$, 300.13 MHz): $\delta = 4.51$–4.32 (m, 4H, OCH$_2$), 2.85–2.71 (m, 4H, NCH$_2$), 2.54 (s, 3H, NCH$_3$), 1.94 (s, 15H, C$_5$(CH$_3$)$_5$). ^{13}C{^{1}H}-NMR (CDCl$_3$, 75.1 MHz): $\delta = 126.3$ (C$_5$(CH$_3$)$_5$), 73.28 (OCH$_2$), 57.99 (NCH$_2$), 45.30 (NCH$_3$), 11.86 (C$_5$(CH$_3$)$_5$). EIMS; m/z (relative intensity): 335 ([M$^+$], 13), 305 ([M$^+$ − CH$_2$O], 100), 275 ([M$^+$ − 2CH$_2$O], 24), 218 ([M$^+$ − CH$_3$N(CH$_2$CH$_2$O)$_2$], 40), 200 ([M$^+$ − Cp*], 9). Anal. Found: C, 54.01; H, 8.00; N, 4.32. Calc. for (C$_{15}$H$_{26}$ClNO$_2$Ti)$_n$ ((335.7)$_n$): C, 53.67; H, 7.81; N, 4.17%.

2.3.2. Cp*ZrCl((OCH$_2$CH$_2$)$_2$NMe) (2)

A yellow solid 2 was prepared in a yield of 70% (1.33 g) by reacting Cp*ZrCl$_3$ (1.66 g, 5.0 mmol) with N-methyldiethanolamine (0.75 g, 5.0 mmol) and triethylamine (2.1 ml, 15 mmol) in a manner analogous to the procedure for 1.

^{1}H-NMR (CDCl$_3$, 300.13 MHz): $\delta = 4.30$–4.19 (m, 4H, OCH$_2$), 2.93–2.85 (m, 2H, NCH$_2$), 2.75–2.67 (m, 2H, NCH$_2$), 2.61 (s, 3H, NCH$_3$), 1.92 (s, 15H, C$_5$(CH$_3$)$_5$). ^{13}C{^{1}H}-NMR (CDCl$_3$, 75.1 MHz): $\delta = 121.0$ (C$_5$(CH$_3$)$_5$), 67.59 (OCH$_2$), 58.76 (NCH$_2$), 45.43 (NCH$_3$), 10.88 (C$_5$(CH$_3$)$_5$). Anal. Found: C, 48.31; H, 7.11; N, 4.01. Calc. for (C$_{15}$H$_{26}$ClNO$_2$Zr)$_n$ (MW (379.0)$_n$): C, 47.53; H, 6.91; N, 3.70%.

2.3.3. Cp*TiCl((OCH$_2$CH$_2$)$_2$NBu) (3)

A yellow solid 3 was prepared in a yield of 76% (1.44 g) by reacting Cp*TiCl$_3$ (1.45 g, 5.0 mmol) with N-butyldiethanolamine (0.81 g, 5.0 mmol) and triethylamine (2.1 ml, 15 mmol) in a manner analogous to the procedure for 1.

^{1}H-NMR (CDCl$_3$, 300.13 MHz): $\delta = 4.44$–4.29 (m, 4H, OCH$_2$), 2.87–2.70 (m, 6H, NCH$_2$CH$_2$O and NCH$_2$CH$_2$CH$_2$CH$_3$), 1.98 (s, 15H, C$_5$(CH$_3$)$_5$), 1.41 (m, 2H, NCH$_2$CH$_2$CH$_2$CH$_3$), 1.27 (m, 2H, NCH$_2$-CH$_2$CH$_2$CH$_3$), 0.895 (t, 3H, $^3J_{HH}$ = 7.2 Hz, NCH$_2$-CH$_2$CH$_2$CH$_3$). ^{13}C{^{1}H}-NMR (CDCl$_3$, 75.1 MHz): $\delta = 126.0$ (C$_5$(CH$_3$)$_5$), 74.66 (OCH$_2$), 54.37 (NCH$_2$-CH$_2$CH$_2$CH$_3$), 53.98 (NCH$_2$CH$_2$O), 25.99 (NCH$_2$CH$_2$-CH$_2$CH$_3$), 20.80 (NCH$_2$CH$_2$CH$_2$CH$_3$), 14.10 (NCH$_2$-CH$_2$CH$_2$CH$_3$), 11.86 (C$_5$(CH$_3$)$_5$). EIMS; m/z (relative intensity): 377 ([M$^+$], 50), 342 ([M$^+$ − CH$_2$O], 100), 312 ([M$^+$ − 2CH$_2$O], 44), 242 ([M$^+$ − Cp*], 40). Anal. Found: C, 58.10; H, 8.70; N, 3.92. Calc. for (C$_{18}$H$_{32}$ClNO$_2$Ti)$_n$ (MW 377.8)$_n$): C, 57.23; H, 8.54; N, 3.71%.

2.4. Polymerization procedure

Ethylene polymerizations were carried out in 250 ml Schlenk flasks with magnetic stirring. Polymerizations were carried out as follows: toluene and MMAO were injected into 250 ml Schlenk flasks with magnetic stirring in that order at the desired temperatures of 30, 50, and 70 °C. The solution was then saturated with 1 atm of ethylene. Polymerization begins with the addition of toluene solution of the metal compound into the 250 ml Schlenk flask. After the desired reaction time was reached, polymerizations were terminated by venting the ethylene gas and quenching with a small volume of MeOH. The polymers were isolated by filtration, washed with MeOH, a solution of 4 M HCl in MeOH and MeOH in that order, and then dried in vacuo.

Styrene polymerizations were carried out in 250 ml Schlenk flasks with magnetic stirring. Toluene, the polymerization solvent, was distilled from sodium–potassium alloy under argon atmosphere just before use. Styrene monomer was distilled from CaH_2 and stored in a refrigerator. Polymerizations were carried out as follows: toluene, styrene, MMAO, and the titanium compound were injected into a 250 ml Schlenk flask with magnetic stirring in that order at the desired temperatures of 30, 50, and 70 °C. After the desired reaction time was reached, the reaction was terminated by the addition of 50 ml MeOH followed by the addition of 50 ml of 10% HCl in MeOH. The resulting precipitated polymer was washed three times each with 500 ml of MeOH and dried in vacuo at 70 °C for 12 h. The polymer was extracted with refluxing 2-butanone for 12 h in order to determine the syndiotacticity of the polymer obtained.

3. Results and discussion

Compounds **1–3** were prepared by synthetic routes outlined in Scheme 1. The reaction of a solution of Cp^*MCl_3 in CH_2Cl_2 with $RN(CH_2CH_2OH)_2$ (R = Me or *n*-Bu) in the presence of triethylamine afforded crystalline solids $Cp^*MCl(DEA–R)$ (DEA = $(OCH_2-CH_2)_2N$) in a yield of 70–76%. Attempted use of di-

lithiated species instead of neutral alkyldiethanolamine in toluene was not successful and a mixture of the desired product with non-separable impurities was obtained, suggesting that mild reaction condition of HCl-elimination is essential and required for the synthesis of $Cp^*MCl(DEA–R)$. In addition, it is worth mentioning that a mixture of several unidentified compounds was obtained when the $(DEA–R)MCl_2$ was reacted with Cp^*TMS in toluene or CH_2Cl_2 as a solvent. They were purified by recrystallization from toluene–pentane. Like other half-sandwich metallocene compounds, yellow crystalline solids **1–3** are freely soluble in toluene and methylene chloride but insoluble in hydrocarbon solvents such as hexane and pentane. Moreover, they are slightly air-sensitive and thermally unstable.

Compounds **1–3** were characterized by various spectroscopic methods including NMR spectroscopy. The ^{1}H- and ^{13}C{^{1}H}-NMR spectra of **1–3** show the presence of only one pure compound. In comparison to the free alkyldiethanolamine precursors, all signals in the ^{1}H- and ^{13}C{^{1}H}-NMR spectra are shifted to downfield, which is a consequence of the high Lewis acidity of titanium metal. In the ^{1}H-NMR spectra, the extent of downfield shift is greater for OCH_2 resonances than for CH_2N resonances. The OCH_2 resonance in the ^{1}H-NMR shifted downfield by approximately 0.8 ppm versus the free ligand. A somewhat smaller downfield shift by 0.3 ppm was observed for the CH_2N resonance. The greater extent of downfield shifts of the OCH_2 NMR resonances than those of the NCH_2 resonances suggests a strong bond between the O and Ti atoms and a weak interaction between the N and the Ti atoms upon complexation. In the ^{1}H-NMR spectra, the methylene NCH_2 and OCH_2 protons are diastereotopic, giving ABXY spin systems (see Fig. 1). Indeed, Fig. 1 shows that NCH_2–OCH_2 couplings are observed. The NMR signals were sharp and variable—temperature studies showed no evidence of inter or intramolecular ligand exchange at ambient temperature. In the absence of X-ray structural determination of the compounds **1–3**, it is not possible to clarify whether **1–3** are monomeric, dimeric or polymeric species. However, we tentatively suggest that **1** and **3** should exist most likely
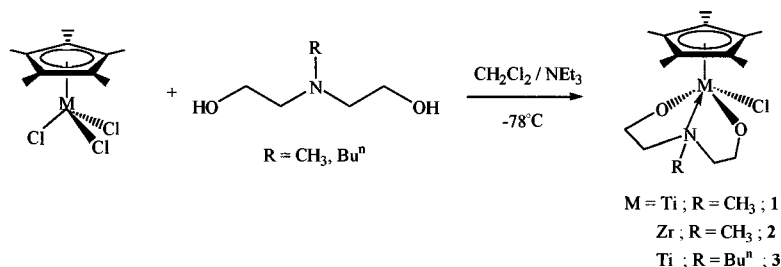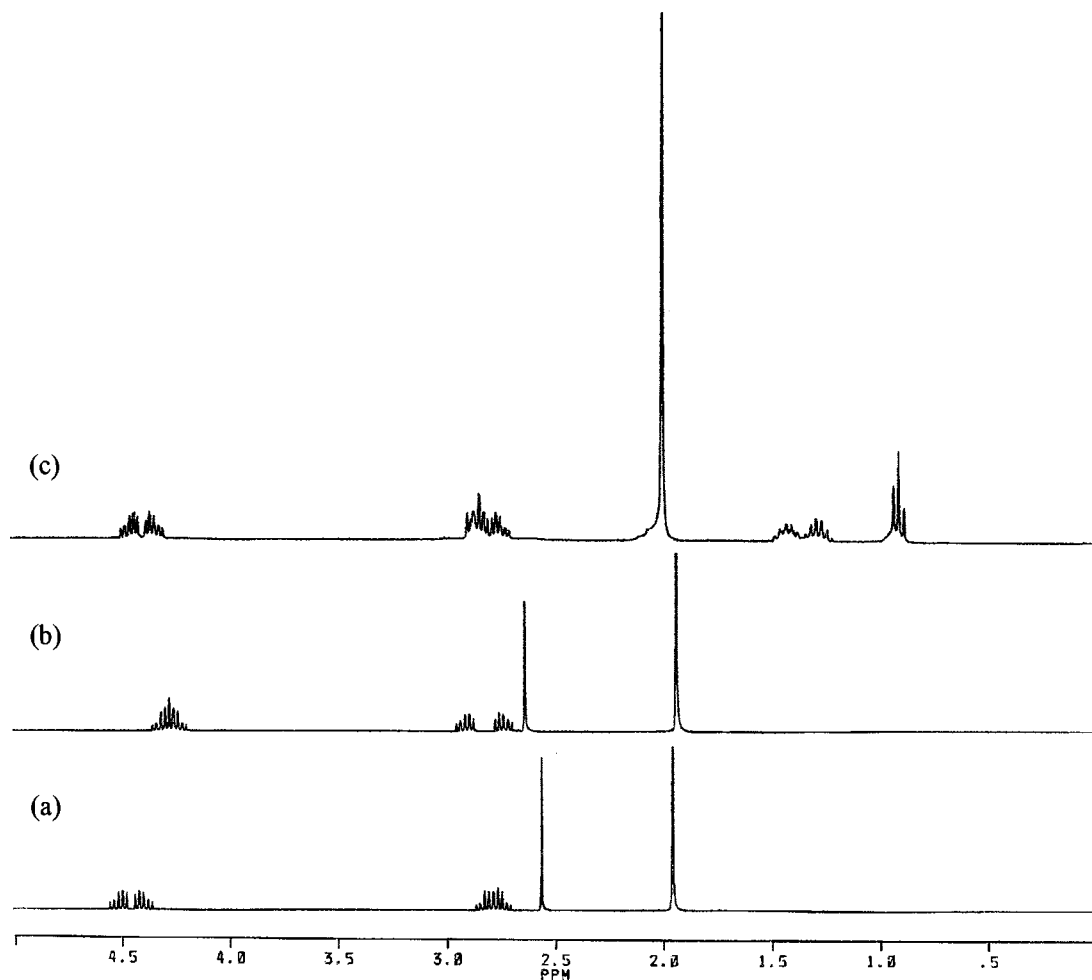

Scheme 1.

Fig. 1. (a) ^{1}H-NMR spectrum of **1**; (b) ^{1}H-NMR spectrum of **2**; (c) ^{1}H-NMR spectrum of **3**.

as monomeric species, because the NMR spectra of compounds **1** and **3** are sharp and they have some volatile nature and the EI mass spectra of the compounds exhibit molecular peaks for the corresponding complexes. The same observation has been made for Cp*Ti(TEA) and its derivatives, recently reported by us [6].

The newly synthesized catalyst precursors **1**–**3** are examined as catalysts for ethylene polymerization in the presence of MMAO. The polymerization results are summarized in Table 1 in terms of the activity of the catalyst, T_m, M_n, M_w, and M_w/M_n. To probe the nature of the polymerization reaction, we carried out polymerizations at various temperatures. In order to assess the significance of the quoted activity values, we also carried out the control polymerization experiment by using a Cp*ZrCl$_3$/MMAO system under the same polymerization condition. The polymerization data in Table 1 reveal that **1**–**3**/MMAO systems showed less catalytic activity than the Cp*ZrCl$_3$/MMAO system and **1**–**3**/MMAO systems gave the highest activity at 50, 70 and 50 °C, respectively. Among **1**–**3**/MMAO catalyst sys-

tems, the **1**/MMAO system is most efficient in producing PE in terms of activity and conversion at polymerization temperatures of below 50 °C. However, the **2**/MMAO system is most efficient in terms of molecular weight at all polymerization temperatures since the **1**–**3**/MMAO system yields M_ws in the range of 13 500–212 900, 78 400–350 700 and 13 200–185 000, respectively. NMR spectroscopy was used to analyze the polyethylene produced by the **1**–**3**/MMAO systems. NMR analysis of the polymers reveals highly linear polyethylene having virtually no branching [11]. In addition, the **2**/MMAO system is interesting in that PE with high T_m is consistently made at all polymerization temperatures. These data also suggest that the produced polymer should be high-density polyethylene. Especially, a broad molecular weight distribution was observed for the polymerization of ethylene using the **2**/MMAO system. We believe at this stage, that the tremendous increase in the PDI values is probably due to the increase in the degree of chain transfer reaction by AlMe$_3$, which excessively exists in the toluene solution of MMAO, though the produced polymers are

highly linear polyethylenes. In addition, Cp*ZrCl$_3$ and **1**–**3**/MMAO systems showed a lowering of T_m value with increasing T_p as in many homogeneous metallocene catalysts based on pentahapto ligands [12].

Polymerizations of styrene [7] with the **1**/MMAO and **3**/MMAO systems were performed in toluene at various conditions. In order to assess the significance of the quoted activity values, we also carried out the control polymerization experiment by using Cp*Ti(TEA)/MMAO and Cp*TiCl$_3$/MMAO systems under the same polymerization condition. The polymerization data, summarized in Table 2, reveal that the catalytic effi-

ciency in terms of activity decreases in the order Cp*Ti(TEA)/MMAO > Cp*TiCl$_3$/MMAO > **3**/MMAO > **1**/MMAO. In the **1**/MMAO and **3**/MMAO catalytic systems, **3**/MMAO is more efficient in producing highly syndiotactic polystyrene in terms of activity, conversion and molecular weight at all polymerization temperatures. Compared with sPS polymers produced by **3**/MMAO, those obtained by **1**/MMAO have higher syndiotacticity. The catalytic activity also increases until the polymerization temperature T_p increases up to 70 °C. The **1**/MMAO and **3**/MMAO systems afford polystyrenes with high stereospecificity of greater than

Table 1
Ethylene polymerization catalyzed by **1**–**3**/MMAO

Catalyst [a]	T_p (°C)	PE (g)	A [b]	T_m (°C) [c]	M_n [d]	M_w [d]	M_w/M_n [d]
	30	0.102	62.8	137.1	78 000	180 700	2.31
Cp*ZrCl$_3$	50	0.17	104.6	133.5	34 700	120 600	3.48
	70	0.265	163.1	132	13 600	64 300	4.7
	30	0.045	27.7	135.9	115 500	212 900	1.84
1	50	0.105	64.6	134.1	37 300	60 400	1.62
	70	0.038	23.4	128.6	3 800	13 500	3.55
	30	0.017	10.5	133.5	9 100	350 700	38.34
2	50	0.048	29.5	131.7	35 400	397 800	11.24
	70	0.071	43.7	131	3 300	78 400	23.44
	30	0.022	13.5	136	118 000	185 000	1.57
3	50	0.091	56	134.4	34 000	52 300	1.54
	70	0.035	21.5	129.8	5 700	13 200	2.32

[a] Polymerization condition: [M] = 9.75 µmol, Al/M = 1000, ethylene pressure = 1 atm, time = 10 min, 50 ml toluene, cocatalyst: modified methylaluminoxane (MMAO).
[b] Activity = kg PE (mol catalyst)$^{-1}$ × h^{-1} × atm^{-1}.
[c] Determined by DSC (heating rate: 10 °C min^{-1}).
[d] Determined by GPC.

Table 2
Polymerization of sPS catalyzed by **1**/MMAO and **3**/MMAO

Catalyst [a]	T_p (°C)	PS (g)	A [b] ($\times 10^{-7}$)	Conversion (%)	T_m [c]	SI [d] (%)	M_n [e]	M_w [e]	M_w/M_n [e]
	30	0.907	0.64	19.9	276.4	98.7	118 000	177 000	1.5
Cp*Ti(TEA)	50	3.36	2.37	73.8	274.6	98.4	115 000	253 000	2.2
	70	4.01	2.83	88.1	273.4	98.2	71 700	292 000	4.07
	30	0.88	0.62	19.3	274.6	97.7	136 000	231 000	1.7
Cp*TiCl$_3$	50	2.62	1.84	57.6	272.9	96	114 000	197 000	1.73
	70	3	2.12	65.9	272.7	95.4	87 000	182 300	2.09
	30	0.21	0.15	4.6	274	98.5	73 000	160 000	2.21
1	50	0.81	0.57	17.8	274.7	98.6	72 000	155 000	2.14
	70	1.71	1.21	37.7	273.8	97.9	62 000	119 000	1.92
	30	0.43	0.3	9.5	275.2	98.7	150 000	301 000	2.01
3	50	1.71	1.21	37.6	272.3	97.5	136 000	262 000	1.92
	70	2.32	1.64	51	274.5	97.7	82 000	151 000	1.83

[a] Polymerization condition: [styrene] = 0.436 M (5 ml); [Ti] = 0.195 mM; time = 10 min.
[b] Activity = g sPS (mol Ti)$^{-1}$ × (mol styrene)$^{-1}$ × h^{-1}.
[c] Determined by DSC (heating rate: 20 °C min^{-1}).
[d] SI = syndiotacticity (2-butanone insoluble portion whose tacticity was established by ^{13}C-NMR in 1,1,2,2-tetrachloroethane-d_2).
[e] Determined by GPC.

97.5% and a high T_m value of 272.3–275.2 °C over the entire T_p range studied. The molecular weights of the resulting polystyrenes from the **1**/MMAO and **3**/MMAO systems are in the range of $M_w = 119\,000$–$160\,000$ with $M_w/M_n = 1.92$–2.21 and $M_w = 151\,000$–$301\,000$ with $M_w/M_n = 1.83$–2.00, respectively. Abnormally, the **1**/MMAO and **3**/MMAO systems showed a lowering of polydispersity index values with increasing T_p. In this regard, two catalytic systems **1**/MMAO and **3**/MMAO are fairly good catalysts in sPS polymerization in the order **3**/MMAO > **1**/MMAO.

4. Conclusions

In this paper, we have demonstrated the synthetic significance of the catalytic system of Cp*MCl-(DEA–R) (DEA = $(OCH_2CH_2)_2N$, R = Me, M = Ti (**1**); R = Me, M = Zr (**2**); R = n-Bu, M = Ti (**3**)) in generating polyethylene with high molecular weight. Especially, the **2**/MMAO system could give polyethylene with broad molecular weight distribution at all polymerization temperatures. In addition, **1**/MMAO and **3**/MMAO also produce syndiospecific polystyrene with a high syndiotacticity index. Further studies on the copolymerization of styrene with ethylene and synthesis of other alkyldiethanolamine metal complexes are now in progress.

Acknowledgements

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