Novel Diphenyl Thioether-Bridged Binuclear Metallocenes of Ti and Zr for Synthesis of Polyethylene with Broad Molecular Weight Distribution

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ABSTRACT: Two diphenyl thioether-bridged binuclear metallocenes of Ti and Zr, $[(C_5H_5)Cl_2MC_5H_4CH_2(p\text{-}C_6H_4)]_2S$ [M = Ti (1) and Zr (2)], have been synthesized by treating the dilithium salts of the corresponding ligand $[(C_5H_5CH_2(p\text{-}C_6H_4)]_2S$ with two equivalents of $C_5H_5TiCl_3$ and $C_5H_5ZrCl_3(DME)$, respectively, in toluene at 0°C. Both new complexes have been characterized by ^{1}H-NMR spectroscopy and elemental analysis. Homogeneous ethylene polymerization using both complexes was performed in the presence of methylaluminoxane (MAO). The influences of molar ratio of [MAO]/[Cat], concentration of the catalysts, time, and temperature have been studied systematically. The catalytic activity of **1** is higher than that of the corresponding oxygen-bridged catalyst $[(C_5H_5)Cl_2TiC_5H_4CH_2(p\text{-}C_6H_4)]_2O$. The catalytic activity of **2** is at least two times higher than that of **1** under any tested polymerization conditions. The melting points of polyethylene (PE) produced by **1** and **2** are higher than 130°C, indicating a highly linear and highly crystalline PE. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 120: 3530–3535, 2011

Key words: binuclear metallocene; diphenyl thioether bridge; metallocene catalyst; polymerization; polyethylene

INTRODUCTION

Polymetallic metallocene complexes having two, three, or more transition metal centers of group 4 elements have been one of the most exciting developments in the area of catalysis and organometallic chemistry.[1–3] The reason for that could be attributed to the unique catalytic transformations arising from cooperative catalytic effects between multiple metal centers and the influence of steric effects, the structure of the bridge, and the metallocene ligands on both sides of the bridge.[4–6] The attraction of those metallocenes catalysts in combination with methylaluminoxane (MAO) for polyolefin industry is the resulting polyolefin having a broad molecular weight distribution (MWD), which is favorable to overcome process difficulties, because mononuclear metallocene catalysts produce polyolefins with a narrow MWD.[7–9]

Up to now, a lot of attention was given to binuclear metallocene complexes of titanium and zirconium containing two equal or different metallocene units linked by various bridges, such as phenylene,[3] biphenyl,[10] polymethylene,[11,12] polysiloxane,[6] 3-oxapentamethylene,[13–15] and others. The insertion of hetero atoms such as oxygen or sulfur into the bridge influences the nature of the bridge and consequently, the catalytic properties of binuclear metallocene complexes. Noh et al.[6] proposed that the interaction of the Lewis acidic cocatalyst MAO with the Lewis basic oxygen of the polysiloxane bridge might withdraw electron density and result in a reduced polymerization activity. We proposed the formation of pseudo five or six-membered rings existing in 3-oxa-pentamethylene-bridged binuclear metallocenes of Ti and Zr through the coordination of the oxygen atom of the bridge with the center metal atom in those metallocene units.[13–15] The partially increased electron density at the metal atom seems to increase the stability of the active centers.

The influence of the heteroatoms of those bridged binuclear metallocenes on the catalytic activity is obviously very complex, and thus it is notable to study it in detail. Recently, we reported upon diphenyl ether-bridged binuclear metallocenes of Ti and their use to produce PE with high MW and broad MWD.[16] Those binulear metallocenes are different from 3-oxapentamethylene-bridged binuclear metallocenes. The former has a rigid phenyl ring sequence in their bridge, and the later has a typical

flexible bridge of 3-oxa-pentamethylene in their molecular structure.

Oxygen and sulfur are elements of main group 16 of the periodic table. In addition of their similarities, the bigger atom radius and the lower electronegativity of sulfur attracted us to use sulfur instead of oxygen in the bridge to look for different catalyic features. In this contribution, two new diphenyl thioether containing binuclear titanocene and zirconocene complexes were prepared and used for ethylene polymerization in the presence of MAO.

EXPERIMENTAL

All manipulations including air- or moisture-sensitive materials were performed under an atmosphere of argon using standard Schlenk techniques.

Materials

Toluene, tetrahydrofuran (THF), diethyl ether, and hexane were freshly distilled under argon from purple sodium/benzophenone ketyl solutions. CH_2Cl_2 was distilled under Argon from CaH_2. Cyclopentadiene was commercially available and used without further purification. MAO (10% in toluene) was purchased from Witco. Ethylene (polymer grade) was purified via bubbling through triisobutylaluminum in toluene. 4,4-Bis(bromomethyl)diphenyl sulfide was synthesized according to the literature.[17]

Measurements

^{1}H-NMR spectra were recorded on a Bruker Advance 300 instrument at an ambient temperature. Chemical shifts were referenced with respect to tetramethylsilane. Elemental analyses were conducted on a Perkin–Elmer 240 elemental analyzer. The intrinsic viscosity [η] of PE in decahydronaphthalene was measured with a modified Ubbelohde viscosimeter at 135°C. The viscosity-averaged molecular weight [M_η] was calculated according to the equation $[\eta] = 6.67 \times 10^{-4} \times [M_\eta]^{0.67}$ (mL/g). The MWD of PE was determined by gel-permeation chromatography (Water 150, 135°C) with standard polystyrene as a calibration reference. The melting point temperatures (T_m) of PE were recorded with a Perkin–Elmer DSC-7 differential scanning calorimeter.

Synthesis

Synthesis of complexes 1 and 2

A solution of 4,4-bis(bromomethyl)diphenyl sulfide (1.85 g, 5.00 mmol) in THF (40 mL) was added slowly to a stirred solution of cyclopentadienyl sodium (10.00 mmol) in THF (30 mL) at 0°C and stirred for 2 h. The solvent was removed in vacuum,

and the resulting mixture was extracted with diethyl ether (3 × 30 mL). The combined ether solutions were added to a stirred solution of n-BuLi (8 mL, 1.5M, and 12 mmol) in hexane at 0°C. The reaction mixture was warmed up to room temperature, stirred overnight, and then filtered. The residue was washed with diethyl ether (3 × 20 mL) and dried in vacuum to yield an air-sensitive pale yellow powder. This was added slowly to a stirred yellow solution of $CpTiCl_3$ (1.31 g, 6.00 mmol) in toluene (60 mL) at 0°C. After stirring overnight at room temperature, the mixture was filtered, and the residue was extracted with CH_2Cl_2 (3 × 40 mL). The combined extraction solutions were concentrated and cooled down to −15°C. Subsequently, a red powder precipitated from the solution was isolated by filtration and washed several times with cold pentane to yield 1 as a red powder.

Yield: 1.43 g (67.4% related to $CpTiCl_3$). Elemental analysis: $C_{34}H_{30}Cl_4STi_2$ (%), found: C 57.03, H 4.20; calcd: C 57.66, H 4.27; ^{1}H-NMR (CDCl$_3$, δ, ppm): 4.09 (s, 4 H, CH$_2$), 6.34 (t, J = 2.4 Hz, 4 H, C$_5$H$_4$), 6.43 (t, J = 2.4 Hz, 4 H, C$_5$H$_4$), 6.52 (s, 10 H, C$_5$H$_5$), 7.13 (d, J = 8.4 Hz, 4 H, C$_6$H$_4$), 7.24 (d, J = 8.4 Hz, 4 H, C$_6$H$_4$).

Complex 2 was synthesized in analogy to 1 and isolated as a pale yellow powder

Yield: 1.63 g (68.5% related to $CpZrCl_3$). Elemental analysis: $C_{34}H_{30}Cl_4SZr_2$ (%), found: C 51.05, H 4.12; calcd: C 51.37, H 3.80; ^{1}H-NMR (CDCl$_3$, δ, ppm): 3.98 (s, 4 H, CH$_2$), 6.21 (t, J = 2.4 Hz, 4 H, C$_5$H$_4$), 6.34 (t, J = 2.4 Hz, 4 H, C$_5$H$_4$), 6.43 (s, 10 H, C$_5$H$_5$), 7.11 (d, J = 8.4 Hz, 4 H, C$_6$H$_4$), 7.24 (d, J = 8.4 Hz, 4 H, C$_6$H$_4$).

Polymerization

The polymerizations were carried out in a 50-mL glass reactor. A solution of MAO in toluene was saturated with ethylene at 1 bar. Then, the polymerization was initiated by the injection of the catalyst solution. After the reaction mixture was stirred for an appropriate period at the desired temperature, an acidic ethanol containing 10% HCl was added. The precipitated PE was filtered, washed repeatedly with water and ethanol, and then dried to constant weight in vacuum at 60°C.

RESULTS AND DISCUSSION

Synthesis and characterization of the binuclear complexes 1 and 2

In analogy to the recently described synthesis of $[(C_5H_5)Cl_2MC_5H_4CH_2(p\text{-}C_6H_4)]_2O$,[16] the new ligand $[C_5H_5CH_2(p\text{-}C_6H_4)]_2S$ was prepared in a "one pot"
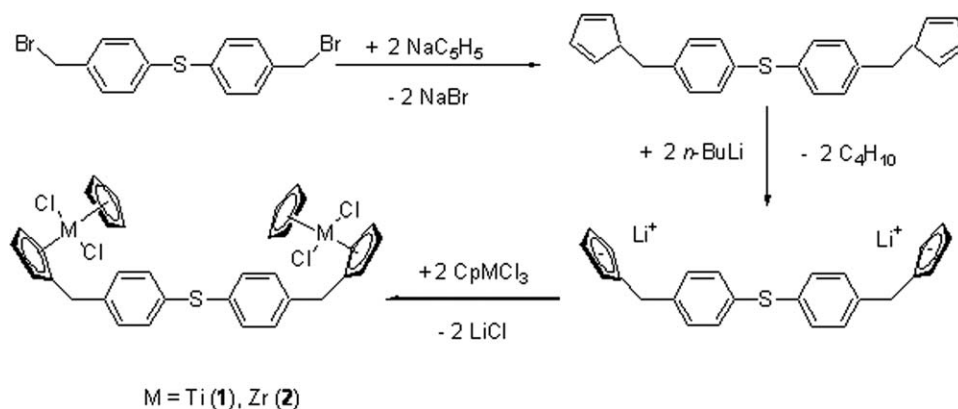
Scheme 1 Synthesis of the binuclear metallocene complexes **1** and **2**.

reaction first by reaction of 4,4-bis(bromomethyl) diphenyl sulfide with two molar equivalents of cyclopentadienyl sodium. After deprotonation of both, cyclopentadienyl ligands using *n*-butyl lithium and reaction with either $C_5H_5TiCl_3$ or $C_5H_5ZrCl_3$ (DME) resulted the related binuclear metallocene complexes $[(C_5H_5)Cl_2TiC_5H_4CH_2(p-C_6H_4)]_2S$ (**1**) and $[(C_5H_5)Cl_2ZrC_5H_4CH_2(p-C_6H_4)]_2S$ (**2**) in yields of 67.4 and 68.5 %, respectively (Scheme 1).

The ^{1}H-NMR spectra show in both cases singlet signals for the terminal cyclopentadienyl ligands and the two methylene groups, two pseudotriplets according to the AABB system of the bridging C_5H_4 groups, and two doublets for the *para*-substituted phenylene unit in the expected range, thus proofing the proposed structure as well as the elemental analysis. Both compounds are sensitive against moisture and air but stable at room temperature.

Homogeneous polymerization of ethylene

The new metallocene complexes **1** and **2** were used for ethylene polymerization in the presence of MAO. The influence of the important reaction parameters, such as the molar ratio [MAO]/[Cat], the catalyst concentration, polymerization temperature, and time have been studied in detail.

Influence of the conditions on ethylene polymerization

The catalytic activity of the metallocene catalysts is strongly dependent on the amount of MAO used for activation. As shown in Figure 1, the activity of both complexes, **1** and **2**, increases rapidly with increasing [MAO]/[Cat] molar ratio, indicating that a high amount of MAO is necessary for the elimination of all kinds of impurities existing in the polymerization medium and especially to generate the catalytic active species. However, the molar ratio of [MAO]/ [Cat] too higher might cause the decrease of catalytic activity. These phenomena of catalytic activity

decrease could be attributed to the formation of inactive species M_t-CH_2-Al by coordination of the oxygen atom of MAO to the complex cation, which was shown by Kaminsky in the study of propene polymerization catalyzed by zirconocene/MAO system.[18]

The molecular weight of the obtained PE increases in both cases constantly until reaching a maximum at a molar ratio [MAO]/[Cat] = 1000 followed by a decrease, which may be due to the excess of MAO causing the chain transfer.

Figure 2 demonstrates the influence of the polymerization temperature on the catalytic activity and the molecular weight of polyethylene. It shows that 0°C is the optimum polymerization temperature for the system **1**/MAO. The activity of this system decreases with increasing polymerization temperature. In contrast, the activity of **2**/MAO increases rapidly between 0 and 60°C, demonstrating that the
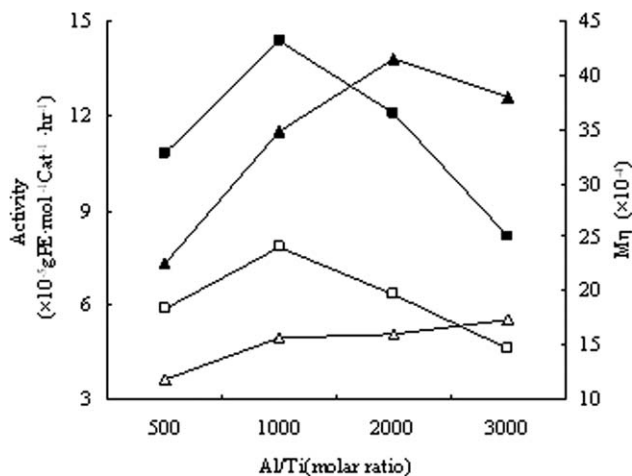

Figure 1 Influence of the [MAO]/[Cat] molar ratio on catalytic activity and molecular weight of PE (△, activity of **1**/MAO; ▲, activity of **2**/MAO; □, Mη of **1**/MAO; ■, Mη of **2**/MAO). Polymerization conditions: [Cat] = 1.0 × 10^{-4} mol/L, T_p = 40°C; t_p = 30 min; P_e = 1 bar, $V_{toluene}$ = 25 mL.
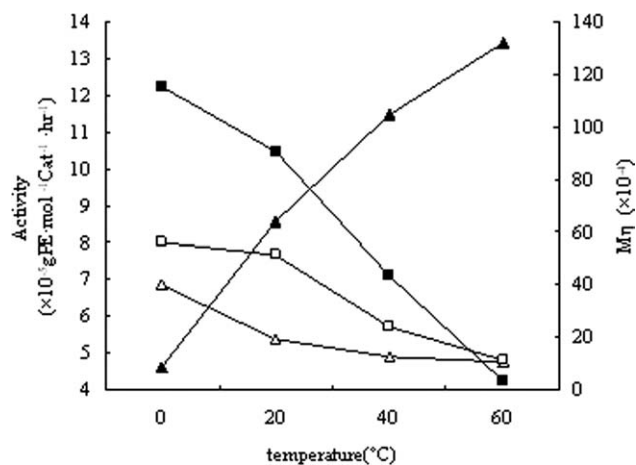
Figure 2 Influence of the polymerization temperature on catalytic activity and molecular weight of PE. ($\triangle$, activity of **1**/MAO; $\blacktriangle$ activity of **2**/MAO; $\square$, Mη of **1**/MAO; $\blacksquare$, Mη of **2**/MAO]. Polymerization conditions: [Cat] $= 1.0 \times 10^{-4}$ mol/L; [MAO]/[Cat] $= 1000$; $t_p = 30$ min; Pe $= 1$ bar; $V_{\text{toluene}} = 25$ mL.

active species of the zirconium complex **2** is more stable than those of the titanium complex **1**. The molecular weight of PE decreases in both cases, but faster using **2**, with increasing polymerization temperature. A competition between the termination and the propagation steps determines the molecular weight of polyethylene. A higher temperature is favorable for increasing the rate of β-hydride chain transfer over the propagation rate causing a polymer with a lower molecular weight.[19]

Figure 3 shows the effect of the catalyst concentration on the polymerization of ethylene. The activity of both systems rises between [Cat] $= 0.5$ and 1.0

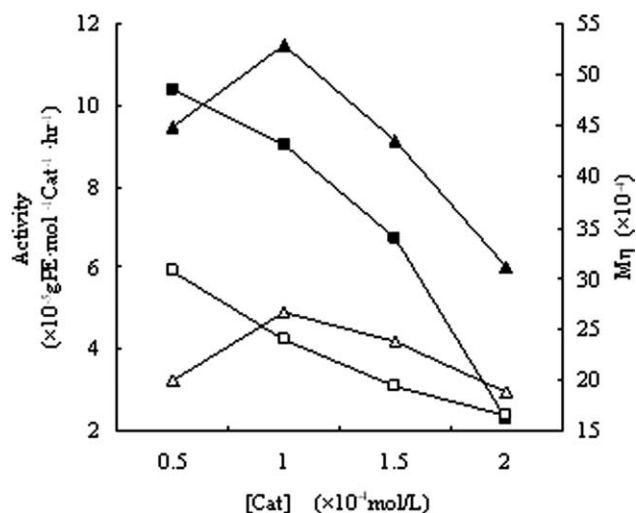**Figure 3** Influence of the catalyst concentration on catalytic activity and molecular weight of PE. ($\triangle$, activity of **1**/MAO; $\blacktriangle$, activity of **2**/MAO; $\square$, Mη of **1**/MAO; $\blacksquare$, Mη of **2**/MAO]. Polymerization conditions: [MAO]/[Cat] $= 1000$, $T_p = 40°C$, $t_p = 30$ min; $P_e = 1$ bar; $V_{\text{toluene}} = 25$ mL.

before it decreases using an increasing catalyst concentration, whereas the molecular weight of PE decreases constantly. Because increasing catalyst concentration implies much more active centers formed in the reaction system, making less ethylene monomers available per mole of active centers, furthermore, it increases the chance of a bimolecular deactivation of the catalyst. Chien[20] and Mülhaupt[4] found a similar phenomenon for the polymerization of propene using Cp_2ZrCl_2/MAO and proposed a mechanism of fast deactivation, which is second order relative to the zirconium catalyst concentration.

It can be found as an interesting phenomenon that the MW of polyethylene showed in both Figures 2 and 3 reveals in general a decreasing trend; however, the reasons for them are different from each other. High temperature causes chain-transfer reaction for former, and the high-concentration catalyst causes deactivation of the catalyst for later.

Figures 2 and 3 show some differences in the developed trends of catalytic activity and molecular weight of polyethylene produced from 1/MAO and 1/MAO. Additionally, it is well acceptable that the catalytic activity of zirconocene is in general higher than titanocene in ethylene or proplene polymerization. All the differences between Ti and Zr could be attributed to the various metals. Both Ti and Zr are the elements in group IV B of the periodic table of the elements. They, although have many similarities, each differs from the other.

Some data listed in Table I indicate that Ti is so much different from Zr and Hf. Jean B showed that zirconium and hafnim are much alike that they always occur together in nature. However, titanium does not occur with zirconium and hafnium. It should be related to lanthanide concentration. As a result of it, the second and third transition series elements of a group have very similar properties, which are different from the properties of the member of the group in the first transition series. For example, the properties of zirconium and hafnium are almost identical but different from the properties of titanium.[21] The great differences between Ti and Zr should display profound effect on the catalytic properties of their metallocene catalytic systems.

TABLE I
Some Data of Ti, Zr, and Hf[21]

Mt	PQN	AR (pm)	EN	SEAM$_t$ $\Delta H_a°$ (kJ/mol)
Ti	4	145	1.3	469
Zr	5	159	1.2	612
Hf	6	156	1.2	611

PQN, principal quantum number; AR, atomic radii (pm); EN, electronegativity; SEAM$_t$, standard enthalpies of atomization of metals $\Delta H_a°$ (kJ/mol).
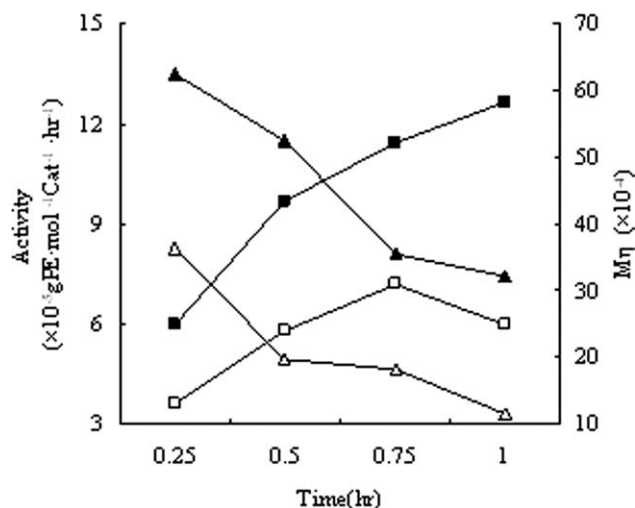
Figure 4 Influence of the polymerization time on catalytic activity and molecular weight of PE. ($\triangle$, activity of **1**/MAO; $\blacktriangle$, activity of **2**/MAO; $\square$, $M\eta$ of **1**/MAO; $\blacksquare$, $M\eta$ of **2**/MAO]. Polymerization conditions: [Cat] = 1.0 × 10^{-4} mol/L, [MAO]/[Cat] = 1000, T_p = 40°C, P_e = 1 bar, $V_{toluene}$ = 25 mL.

The influence of the polymerization time on the ethylene polymerization is depicted in Figure 4. The activity of both catalysts decreases with prolonging reaction time, due to the deactivation of the active centers. The molecular weight of PE is higher using the zirconium complex **2** and constantly increasing during the polymerization time. In contrast, M_η reaches a maximum after 0.75 h using the titanium complex **1** and then reveals a little decrease trend with prolonging polymerization time, which might be arisen from a faster deactivation of **1** compared to **2**.

The catalysts of 1 and 2 with correspondent catalysts Cat 3, Cat 4, and Cat 5 effectly producing polyethylene Cat 5 broad MWD

Table II demonstrates that the catalytic activities of the binuclear metallocene complexes of Ti and Zr as well as the MWD of the produced PE are similar to the results of biphenyl-bridged dinuclear *ansa*-zirconocenes[10] and polymethylene-bridged binuclear zirconocenes.[11] That indicates that optimized bridges in binuclear metallocenes are effective to improve the catalytic properties and broaden the MWD of polyolefins.

Another interesting phenomenon is the fact that the diphenyl ether-bridged binuclear titanocene (Cat 3) as well as the diphenyl thioether-bridged binuclear metallocenes of Ti and Zr (Cat 1 and Cat 2) display higher or slightly higher catalytic activities in comparison with the biphenylene-bridged binuclear metallocenes of Ti and Zr, which should be attributed to the effect of the longer length of the bridge[11] because of the additional heteroatom, oxygen, or sulfur inserted into their bridges.

The larger sulfur atom increases the lengths of the bridge and the lower electronegativity of sulfur causes a smaller inductive effect than oxygen in withdrawing electron density from the cationic active metallocene species.

Table II indicates that polyethylene produced by **1**/MAO and **2**/MAO has a broad MWD. Like in our previous investigations,[3,14,15,22] their higher melting points imply a polyethylene having a long linear chain structure and a lower crystallinity.

CONCLUSIONS

Two new diphenyl thioether-bridged binuclear metallocenes of Ti and Zr have been synthesized and successfully used as catalysts in combination with MAO in ethylene polymerization. The resulting polyethylene has a high-molecular weight and a broad MWD. In comparison with the biphenyl ether-bridged binuclear metallocene of Ti, the thioether-bridged binuclear metallocene complex has a higher catalytic activity, which is in accordance with the anticipation of the results of steric and electronic effects on the active species. The high-melting points of polyethylene obtained from **1**/MAO and **2**/MAO indicate a high linear and crystalline polyethylene.

TABLE II
Comparison of Catalytic Behaviors of Dinuclear Metallocene Catalysts

Entry	[Cat] (10^{-4} mol/L)	n(Al)/n(Cat)	Temp. (°C)	Time (h)	Activity × 10^{-5} g PE/mol Cat h	M_n × 10^{-4}	MWD	T_m (°C)
Cat 1	1.0	1000	40	0.5	4.93	24.06	10.11	130.5
Cat 2	1.0	1000	40	0.5	11.48	34.11	6.02	130.9
Cat 3[16]	1.0	1000	40	0.5	4.02	31.99	6.17	132.1
Cat 4[22]	1.0	1000	40	0.5	3.89	14.70	4.28	134.0
Cat 5[22]	1.0	1000	40	0.5	8.87	17.70	3.18	131.9

Cat 3[16]: $(C_5H_5TiCl_2)_2(C_5H_4CH_2)(p\text{-}C_6H_4)O(C_6H_4\text{-}p)(CH_2C_5H_4)$.
Cat 4[22]: $(CpTiCl_2)_2[C_5H_4CH_2C_6H_4\text{-}p\text{-}C_6H_4CH_2C_5H_4]$.
Cat 5[22]: $(CpZrCl_2)_2[C_5H_4CH_2C_6H_4\text{-}p\text{-}C_6H_4CH_2C_5H_4]$.
Polymerization conditions: P_e = 1 bar, $V_{toluene}$ = 25 mL.

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