

Living Polymerization of 1,3-Butadiene Catalyzed by Half-titanocene Complex Bearing Dibenzhydryl-substituted Aryloxy Ligand*

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Abstract Half-titanocene complexes bearing dibenzhydryl-substituted aryloxy ligands (**2a–2d**) were prepared. Among them, **2c** adopted a three-legged distorted tetrahedral geometry evidenced by X-ray crystallography. The poly-1,3-butadiene with high molecular weight and narrow molecular weight distribution was obtained by using these complexes as the catalysts activated with methylaluminoxane (MAO). The catalytic activities of the complexes depended on their structures. The Ti—O—C bond in the complexes with large angle afforded them with higher activity, while Cp*-based complexes exhibited lower activities than the Cp-based analogues. The activity of complex increased with increasing the polymerization temperature while the selectivity remained no change, indicating the high thermal stability. Furthermore, the polymerization of 1,3-butadiene catalyzed by **2a**/MAO at 0 °C has been found in a living fashion.

Keywords Half-titanocene complexes; 1,3-Butadiene; Thermal stability; Living polymerization

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INTRODUCTION

Polyolefin as one of the largest commodity materials have found versatile applications in our daily life. A long-standing research subject in polyolefin synthesis is the design and synthesis of highly efficient catalysts^[1, 2]. Decades after the discovery of Ziegler-Natta catalysts, promising advances have been made in the development of metallocene and non-metallocene catalysts for olefin polymerization^[3–9]. Whereas non-metallocene catalysts received great interests recently, early transition metal metallocene complexes are the most important catalysts for olefin polymerization due to their high activities, well known structures, and accessibility of producing new polymer architectures, *etc.* and have been used in industry^[10, 11]. Many efforts have also been devoted to the 1,3-diene polymerization. Some metallocene catalysts exhibited high activity and stereoselectivity in the 1,3-butadiene polymerization. In some cases living polymerization was achieved, allowing to produce polymers with regulated structures. For instance, traditional CpTiCl₃/MAO system afforded single active site to induce the

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living polymerization of 1,3-butadiene^[12]. Half-titanocene bearing coordinative ether and ester side chains promoted living polymerization of 1,3-butadiene to give the polymers with high *cis*-1,4 stereoregularity (up to 99.2%)^[13]. Alkyl and alkylsilyl substituted cyclopentadienyl titanium trichlorides were highly active and selective catalyst precursors for 1,3-butadiene polymerization with a living nature at $-25\text{ }^{\circ}\text{C}$ ^[14].

Recently, numerous studies focused on the preparation of half-metallocene type precatalysts bearing bulky anionic ancillary ligands^[15, 16]. Indeed, theoretical and experimental studies revealed that the presence of bulky ligand could stabilize the generated active species, and thus give rise to high catalytic activity. Sun and Redshaw reported the synthesis of half-titanocene dichloride 2-aryliminoquinolin-8-olates, which displayed high activities in ethylene polymerization even at high temperatures^[17]. Li *et al.* synthesized a series of half-zirconocenes bearing phosphine oxide phenolate chelating ligands with high activity, which could be used to polymerize ethylene at high temperature of $75\text{ }^{\circ}\text{C}$ ^[18]. Mu *et al.* reported that half-titanocene anilide complexes were the efficient catalyst precursors for ethylene polymerization and ethylene/1-hexene copolymerization^[19]. Bulky aryloxide as an important class of ligands has been widely used for the stabilization of metal complexes in coordination chemistry. Nomura *et al.* synthesized a series of half-titanocenes containing aryloxide ligands which exhibited not only notable catalytic activities for olefin polymerization but also high comonomer incorporation for the copolymerization of ethylene with α -olefin, cycloolefins, and styrene^[20–22]. We also reported the high activities and comonomer incorporation properties of half-titanocenes bearing dibenzhydryl-substituted aryloxide ligands for ethylene polymerization and ethylene/1-hexene copolymerization^[23]. Despite the above-mentioned successful examples of olefin polymerization, to our knowledge, half-titanocenes containing bulky aryloxide ligands for 1,3-diene polymerization have not yet been explored. Therefore, in this study, half-titanocene complexes bearing dibenzhydryl-substituted aryloxide ligands were prepared and employed for the 1,3-butadiene polymerization. The influences of ligand structure and reaction parameters on the polymerization were investigated in detail.

EXPERIMENTAL

Chemicals and Measurements

All the manipulations were carried out under argon by using standard Schlenk techniques or in a glove box. Methylaluminoxane (MAO, 1.5 mol/L in toluene) was commercially available from Akzo Nobel Chemical Inc. 1,3-Butadiene was donated by Jinzhou petrochemical Corporation, PetroChina. *n*-Butyllithium (1.6 mol/L in hexane), trichloro (cyclopentadienyl) titanium (CpTiCl_3) and trichloro (pentamethylcyclopentadienyl) titanium (Cp^*TiCl_3) were purchased from Aldrich. 2,6-Bis(diphenylmethyl)-4-methoxyl phenoxide was synthesized according to the procedures reported in the literature^[24]. Toluene was distilled from sodium/diphenyl ketone and stored under dry nitrogen.

The molecular weights (M_n) and molecular weight distributions (M_w/M_n) of polymers were measured at $30\text{ }^{\circ}\text{C}$ by gel permeation chromatography (GPC) equipped with a Waters 515 HPLC pump, four columns (HMW 7 THF, HMW 6E THF $\times 2$, HMW 2 THF), and a Waters 2414 refractive index detector. THF was used as the eluent at a flow rate of 1.0 mL/min. The experiment settings were calibrated by polystyrene standard. The structure of polymers was determined by NMR on a Bruker-300 MHz at ambient temperature with CDCl_3 as a solvent. IR spectra were recorded on a BRUKE Vertex-70 FTIR spectrophotometer. The proportion of *cis*-1,4, 1,2, and *trans*-1,4 units of polymers were determined with the method reported in the literature^[25].

Synthesis of the Complexes (2a–2d)

The bulky aryloxide half-titanocene complexes **2a**, **2b**, and **2d** were synthesized according to our previous work^[23]. The synthetic method of **2c** was as follows: a solution of 2,6-bis(diphenylmethyl)-4-methoxyl phenoxide (1.0 g, 2.19 mmol) in 15 mL of toluene was added dropwise into a hexane solution of *n*-butyllithium (1.43 mL, 2.29 mmol) at $-78\text{ }^{\circ}\text{C}$, then the mixture was warmed to room temperature and stirred for 4 h. *In situ* prepared $\text{LiO}(2,6\text{-Ph}_2\text{CH-C}_6\text{H}_2\text{-4-OMe})$ was added to the toluene solution of (pentamethylcyclopentadienyl) titanium trichloride (0.63 g, 2.19 mmol) slowly and stirred for 12 h. The mixture was filtered through celite, and

the filtrate was dried under vacuum to get a red residue. The powder was washed twice with diethyl ether (10 mL) and filtered. Recrystallization of the crude product from CH_2Cl_2 /hexane at $-30\text{ }^\circ\text{C}$ gave the desired product (0.86 g, 52% yield). $^1\text{H-NMR}$ (CDCl_3 , δ): 7.22–7.18 (m, 12H, Ar–H), 7.13–7.12 (m, 8H, Ar–H), 6.42 (s, 2H, Ar–H), 6.21 (s, 2H, $\text{CH}(\text{Ph})_2$), 3.4 (s, 3H, OMe), 1.74 (s, 15H, Cp^*). $^{13}\text{C-NMR}$ (CDCl_3 , δ): 159.57, 144.64, 131.18, 129.92, 129.03, 128.61, 127.13, 126.63, 51.02, 48.72, 12.76. Anal. Calcd. for $\text{C}_{43}\text{H}_{42}\text{Cl}_2\text{O}_2\text{Ti}$: C, 72.79; H, 5.97; Found: C, 72.17; H, 5.56.

X-ray Crystallographic Details

Data collections were performed at $-88.5\text{ }^\circ\text{C}$ on a Bruker SMART APEX diffractometer with a CCD area detector using graphite monochromated Mo K radiation ($\lambda = 0.0771\text{ nm}$). The determination of crystal class and unit cell parameters was carried out by the SMART program package. The raw frame data were processed using SAINT and SADABS to collect the reflection data file. Refinement was performed on F^2 anisotropically for all non-hydrogen atoms by full-matrix least-squares method. Details of X-ray structure determinations and refinements are shown in Table S1 (in the Supporting Information, SI). The CCDC number is 1483557.

Polymerization Procedure

A typical procedure for the 1,3-butadiene polymerization was as follows (Entry 4, Table 1): at first, the desired amount of MAO and toluene solution (10 mL) of 1,3-butadiene (1 g, 18.5 mmol) were added into a glass bottle and stirred at room temperature for 15 min. Then, the toluene solution of half-titanocene complex (10 μmol , 1 mL) was injected to initiate the polymerization at $20\text{ }^\circ\text{C}$. After a desired time, the polymerization was quenched by addition of acidified ethanol (10 mL, 10% HCl) containing 2,6-di-*tert*-butyl-4-methylphenol (1.0 wt%) as a stabilizer. The polymer was washed with ethanol repeatedly, and then dried under vacuum at $40\text{ }^\circ\text{C}$ to constant weight. The polymer yield was determined by gravimetry.

RESULTS AND DISCUSSION

Molecular Structures

Single crystal of complex **2c** was obtained by slow diffusion of *n*-hexane into its dichloromethane solution. The molecular structure is shown in Fig. 1, and the selected bond lengths and angles are summarized in Table S2 (in SI). The solid state structure of **2c** is similar to our previously reported bulky aryloxy half-titanocene complexes, which adopts three-legged distorted tetrahedral geometry around the metal center^[23]. The selected Ti–C (in the Cp ring) bond lengths of the complexes are ranging from 0.2323 nm to 0.2405 nm and the observed singlet of Cp ring in the NMR spectra indicates their conjugated characteristics^[26].

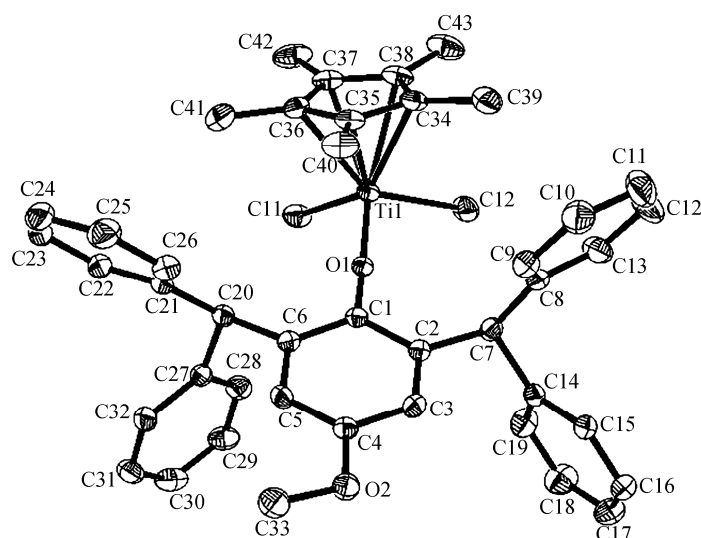


Fig. 1 ORTEP view of complex **2c**, drawn at 35% probability (Hydrogen atoms were omitted for clarity.)

As shown in Fig. 2, complex **2c** has the longest Ti—O bond distance (0.2036 nm), and the Ti—O—C angles in the complexes are in the order of **2c** (169.1°) > **2a** (167.2°) > **2b** (162.9°). Moreover, due to the relatively large $\text{Cp}_{\text{cent}}\text{—Ti—O1}$ angles ($118.9^\circ\text{--}120.9^\circ$) of the complexes, the bulky aryloxy ligand can rotate in the Ti—O—C axial position flexibly in the solution state to provide the open space for the monomer coordination^[27].

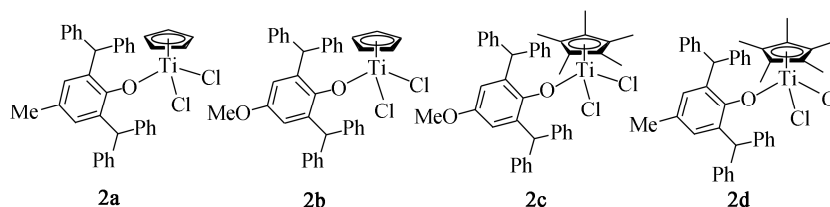


Fig. 2 The structures of the half-titanocene bearing bulky aryloxy ligands

Polymerization of 1,3-Butadiene

All the complexes activated with MAO were investigated for the polymerization of 1,3-butadiene. The results are summarized in Table 1. According to the observed polymer yields, the activity of the complex increased in the order of **2c** < **2d** < **2b** < **2a**. The activity trend is in line with the order of Ti—O—C angle of the complex, possibly because the more open angle favors the coordination of monomer to the metal center^[3]. On the other hand, Cp*-based complexes **2c** and **2d** exhibited lower activities than their Cp-based counterparts **2a** and **2b**, which might be owing to the steric hindrance^[9]. These complexes exhibited somewhat low selectivity which was similar to that of traditional half-titanocene; the *cis*-1,4 contents ranged from 72.9% to 80.5%. All the resulting polymers had high molecular weights ($M_n = 15.3 \times 10^4\text{--}22.7 \times 10^4$) and relatively narrow molecular weight distribution ($M_w/M_n = 2.1\text{--}2.3$).

Table 1 Polymerization of 1,3-butadiene by using Cp/Ti(OAr)Cl₂/MAO catalytic systems^a

Entry	Molar ratio Al/Ti	Cat	<i>T</i> (°C)	Yield (wt%)	Microstructure ^b (%)			M_n^c $\times 10^{-4}$	M_w/M_n^c
					<i>Trans</i> -1,4	<i>Cis</i> -1,4	1,2		
1	1000	2a	20	40.8	2.3	80.5	17.1	22.7	2.2
2	1000	2b	20	32.6	2.9	78.6	18.4	19.8	2.1
3	1000	2c	20	15.7	3.6	72.9	23.5	17.4	2.3
4	1000	2d	20	18.2	2.7	73.6	23.7	15.3	2.2
5	500	2a	20	12.0	2.4	79.6	17.9	20.0	2.3
6	1500	2a	20	53.1	4.0	75.7	20.3	22.0	2.1
7	2000	2a	20	60.0	4.1	78.7	17.2	20.4	2.3
8	2000	2a	0	14.1	0.7	82.3	17.0	4.9	1.4
9	2000	2a	50	92.1	4.7	76.6	18.7	12.9	2.6
10	2000	2a	70	82.7	5.9	75.2	18.9	11.0	2.7

^a Polymerization: carried out in 23.3 mL of toluene for 1 h with 10 μmol of Ti, 1.0 g Bd, $[\text{Bd}]/[\text{Ti}] = 1850$; ^b Determined by IR and NMR; ^c Determined by GPC using polystyrene standards

The influences of reaction parameters such as Al/Ti ratio and temperature on the polymerization were further examined with complex **2a** as precatalyst. When the reaction temperature fixed at 20 °C, varying the Al/Ti ratio from 500 to 2000, the polymer yield increased with the increase of Al/Ti ratio. Meanwhile, the molecular weight of the obtained polymers hardly changed ($M_n \sim 21 \times 10^4$) and the molecular weight distributions remained relatively narrow ($M_w/M_n \sim 2.2$), indicating the negligible chain transfer reaction to the cocatalyst. The polymerization rate remarkably accelerated with increasing the reaction temperature; the polymer yield at 0 °C was 14.1%, whereas the yield at 50 °C reached 92.1%. However, further increasing temperature to 70 °C resulted in a slight decrease in polymer yield (82.7%). This result is different from other metallocene catalysts whose activity remarkably decreased as the polymerization temperature increased to 50 °C and

above^[28–30]. The high thermal stability of the present catalyst might be due to the fact that the bulky aryloxo ligand played an important role in preventing the precatalyst from decomposition at elevated temperature. On the other hand, the molecular weight of the resulting polymer decreased and the molecular weight distribution became broader with the increment of temperature due to the accelerated chain transfer reaction at high temperatures. It should be noted that the *cis*-1,4 content of the resultant polybutadiene keep almost unchanged (*ca.* 77%) even at 70 °C (shown in Figs. 3 and 4), although the present catalyst has low selectivity.

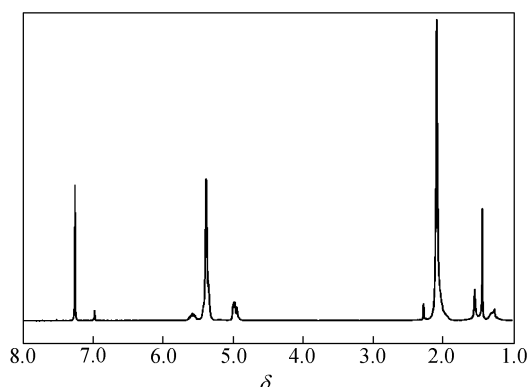


Fig. 3 ^1H -NMR spectrum of polybutadiene obtained with **2a**/MAO catalytic system (Table 1, Entry 10)

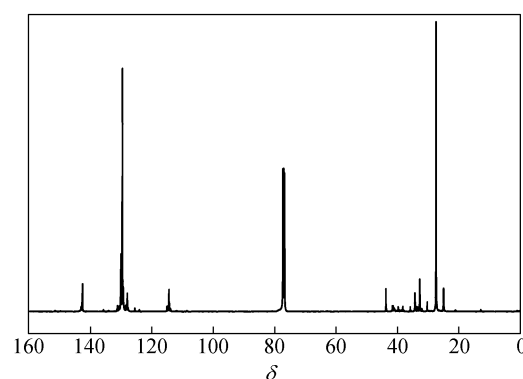


Fig. 4 ^{13}C -NMR spectrum of polybutadiene obtained with **2a**/MAO catalytic system (Table 1, Entry 10)

Living Polymerization of 1,3-Butadiene

The narrow molecular weight distributions of polybutadienes especially that obtained at 0 °C suggested that the polymerization might proceed in a living manner. Thus, the polymerization of 1,3-butadiene with **2a**/MAO in 23.3 mL of toluene at 0 °C, 1.0 g Bd, $[\text{Bd}]/[\text{Ti}] = 1850$, $[\text{Al}]/[\text{Ti}] = 2000$ was investigated in more details. As shown in Fig. 5, although the catalytic system gave a low chain propagation rate, the yield reached *ca.* 70% with prolonging the polymerization time to 8 h. The plot of $\ln([M]_0/[M]_t)$ versus polymerization time revealed that the polymerization was of first-order with respect to the concentration of monomer. A plot of M_n versus polymer yield showed a linear relationship, while the molecular weight of the resultant polybutadiene increased with prolonging the reaction time (shown in Fig. 6) and molecular weight distributions kept narrow (shown in Fig. 7), indicating that the chain transfer and termination reactions hardly occur during the polymerization process^[31]. Furthermore, the seeding polymerization was carried out by sequential monomer addition, and indeed chain extension was achieved (Fig. 8). The first stage polymerization was almost complete within 10 h (yield *ca.*

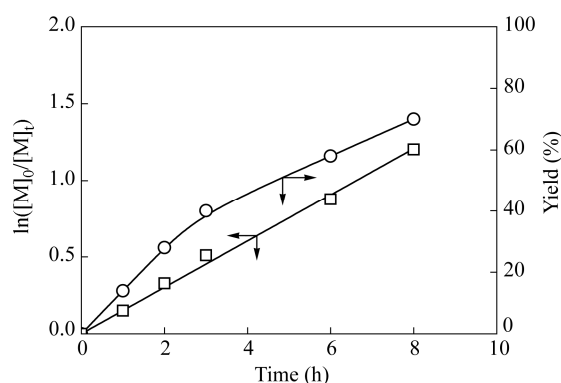


Fig. 5 Plots of $\ln([M]_0/[M]_t)$ and polymer yield against polymerization time
Polymerization conditions: in toluene (23.3 mL) at 0 °C, 1.0 g Bd, $[\text{Bd}]/[\text{Ti}] = 1850$, $[\text{Al}]/[\text{Ti}] = 2000$

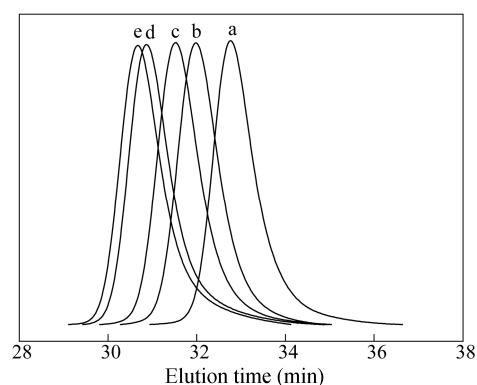


Fig. 6 GPC profiles of polymers obtained at different polymerization time: (a) 1 h, (b) 2 h, (c) 3 h, (d) 6 h, and (e) 8 h
Polymerization conditions: in toluene (23.3 mL) at 0 °C, 1.0 g Bd, $[\text{Bd}]/[\text{Ti}] = 1850$, $[\text{Al}]/[\text{Ti}] = 2000$

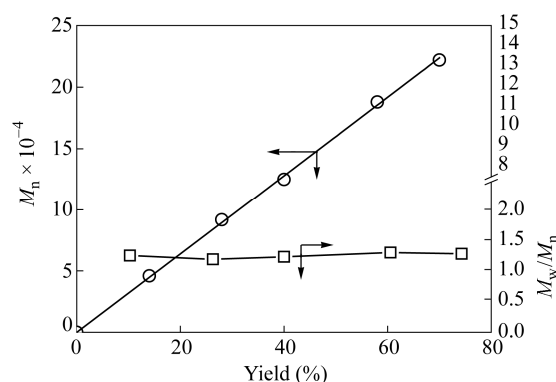


Fig. 7 Plots of M_n and M_w/M_n against polymer yield
Polymerization conditions: in toluene (23.3 mL) at 0 °C, 1.0 g Bd, $[Bd]/[Ti] = 1850$, $[Al]/[Ti] = 2000$

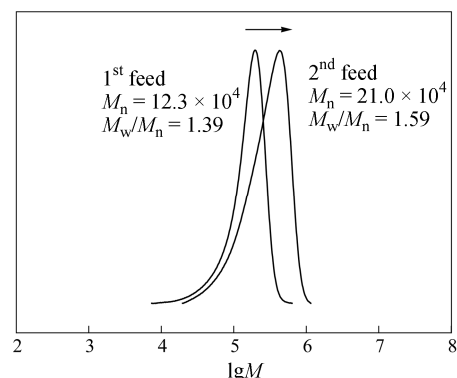


Fig. 8 GPC profiles of polymers obtained with the sequential polymerization of 1,3-butadiene

Polymerization conditions: in toluene at 0 °C, MAO as cocatalyst, $[Bd]_0 = 0.184$ mol/L, $[Bd]_0/[Ti] = 462$, $[Al]/[Ti] = 1000$, $[Bd]_{add} = 0.184$ mol/L, $[Bd]_{add}/[Ti] = 1000$

95%) and gave the polymer with M_n of 12.3×10^4 and M_w/M_n of 1.39. After that, the second portion of monomer was added. After additional 10 h, the polymer with a total yield of 90% had approximately doubled M_n of 21.0×10^4 and kept narrow M_w/M_n of 1.59. These results clearly demonstrated the living character of the polymerization system.

CONCLUSIONS

Half-titanocenes **2a–2d** bearing bulky dibenzhydryl-substituted aryloxy ligands activated with MAO were studied for 1,3-butadiene polymerization. The resulting polybutadienes had high molecular weight and narrow molecular weight distribution. The structure of the complexes significantly influenced their catalytic performance. The catalytic activity of the complex increased in the order of **2c** < **2d** < **2b** < **2a**, which followed the trend of the Ti–O–C angle, while Cp*-based complexes **2c** and **2d** showed lower activities than their Cp-based counterparts **2a** and **2b**. The bulky aryloxy ligand-containing complex exhibited higher thermal stability than the traditional metallocenes; even at high reaction temperature the complex displayed high activity and good selectivity. Moreover, the polymerization of 1,3-butadiene using complex **2a** as precatalyst exhibited the features of a living process.

REFERENCES

- 1 Makio, H., Terao, H., Iwashita, A. and Fujita, T., *Chem. Rev.*, 2011, 111: 2363
- 2 Redshaw, C. and Tang, Y., *Chem. Soc. Rev.*, 2012, 41: 4484
- 3 Nomura, K. and Liu, J., *Dalton Trans.*, 2011, 40: 7666
- 4 Britovsek, G.J., Cohen, S.A., Gibson, V.C. and van Meurs, M., *J. Am. Chem. Soc.*, 2004, 126: 10701
- 5 Wasilke, J.C., Obrey, S.J., Baker, R.T. and Bazan, G.C., *Chem. Rev.*, 2005, 105: 1001
- 6 Kretschmer, W.P., Dijkhuis, C., Meetsma, A., Hessen, B. and Teuben, J.H., *Chem. Commun.*, 2002, 114(6): 608
- 7 Alt, H.G. and Koppl, A., *Chem. Rev.*, 2000, 100: 1205
- 8 Flisak, Z. and Sun, W.H., *ACS Catal.*, 2015, 5: 4713
- 9 Ikai, S., Yamashita, J., Kai, Y., Murakami, M., Yano, T., Qian, Y.L. and Huang, J.L., *J. Mol. Catal. A: Chem.*, 1999, 140: 115
- 10 Shapiro, P.J., Schaefer, W.P., Labinger, J.A., Bercaw, J.E. and Cotter, W.D., *J. Am. Chem. Soc.*, 1994, 116: 4623
- 11 McKnight, A.L. and Waymouth, R.M., *Chem. Rev.*, 1998, 98: 2587

- 12 Miyazawa, A., Kase, T. and Soga, K., *J. Polym. Sci., Part A: Polym. Chem.*, 1999, 37: 695
- 13 Miyazawa, A., Kase, T., Hashimoto, K., Choi, J.C., Sakakura, T. and Ji, Z.J., *Macromolecules*, 2004, 37: 8840
- 14 Miyazawa, A., Kase, T. and Soga, K., *Macromolecules*, 2000, 33: 2796
- 15 Nomura, K., Liu, J.Y., Padmanabhan, S. and Kitiyanan, B., *J. Mol. Catal. A: Chem.*, 2007, 267: 1
- 16 Nomura, K., Naga, N., Miki, M., Yanagi, K. and Imai, A., *Organometallics*, 1998, 17: 2152
- 17 Huang, W., Li, B.X., Wang, Y.H., Zhang, W.J., Wang, L., Li, Y.S., Sun, W.H. and Redshaw, C., *Catal. Sci. Technol.*, 2011, 1: 1208
- 18 Tang, X.Y., Wang, Y.X., Liu, S.R., Liu, J.Y. and Li, Y.S., *Dalton Trans.*, 2013, 42: 499
- 19 Liu, K.F., Wu, Q.L., Gao, W., Mu, Y. and Ye, L., *Eur. J. Inorg. Chem.*, 2011, 1901
- 20 Nomura, K., Oya, K. and Imanishi, Y., *J. Mol. Catal. A: Chem.*, 2001, 174: 127
- 21 Apisuk, W. and Nomura, K., *J. Polym. Sci., Part A: Polym. Chem.*, 2016, 54: 1902
- 22 Wang, W., Fujiki, M. and Nomura, K., *J. Am. Chem. Soc.*, 2005, 127: 4582
- 23 Dong, B., Zhang, H.X., Li, H., Liu, H., Guo, J., Zhang, C.Y., Zhang, X., Hu, Y.M., Sun, G.P. and Zhang, X.Q., *Polymer*, 2016, 100: 188
- 24 Franke, S.M., Tran, B.L., Heinemann, F.W., Hieringer, W., Mindiola, D.J. and Meyer, K., *Inorg. Chem.*, 2013, 52: 10552
- 25 Tanaka, Y., Takeuchi, Y., Kobayashi, M. and Tadokoro, H., *J. Polym. Sci. Part A-2, Polym. Phys.*, 1971, 9: 43
- 26 Sun, W.H., Liu, S.F., Zhang, W.J., Zeng, Y.N., Wang, D. and Liang, T.L., *Organometallics*, 2010, 29: 732
- 27 Nomura, K., Oya, K., Komatsu, T. and Imanishi, Y., *Macromolecules*, 2000, 33: 3187
- 28 Srebro, M., Piekos, L., Kim, T.J., Cheong, M., Ok, M.A., Kang, S.O. and Michalak, A., *Organometallics*, 2010, 29: 5341
- 29 Liu, S.F., Sun, W.H., Zeng, Y.N., Wang, D., Zhang, W.J. and Li, Y., *Organometallics*, 2010, 29: 2459
- 30 Brintzinger, H.H., Fischer, D., Mülhaupt, R., Rieger, B. and Waymouth, R.M., *Angew. Chem. Int. Ed.*, 1995, 34: 1143
- 31 Gong, D.R., Dong, W.M., Hu, J.C., Zhang, X.Q. and Jiang, L.S., *Polymer*, 2009, 50: 2826