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ARTICLE

Extremely Active α -Olefin Polymerization and Copolymerization with Ethylene Catalyzed by dMAO-Activated Zirconium(IV) Dichloro Complex Having an [OSSO]-Type Ligand

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The ability of zirconium(IV) dichloro complex (**6b**) incorporating an [OSSO]-type ligand **5** with dMAO as an activator for the polymerization of 1-hexene and 4-methyl-1-pentene (4-MP) is described. In the polymerization of 1-hexene, the combination of **6b**/dMAO catalyst system efficiently provided poly(1-hexene)s with completely isotactic [*mmmm*] pentad more than 95% and relatively large molecular weight ($M_w = 40,000$ – $150,000$ g mol⁻¹). The corresponding activity was recorded with quite high values up to $18,100$ g mmol(**6b**)⁻¹ h⁻¹, which increased extremely compared with those of the related non-Cp complexes. The polymerization of 4-MP using the **6b**/dMAO system at different temperatures also gave perfect isotactic poly(4-MP)s ([*mmmm*] > 95%) with moderate molecular weight ($M_w = 7,000$ – $21,300$ g mol⁻¹), relatively narrow polydispersity ($M_w/M_n = 1.5$ – 1.7), and activities of $1,220$ – $1,690$ g mmol(**6b**)⁻¹ h⁻¹. This catalyst system was also found to promote ethylene copolymerization with different amounts of 1-hexene at 25 °C under atmospheric pressure producing random ethylene/1-hexene copolymers ($M_w = 10,100$ – $17,300$ g mol⁻¹, $M_w/M_n = 1.8$ – 1.9 , 1-hexene contents = 37.3–66.7 mol %) with fairly high activity up to $2,700$ g mmol(**6b**)⁻¹ h⁻¹.

Introduction

The conversion of α -olefins into polyolefins by effective transition metal catalysts is a field of research that receives continuous attention from groups in both academia and industry since the discovery of the Ziegler-Natta catalyst and the metallocene catalyst.¹ In particular, considerable attention has been paid to the development of Group 4 metal complexes supported by non-Cp (cyclopentadienide) ligands that perform highly stereocontrolled polymerization of α -olefin with high activity.² Among these systems, since a zirconium complex featuring an [ONNO]-type diamine bis(phenolate) Salan ligand has been reported by Kol et al. to promote the living polymerization of 1-hexene with high isospecificity at ambient temperature, several related studies on Group 4 metal complexes bearing mixed-donors based on [ONNO]-,³ [OSSO]-,⁴⁻⁸ [OOOO]-,⁹ and [ONSO]-type¹⁰ tetradentate ligands were published to date. As a pioneering work for sulfur-containing [OSSO]-type bis(phenolate) ligands, Okuda et al. have demonstrated that a methylaluminoxane (MAO)-activated titanium(IV) dichloro complex with 1,4-dithiabutanediyl linked [OSSO]-type ligand **1** could be used as a highly active pre-

catalyst for the isospecific polymerization of styrene.^{5a} In addition, they have described that optically active copolymers that involve isotactic polystyrene and atactic oligo(1-hexene) segments could be generated by titanium catalysts with enantiopure 1,2-dithiocyclohexanediyl-linked [OSSO]-type bis(phenolate) ligand **2**.^{5k,5o} As [OSSO]-type ligands having the 6-5-6 array of chelate rings toward central metal, the syntheses and α -olefin polymerization activity of several Group 4 metal complexes with 1,4-dithiabutanediyl-linked [OSSO]-type bis(phenolate) ligand **3** have independently reported by Kol's⁶ and Miyatake's⁷ groups. Jin et al. also have developed Group 4 metal complexes that contain *o*-carborane-bridged [OSSO]-type bis(phenolate) ligand **4**.⁸ Recently, we have succeeded in the development of new [OSSO]-type bis(phenolate) **5** incorporating with a *trans*-1,2-cyclooctanediyl platform and in the complexation of the pre-ligand **5** with Zr(CH₂Ph)₄ to form the corresponding zirconium(IV) dibenzyl complex **6a**.¹¹ Upon activation with B(C₆F₅)₃ or (Ph₃C)[B(C₆F₅)₄], complex **6a** achieved highly active (1610 – 2500 g mmol(**6a**)⁻¹ h⁻¹) and completely isospecific polymerization of 1-hexene ([*mmmm*] > 95%). Very recently, we have also presented that hafnium(IV) complexes **7a** (L = CH₂Ph) and **7b** (L = Cl) supported by the ligand **5** could promote precisely isospecific polymerizations of 1-hexene as well as 4-methyl-1-pentene involving high activity and significantly large molecular weight.¹² Moreover, the dibenzyl complex **7a** activated with dMAO (dried methylaluminoxane) led to excellent activity [500 – $17,000$ g mmol(**7a**)⁻¹ h⁻¹] and fairly high isotacticity ([*mmmm*] = 86.8–93.7%) in the polymerization of propylene at different temperatures from 0 to 70 °C. These successful

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† Electronic Supplementary Information (ESI) available: [¹³C{¹H}] NMR charts and DSC curves of the produced polymers. See DOI: 10.1039/x0xx00000x

results with [OSSO]-type Group 4 complexes stimulated us further to explore the performance of an alternative zirconium(IV) dichloro complex with **5**, in the polymerization of various α -olefins. Herein we describe the extremely high catalytic activity in several olefin (co)polymerization by **6b**/dMAO catalyst system, as a part of our investigation on [OSSO]-type ligand **5** in the single-site non-Cp catalysis.

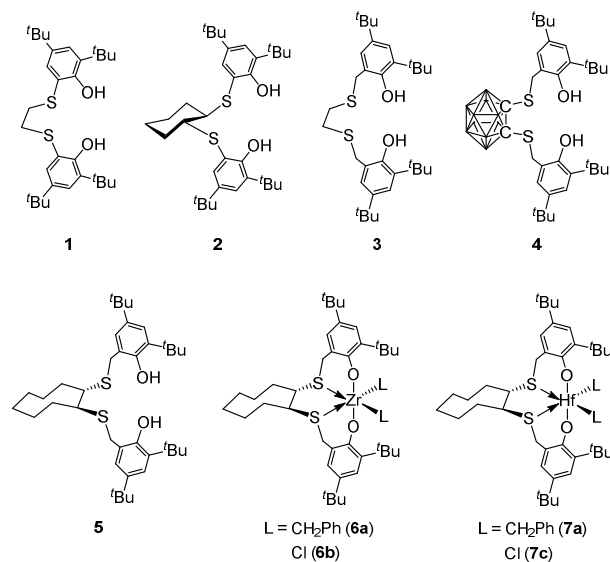


Chart 1

Experimental

General Procedures

All manipulations of air- and/or moisture-sensitive compounds were performed either using standard Schlenk-line techniques or in an MBRAUM LABmaster Glovebox under an inert atmosphere of argon. Anhydrous toluene was further dried by passage through columns of activated alumina and supported copper catalyst supplied by Hansen & Co., Ltd. Other chemicals and gases were used as received. ¹H (400 MHz) and ¹³C (100.5 or 125.8 MHz) NMR spectra were obtained with Bruker DRX400, AVANCE500-T or JEOL JNM-ECS400 spectrometers. The ¹³C NMR data of poly(1-hexene) and ethylene/1-hexene copolymer were obtained in CDCl₃ at room temperature. The ¹³C NMR data of poly(4-methyl-1-pentene) were obtained in C₂D₂Cl₄ at 130 °C. The molecular weights and molecular weight distributions of poly(1-hexene) were determined against polystyrene standard by gel permeation chromatography on a HLC-8220 GPC apparatus (Tosoh Corporation) with THF as the eluent at a flow rate of 0.35 mL/min at 40 °C. The calibration was made by polystyrene standard. The molecular weights and the molecular weight distributions of the poly(4-methyl-1-pentene) and copolymer samples were determined at 140 °C by high-temperature gel permeation chromatography (HT-GPC) on a PL220/HT apparatus (Tosoh Corp.) against polystyrene standard; *o*-dichlorobenzene was employed as the eluent at a flow rate of 1.0 mL/min. Both of the GPC

apparatuses were placed in the laboratory of Dr. Zhaomin Hou (Organometallic Chemistry Laboratory, RIKEN). DSC measurements were performed on a DSC6220 (SII) at a rate of 10 °C/min. Any thermal history difference in the poly(4-methyl-1-pentene) was eliminated by first heating a sample to 300 °C and cooling at 20 °C/min to -100 °C, and then recording the second DSC scan. Zirconium complexes (**6a**^{11a} and **6b**^{11b}) and dMAO¹³ were prepared by the literature procedures.

General Procedure for 1-Hexene Polymerization.

A 50 mL Schlenk flask was charged sequentially with 1-hexene (3.0 g, 35.6 mmol), dMAO, and toluene at room temperature. After stirring for 5 min at room temperature, a toluene solution of catalyst precursor **6** (0.0020 mmol) was added to the reaction mixture. The mixture was stirred for 10–30 min at 0–70 °C. The reaction was quenched by addition of methanol and concentrated hydrochloric acid. The mixture was extracted with toluene, and the organic layer was washed with methanol and dried over MgSO₄. The solvent was removed in vacuo at 70 °C during an overnight to leave poly(1-hexene).

General Procedure for 4-Methyl-1-pentene Polymerization.

A 50 mL Schlenk flask was charged sequentially with 4-methyl-1-pentene (3.0 g, 35.6 mmol), dMAO, and toluene at room temperature. After stirring for 5 min at room temperature, a toluene solution of catalyst precursor **6** (0.0020 mmol) was added to the reaction mixture. The mixture was stirred for 10 min at 25–70 °C. The reaction was quenched by addition of methanol and concentrated hydrochloric acid. The formed precipitates were collected by filtration and washed with methanol. The white solid was dried in vacuo at 70 °C overnight to leave poly(4-methyl-1-pentene).

General Procedure for Propylene Polymerization.

A 400 mL autoclave was charged sequentially with propylene (80 g, 11.9 mmol) and toluene at room temperature. After setting at desired temperature, dMAO and toluene solution of catalyst precursor **5** was added to the reaction mixture. The mixture was stirred for 1 h at 0–70 °C. Then, the reaction was quenched by addition of methanol. After a few minutes the gas was vented, and the mixture was then poured into methanol (1.0 L) with hydrochloric acid (1 M, 10 mL). The polymer was isolated by filtration, washed with methanol, and dried in a high vacuum at 80 °C for 4 h.

General Procedure for Ethylene/1-Hexene Copolymerization.

A 100 mL Schlenk flask was charged sequentially with 1-hexene (1.0–3.0 mL), dMAO, and toluene at room temperature in a glovebox. After stirring for 5 min at room temperature outside the glovebox, the flask was flushed and refilled with ethylene five times. A toluene solution of catalyst precursor **6** (0.0020 mmol) was added to the reaction mixture with ethylene flow (1 atm). The mixture was stirred for 10 min at 25 °C. The reaction was quenched by addition of methanol and concentrated hydrochloric acid. The mixture was extracted with toluene, and the organic layer was

washed with water. The solvent was removed in vacuo at 70 °C during an overnight to leave copolymer.

Results and discussion

In our previous work, we have found that the combination of hafnium(IV) complexes **7** and dMAO was the best one to achieve precisely isospecific polymerization of α -olefins. Thus, we first examined 1-hexene polymerization with dichloro complex **6b** as a pre-catalyst with dMAO as the activator under different reaction conditions, and the results are shown in Table 1. The polymerization of 1-hexene (3.0 g) with **6b** (20 μ mol) activated by dMAO ([dMAO]/**6b** = 250) at ambient temperature in toluene proceeded vigorously and exothermically to give 2.93 g of poly(1-hexene) (Run 1). Under these conditions, most of 1-hexene was consumed within 5 min, which corresponds to an activity over $1,800 \text{ g mmol}(\mathbf{6b})^{-1} \text{ h}^{-1}$. Despite such an exothermic reaction, the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the obtained polymer exhibited a relatively good isotacticity ([*mmmm*] = 88%). The GPC analysis of the product showed that the obtained polymer had a weight-averaged molecular weight M_w of $12,500 \text{ g mol}^{-1}$ and a relatively narrow polydispersity (M_w/M_n) of 2.0, consistent with a single-site catalyst. The polymerization conducted with a reduced amount of **6b** (2.0 μ mol) and quenched with MeOH before completion (3 min) produced 1.81 g of highly isotactic poly(1-hexene) ([*mmmm*] = 95%) with moderate M_w of $40,000 \text{ g mol}^{-1}$ and a narrow polydispersity of 1.9 (Run 2). In this case, the corresponding activity was recorded with $18,100 \text{ g mmol}(\mathbf{6b})^{-1} \text{ h}^{-1}$, which is much larger than those of the previous **6a**/(Ph_3C)[$\text{B}(\text{C}_6\text{F}_5)_4$] ($2,500 \text{ g mmol}(\mathbf{6a})^{-1} \text{ h}^{-1}$) and **7b**/dMAO systems ($3,180 \text{ g mmol}(\mathbf{7b})^{-1} \text{ h}^{-1}$) and the system of MAO-activated hafnium(IV) complex supported by an [OOOO]-type ligand reported by Waymouth ($4,900 \text{ g mmol}(\text{Cat.})^{-1} \text{ h}^{-1}$).^{9c} The polymerization at lower temperatures (0 or -40 °C) also proceeded efficiently to give completely isotactic poly(1-hexene)s ([*mmmm*] > 95%, Figure 1) with remarkably larger molecular weight ($M_w = 146,000$ – $150,000 \text{ g mol}^{-1}$) (Runs 3 and 4). It is noteworthy that in the all cases, the ^1H NMR spectra of

the poly(1-hexene)s displayed no resonance due to terminal olefinic protons, suggesting that the main step in the termination of the polymerization reaction did not involve the β -hydride elimination process. The system of dMAO-activated dibenzyl complex **6a** was next examined as listed in Runs 5 and 6. The polymerization at room temperature employing 2.0 μ mol of **6a** promoted the perfect isospecific 1-hexene polymerization ([*mmmm*] > 95%) involving an excellent activity up to $17,300 \text{ g mmol}(\mathbf{6a})^{-1} \text{ h}^{-1}$ ($M_w = 56,500 \text{ g mol}^{-1}$, $M_w/M_n = 2.1$). These results suggest that dMAO played a role not only as the cocatalyst but also as the scavenger toward moisture contaminated in the monomer and solvents effectively, in particular, for the polymerization with a small amount of catalyst.

Some non-Cp catalysts that are the stereospecific and highly active polymerization catalysts of 1-hexene are known to serve as suitable polymerization catalysts of more sterically bulky monomers such as 4-methyl-1-pentene (4-MP). However, while Group 4 metal complexes based on [ONNO]-

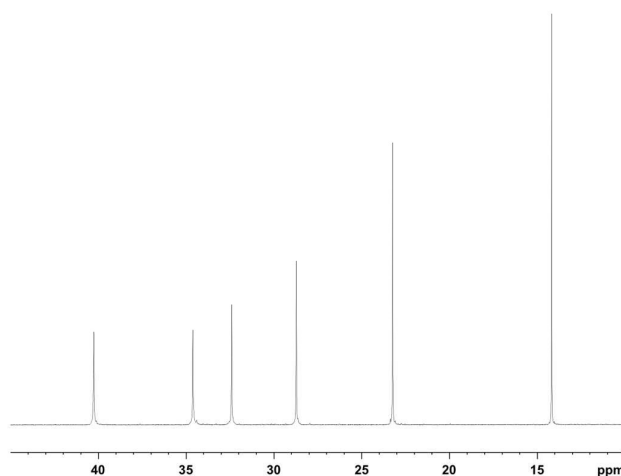


Figure 1. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of poly(1-hexene) obtained by the **6b**/dMAO system at 0 °C (Table 1, Run 3).

Table 1. 1-Hexene Polymerization Catalyzed by Complexes **6** and dMAO Systems^a

Run	Cat. [mmol]	toluene [mL]	Time [min]	Temp. [°C]	Yield [g]	Activity ^c	M_w [g mol ⁻¹]	PDI ^d	[<i>mmmm</i>] ^e [%]
1	6b 20	5	5	RT ^b	2.93	> 1,800	12,500	2.0	88
2	6b 2.0	1	3	RT ^b	1.81	18,100	40,000	1.9	95
3	6b 2.0	1	5	0	0.93	5,580	146,000	2.3	> 95
4	6b 10	10	120	-40	1.56	78	150,000	2.2	> 95
5	6a 20	5	3	RT ^b	2.60	> 2,600	13,400	1.7	> 95
6	6a 2.0	1	3	RT ^b	1.73	17,300	56,500	2.1	> 95

^aConditions: [dMAO]/[Cat.] = 250; 1-hexene 3.0 g (35.6 mmol). ^bActivation temperature. ^cIn g mmol(Cat.)⁻¹ h⁻¹. ^dPDI = M_w/M_n . Determined by GPC with polystyrene standards. ^eDetermined by $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy.

t y p e isotactic poly(4-MP) ($[mmmm] > 95\%$)¹⁵ (Figure 2). It is well

Table 2. 4-Methyl-1-pentene Polymerization Catalyzed by Complex **6b** and dMAO System^a

Run	6b [mmol]	Temp. [°C]	Yield [mg]	Activity ^b	M_w [g mol ⁻¹]	PDI ^c	$[mmmm]^d$ [%]	T_m^e [°C]
1	2.0	25	562.2	1,690	21,300	1.7	> 95	223
2	2.0	40	418.4	1,260	11,100	1.6	> 95	216
3	2.0	70	405.8	1,220	7,000	1.5	> 95	204

^aConditions: [dMAO]/[**6b**] = 250; 4-methyl-1-pentene, 3.0 g (35.6 mmol); toluene, 20 mL; time, 10 min. ^bIn g mmol(**6b**)⁻¹ h⁻¹.

^cPDI = M_w/M_n . Determined by GPC with polystyrene standards. ^dDetermined by ¹³C{¹H} NMR spectroscopy. ^eDetermined by DSC.

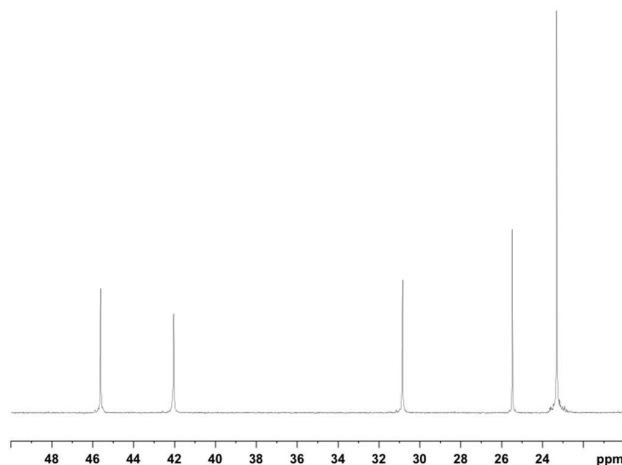


Figure 2. ¹³C{¹H} NMR spectrum of poly(4-methyl-1-pentene) obtained by the **6b**/dMAO system at 25 °C (Table 2, Run 1).

high activity and stereospecificity in the 4-MP polymerization have been quite limited until now. We reported recently that the hafnium pre-catalyst **7a** and dMAO system achieved precisely isospecific 4-MP polymerization with good activity of 54–101 g mmol(**7a**)⁻¹ h⁻¹ and significantly large molecular weight up to 102,000 g mol⁻¹.¹² As a next examination in the α -olefin polymerization catalyzed by complex **6**, we carried out the polymerization of 4-MP at different temperatures. The polymerization results are summarized in Table 2. Upon activation with dMAO (500 μ mol) at 25 °C in toluene, the zirconium complex **6b** (2.0 μ mol) efficiently served as an active catalyst (activity = 1,690 g mmol(**6b**)⁻¹ h⁻¹) to produce a crystalline poly(4-MP) with moderate molecular weight of 21,300 g mol⁻¹ and monomodal PDI value of 1.7 (Run 1). The ¹³C{¹H} NMR spectrum of the obtained polymer showed only five sharp signals indicating the formation of completely

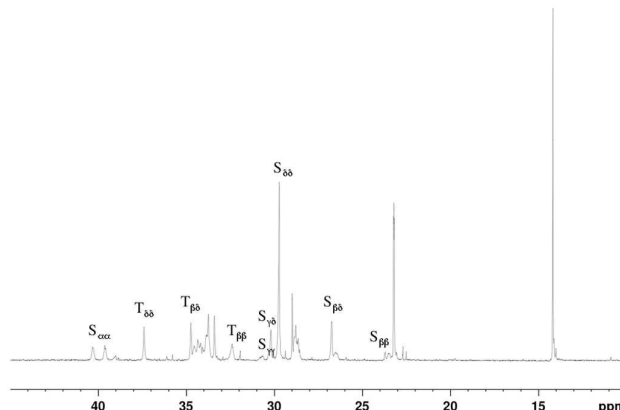


Figure 3. ¹³C{¹H} NMR spectrum of ethylene/1-hexene copolymer obtained by the **6b**/dMAO system (Table 3, Run 1). S and T indicate secondary and tertiary backbone carbons, respectively. The Greek subscripts provide a measure of the distance of neighboring butyl branches.¹⁸

known that highly isotactic poly(4-MP)s have high melting temperatures ($T_m > 220$ °C).¹⁶ In the DSC analysis, T_m of the obtained polymer showed a significantly high temperature of 223.5 °C. In Runs 2 and 3, the **6b**/dMAO system at higher temperatures (40 or 70 °C, respectively) also behaved as a good active catalyst for 4-MP polymerization to afford isotactic poly(4-MP)s. These obtained polymers have lower melting points ($T_m = 216$ °C for Run 2, $T_m = 204$ °C for Run 3) than that of the poly(4-MP) obtained in Run 1 probably because of their decrease of molecular weights.^{3c} The corresponding catalytic activities (1,260 (Run 2) and 1,220 (Run 3) g mmol(**6b**)⁻¹ h⁻¹) and the molecular weights ($M_w = 11,100$ (Run 2) and 7,000 (Run 3) g mol⁻¹ at 70 °C) were somewhat decreased compared with those of the polymerization at 25 °C, probably due to the transmetalation of growing polymer chains toward alkyl

Table 3. Ethylene/1-Hexene Copolymerization Catalyzed by Complex **6b** and dMAO System^a

Run	6b [mmol]	1-hexene [mL]	Conc. of 1-hexene [mol L ⁻¹]	Yield [g]	Activity ^b	M_w [g mol ⁻¹]	PDI ^c
1	5.0	1.0	0.27	0.927	1,110	10,100	1.9
2	5.0	2.0	0.53	1.700	2,040	13,000	1.8
3	5.0	3.0	0.80	2.246	2,700	17,300	1.8

^aConditions: [dMAO]/[**6b**] = 250; ethylene pressure, 1 atm; time, 10 min; temperature, 25 °C; toluene + 1-hexene, total 30 mL.

^bIn g mmol(**6b**)⁻¹ h⁻¹. ^cPDI = M_w/M_n . Determined by GPC with polystyrene standards.

aluminum species at higher temperatures. Thus, zirconium

Table 4. ^{13}C NMR Characterization of Ethylene/1-Hexene Copolymers Prepared with Complexes **6b** and dMAO Systems^a

Run	H content (mol %)	triad (%)						diad (%)			$r_{\text{E}}r_{\text{H}}^b$
		[EEE]	[HEE]	[HEH]	[EHE]	[HHE]	[HHH]	[EE]	[HE]	[HH]	
1	37.3	0.339	0.243	0.034	0.111	0.123	0.138	0.472	0.310	0.218	1.34
2	51.0	0.241	0.208	0.041	0.093	0.151	0.266	0.346	0.289	0.365	1.75
3	66.7	0.148	0.146	0.036	0.073	0.183	0.411	0.224	0.218	0.558	2.29

^aDetermined by $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy. ^b $r_{\text{E}}r_{\text{H}} = 4[\text{EE}][\text{HH}]/[\text{HE}]$.

pre-catalyst **6b** exhibited much greater activity in comparison with those of the reported single-site zirconium complexes with an [ONNO]-type tetradentate ligand (activity = 0.25 g mmol(cat)⁻¹ h⁻¹, $M_w = 15,000 \text{ g mol}^{-1}$)^{3c} and a half-metallocene ligand (activity = 7.4 g mmol(cat)⁻¹ h⁻¹, $M_w = 17,700 \text{ g mol}^{-1}$)¹⁷ in the isospecific polymerization of 4-MP. This catalyst system showed over 10-times higher activity compared with those of **7a**/dMAO system (activity = 101 g mmol(**7a**)⁻¹ h⁻¹) we reported previously.¹²

We next explored the ability of zirconium complex **6b** with dMAO toward ethylene/1-hexene copolymerization under atmospheric pressure. The experimental results are compiled in Table 3. Pre-catalyst **6b** activated with 250 equivalents of dMAO efficiently initiated ethylene copolymerization with different amounts of 1-hexene at ambient temperature to provide viscous, colorless poly(ethylene-co-1-hexene)s possessing M_w of 10,100–17,300 g mol⁻¹ (Runs 1–3). The molecular weight distributions of the copolymers were relatively narrow (PDI = 1.8–1.9), indicating that the complex **6b** could act as a single-site catalyst even in this copolymerization. The activity increased up to 2,700 g mmol(**6b**)⁻¹ h⁻¹ with increase of the feed concentration of 1-hexene up to 0.8 mol L⁻¹. Notably, the activity of this catalyst system are remarkably high in comparison with that of the catalyst system with the zirconium complex having the related *o*-carborane-bridged [OSSO]-type ligand **4** (200 g mmol(Cat.)⁻¹ h⁻¹).⁸ The microstructures of the obtained ethylene/1-hexene copolymers were analyzed by ^{13}C NMR spectra.¹⁸ The possible monomer sequences in the copolymers were summarized in Table 4, and the $^{13}\text{C}\{^1\text{H}\}$ NMR chart of the copolymer obtained in Run 1 is depicted in Figure 3. The contents of 1-hexene were found to increase from 37.3 mol % to 66.7 mol %, being dependent on the feed concentration of 1-hexene. In the ^{13}C NMR spectra, the characteristic low-field signals due to the α,α -carbon in [HH] diad fragment were observed at δ 39–41, indicating that 1-hexene block ([HH]) of 21.8–55.8% are essentially isolated by ethylene units in the polymer chains. According to the previous literatures,^{9d,19} the calculated $r_{\text{E}}r_{\text{H}}$ values for copolymerization of ethylene/1-hexene are in the range of 1.3–2.3, suggesting that this catalyst system allowed the production of high random copolymer sequence distribution.

Conclusions

We have found that the combination of zirconium(IV) dichloro complex **6b** bearing [OSSO]-type ligand **5** with dMAO as the activator led to both of isospecificity and high activity in α -olefin polymerizations. In particular, the activity of 18,100 g mmol(**6b**)⁻¹ h⁻¹ in the polymerization of 1-hexene is over 200 times greater than those of reported single-site Group 4 metal complexes having mixed donor [OEEO]-type tetradentate ligands (E = N, O, and S). The 1-hexene polymerization at 0 or –40 °C also proceeded efficiently affording completely isotactic poly(1-hexene)s ([*mmmm*] > 95%) with remarkably large molecular weight ($M_w = 146,000$ – $150,000 \text{ g mol}^{-1}$). In addition, the polymerization of 4-MP catalyzed by the **6b**/dMAO system at 25–70 °C produced completely isotactic poly(4-MP)s with good activities (1,220–1,690 g mmol(**6b**)⁻¹ h⁻¹) and relatively narrow polydispersities ($M_w/M_n = 1.8$ – 1.9). Furthermore, this catalyst system demonstrated the ethylene-1-hexene copolymerization at 25 °C under atmospheric pressure to form highly random copolymers with 1-hexene content levels in the range of 37.3–66.7 mol % and an activity of 2,700 g mmol(**6b**)⁻¹ h⁻¹.

Acknowledgements

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