

SYNTHESIS OF NOVEL THIOPHENEDIMETHYLENE BRIDGED HOMOBINUCLEAR METALLOCENES AND THEIR CATALYTIC PROPERTIES FOR ETHYLENE POLYMERIZATION*

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Abstract By treating disodium(thiophenedimethylene)dicyclopentadienide $C_4H_2S(CH_2C_5H_4Na)_2$ with two equivalent of $CpTiCl_3$ or $CpZrCl_3$ DME at $0^\circ C$ in THF, two new thiophenedimethylene bridged binuclear metallocenes $[Cl_2MC_5H_5][C_5H_4CH_2C_4H_2SCH_2C_5H_4][C_5H_5MCl_2]$ ($M = Ti$ **3**, $M = Zr$ **4**) were synthesized in high yield and their structures were characterized by ^1H -NMR. These complexes were used as catalysts for ethylene polymerization in the presence of methylaluminoxane (MAO). The effects of polymerization temperature, time, concentration of catalyst, molar ratio of MAO/Cat on polymerization were studied in detail. The catalytic activities of thiophenedimethylene bridged binuclear metallocene catalysts (**3**, **4**) reached 2.44×10^5 g PE $mol^{-1} \cdot cat^{-1} \cdot h^{-1}$, 9.61×10^5 g PE $mol^{-1} \cdot cat^{-1} \cdot h^{-1}$ respectively, which are higher than that of phenyldimethylene bridged binuclear metallocene catalysts and much higher than that of corresponding mononuclear metallocenes (Cp_2TiCl_2 and Cp_2ZrCl_2). The molecular weight distribution curves of polyethylenes produced by binuclear metallocene catalysts (**3**, **4**) and by mononuclear metallocene catalyst have only single peak, but the former ($MWD = 3.5\text{--}4.7$) is obviously broader than the latter ($MWD = 2.0\text{--}2.2$).

Keywords: Binuclear metallocene; Thiophenedimethylene bridged; Ethylene polymerization.

INTRODUCTION

Metallocene activated with methylaluminoxane (MAO) are well known, highly active homogeneous Ziegler-Natta catalysts that produce polyolefins with controlled stereo-regularity and narrow molecular weight distributions^[1–3]. However, these molecular characters can be disadvantageous for industrial processing, such as causing high shear viscosity and low melt extensional viscosity of the product. In order to overcome these problems, recently a variety of binuclear metallocene compounds, which contain two mechanically linked metallocene unit, have been prepared to examine their catalytic properties since binuclear complexes could be potentially useful as a new polymerization catalysts which is operated on the cooperative electronic and chemical interaction between two centers. Presently, it can be divided roughly into two kinds of bridges in binuclear metallocene catalysts, namely flexible bridge as polymethylene^[4, 5], polysiloxane^[6, 7] and rigid bridge containing phenyl ring or double bridges^[8, 9]. Our research interest is focused on the binuclear metallocene containing rigid bridge, which could avoid the bimolecular deactivation^[10]. To our knowledge, the synthesis as well as the polymerization of thiophenedimethylene bridged binuclear metallocene has never been reported in literature. In the present paper, the synthesis of two new bridged homobinuclear compounds $[Cl_2MC_5H_5][C_5H_4CH_2C_4H_2SCH_2C_5H_4][C_5H_5MCl_2]$ ($M = Ti$ **3** and $M = Zr$ **4**) and the effects of all variants on ethylene polymerization are reported.

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EXPERIMENTAL

All manipulations of air-sensitive materials were performed in thoroughly dried Schlenk-type glassware under strict exclusion of oxygen and moisture by connecting to a high vacuum line.

Materials

THF and toluene were distilled under argon from sodium benzophenone ketyl prior to use. Methylene chloride was distilled under argon from CaH_2 . Other solvents were dried and distilled according to standard methods before use. Methylaluminoxane (MAO) (10 wt% in toluene) was provided by Witco. Ethylene (polymer grade) was purified by bubbling through triisobutylaluminum in toluene.

Measurements

^1H -NMR spectra were recorded on a Bruker Advance DMX500 spectrometer at an ambient temperature. Chemical shifts were referenced with respect to tetramethylsilane. EI mass spectra were measured on a HP 6890/5973 GC-MS instrument, 70 eV, 50–270°C. The viscosity of polyethylene was measured in decahydronaphthalene at 135°C by a modified Ubbelohde-type viscometer and the molecular weight was calculated according to $[\eta] = 6.67 \times 10^{-4} M_w^{0.67}$ (mL/g). Molecular weight distribution of some polymers were determined by using gel-permeation chromatography (GPC, Waters 150) at 135°C using standard polystyrene as calibration reference. The melting temperature of the polymer was measured by differential scanning calorimetry (Perkin Elmer DSC-7).

Synthesis

Synthesis of starting materials

Compounds CpTiCl_3 ^[11], CpZrCl_3 DME^[12] and 2,5-bis(chloromethyl)thiophene^[13] were synthesized according to the literatures: CpZrCl_3 DME. ^1H -NMR (500 MHz, CDCl_3 , δ): 3.88 (brs, 6H, $2 \times \text{OCH}_3$), 4.10 (brs, 4H, $2 \times \text{OCH}_2$), 6.69 (s, 5H, C_5H_5). $\text{C}_4\text{H}_2\text{S}$ (CH_2Cl)₂: ^1H -NMR (500 MHz, CDCl_3 , δ): 4.89(s, 4H, $2 \times \text{CH}_2\text{Cl}$), 7.01 (s, 2H, $\text{C}_4\text{H}_2\text{S}$). *m/z* (%): (M^+ , 181, 21), ($\text{M}^+ - \text{Cl}$, 145, 100), ($\text{M}^+ - 2\text{Cl}$, 110, 65).

Synthesis of 2,5-bis(cyclopentadienylmethyl)thiophene(**1**) $\text{C}_4\text{H}_2\text{S}(\text{CH}_2\text{C}_5\text{H}_5)$

2,5-bis(chloromethyl)thiophene (1.5 g, 8.3 mmol) in 30 mL THF was added to a solution of cyclopentadienyl-sodium (16.6 mmol) in 20 mL THF at -78°C with stirring. The temperature of the reaction mixture was allowed to rise gradually to 0°C . The mixture was stirred for an additional 45 min at 0°C and then filtered. The NaCl formed was washed with 2×7 mL of THF and the filtrated solution was added to the filtrate. The remaining NaCl was dried under vacuum and could be isolated in nearly-quantitative yields (95%–98%).

Synthesis of disodium(thiophenedimethylene)dicyclopentadienide $\text{C}_4\text{H}_2\text{S}(\text{CH}_2\text{C}_5\text{H}_4\text{Na})_2$

The yellow filtrate containing **1** was added with stirring over a 25 min period to a suspension of sodium hydride (2.0 g) in 10 mL of THF at 0°C . The reaction mixture was allowed to warm up to room temperature after completion of the addition and stirred until no gas was evolved. The mixture was then filtered and the clear, orange filtrate was used *in situ* for further reactions. Like other cyclopentadienide salts, **2** is very air sensitive and the color of the solution may be varied from orange to reddish brown.

Synthesis of $[\text{Cl}_2\text{MC}_5\text{H}_5][\text{C}_5\text{H}_4\text{CH}_2\text{C}_4\text{H}_2\text{SCH}_2\text{C}_5\text{H}_4][\text{C}_5\text{H}_5\text{MCl}_2]$ ($\text{M}=\text{Ti}$ **3**, $\text{M}=\text{Zr}$ **4**)

To a solution of CpTiCl_3 (3.64 g, 16.6 mmol) or CpZrCl_3 DME (5.86 g, 16.6 mmol) in THF (30 mL), the filtrate **2** was added dropwise over a period of 0.5 h at 0°C with stirring. After stirring at room temperature overnight, the solvent was removed under vacuum, and the residue was extracted with methylene chloride. The solution was concentrated and cooled to -15°C yielding the compound.

Compound **3**: red powder, yield 2.69 g (53.4 %), ^1H -NMR (500 MHz, CDCl_3 , δ): 4.21 (s, 4H, $2 \times \text{CH}_2$), 6.37 (t, 2.5 Hz, 4H, C_5H_4), 6.42 (t, 2.5 Hz, 4H, C_5H_4), 6.53 (s, 10H, $2 \times \text{C}_5\text{H}_5$), 6.68 (m, 2H, $\text{C}_4\text{H}_2\text{S}$).

Compound **4**: white powder, yield 2.75 g (47.8 %), ^1H -NMR (500 MHz, CDCl_3 , δ): 4.12 (s, 4H, $2 \times \text{CH}_2$), 6.26 (t, 2.6 Hz, 4H, C_5H_4), 6.35 (t, 2.6 Hz, 4H, C_5H_4), 6.49 (s, 10H, $2 \times \text{C}_5\text{H}_5$), 6.64 (m, 2H, $\text{C}_4\text{H}_2\text{S}$).

Following the procedure described above, phenylenedimethylene bridged binuclear compounds **5** and **6** have been synthesized.

Compound **5**: red powder, yield 1.58 g (40.5 %), $^1\text{H-NMR}$ (CDCl_3 , 20°C , δ): 4.08 (s, 4H, $2 \times \text{CH}_2$), 6.36 (t, 2.5 Hz, 4H, C_5H_4), 6.44 (t, 2.5 Hz, 4H, C_5H_4), 6.51 (s, 10H, $2 \times \text{C}_5\text{H}_5$), 7.10 (m, 4H, C_6H_4).

Compound **6**: white powder, yield 1.94 g (49.7 %), $^1\text{H-NMR}$ (CDCl_3 , 20°C , δ): 3.97 (s, 4H, $2 \times \text{CH}_2$), 6.22 (t, 2.6 Hz, 4H, C_5H_4), 6.33 (t, 2.6 Hz, 4H, C_5H_4), 6.49 (s, 10H, $2 \times \text{C}_5\text{H}_5$), 7.13 (m, 4H, C_6H_4). MS (m/e , %): (M^+ , 686.9), (620.6, 4.5), (421.8, 20.5), (385.9, 7.1), (357.8, 14.7), (330.8, 21.1), (291.7, 19.2), (254.8, 10.9), (226.7, 63.5), (206.9, 25), (163.8, 15.4), (152.8, 12.2), (104.9, 12.8), (65.0, 48.1), (43.8, 100).

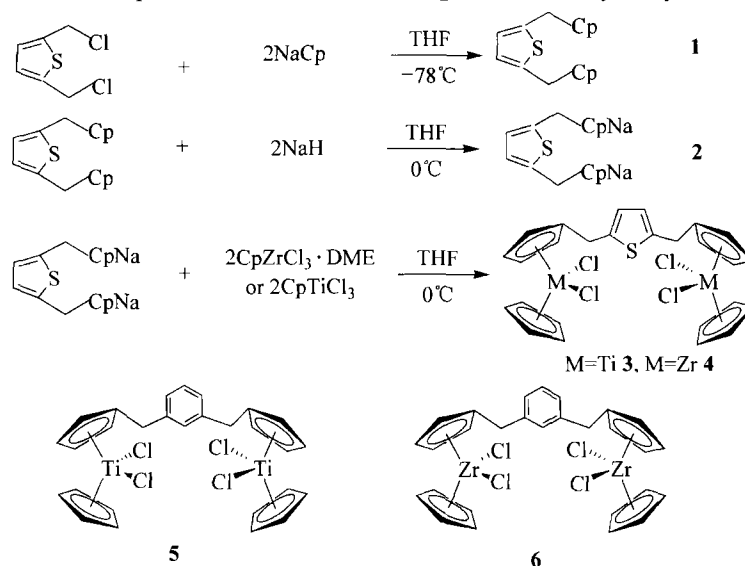
Polymerization

Polymerizations were carried out in a 50 mL Schlenk flask, which was first evacuated and flushed with argon thoroughly. The catalyst solution in toluene was introduced into the flask and then saturated with ethylene. After reaching the given temperature, MAO solution was injected into the reaction system. Ethylene was introduced into the flask with stirring. The polymerization mixture was quenched by the addition of acidic ethanol (containing 10% HCl), filtered, washed with excess ethanol and dried at 60°C in vacuum to a constant weight.

RESULTS AND DISCUSSION

Preparation of Binuclear Catalysts **3** and **4**

The bridged binuclear catalysts **3** and **4** could be prepared according to the reaction routes shown in Scheme 1. The yield of the ligand **1** depends on the order of addition and the reaction temperature. When cyclopentadienylsodium (CpNa) was added to 2,5-bis(chloromethyl)thiophene in THF solution over 0°C with stirring, the yield of ligand **1** decreased due to a competing intramolecular cyclization^[14]; if the reaction was carried out between -78°C and 0°C with adding 2,5-bis(chloromethyl)thiophene to cyclopentadienylsodium in THF, the ligand **1** could be obtained in nearly quantitative yield. The product was not isolated and used directly for the next reaction step. The $^1\text{H-NMR}$ spectra of the new complexes **3** and **4** are similar and show one CH_2 singlet, a singlet due to C_5H_5 , one $\text{C}_4\text{H}_2\text{S}$ singlet and two pseudo triplets corresponding to the A_2B_2 pattern for the bridged C_5H_4 groups^[15]. Because the compounds are air-sensitive, the good elementary analysis data was not obtained.



Scheme 1 Route of synthesis of complexes

Influences of Conditions on Ethylene Polymerization

Complexes **3** and **4** were studied as catalysts in combination with MAO for ethylene polymerization. In order to fully understand the effects of experimental parameters on the polymerization, variation in molar ratio of MAO/Cat, time, temperature and catalyst concentration on ethylene polymerization have been examined in detail.

The dependences of activities and polymer molecular weights on the MAO/Cat molar ratio were presented in Fig. 1. The catalytic activity of complex **4** increases with MAO/Cat molar ratio up to 1000, after which the catalytic activity decreases, but the activity of catalyst **3** increases consistently with increasing MAO/Cat molar ratio. A high MAO/Cat molar ratio is necessary for eliminating all kinds of impurities existing in the polymerization medium and generating the active species. But a MAO/Cat molar ratio higher than 1000 contributes to the reversible deactivation of active centers due to the coordination of the oxygen atoms of MAO to the complex cation or a deactivation process, in which inactive $\text{Zr}-\text{CH}_2-\text{Al}$ might be formed by the evolution of methane, as shown by Kaminsky^[16]. The molecular weight of the polymer obtained by catalyst **4** increases rapidly with increasing MAO/Cat molar ratio upto a maximum and then decreases rapidly at MAO/Cat molar ratio greater than 1000, however there is no apparent effect on the molecular weight of the polymer obtained by catalyst **3** with increasing MAO/Cat molar ratio continuously in the examined region. Increasing the MAO amount, the rate of chain propagation increases also, so the molecular weight of the polymer will rise. However, the excess of MAO may result in increasing the rate of chain transfer, so the molecular weight of the polymer will decrease.

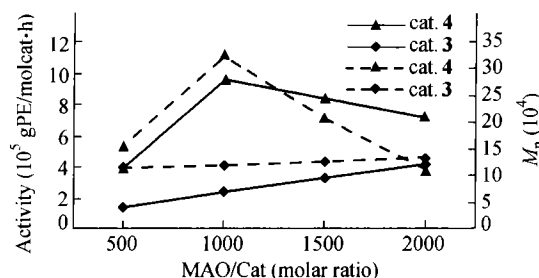


Fig. 1 Influences of MAO/Cat molar ratio on catalytic activity and molecular weight of polyethylene
Solid line denotes activity and dotted line denotes molecular weight of polyethylene.

Polymerization conditions: $[\text{Cat.}] = 1 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$, $T = 40^\circ\text{C}$, $t = 0.5 \text{ h}$, 10^5 Pa , $V(\text{toluene}) = 25 \text{ mL}$

The results of the effects of polymerization time were shown in Fig. 2. It can be seen that the catalyst activity of complex **4** increases rapidly to a peak value roughly within 0.5 h, after which the activity drops, due probably to a deactivation of catalyst. Meanwhile, the activity of complex **3** keeps at a lower level with prolonging polymerization time. In propene polymerization catalyzed by bimetallic zirconium/MAO, Jüling^[17] observed that the initial polymerization rate decreased after a few minutes. Therefore, the catalytic systems we have employed are much more stable. The molecular weight of polyethylene obtained by using catalyst **4** shows a maximum value at 0.5 h. The reason may be that the polymer chains are isolated from the active species and only some of this active species continue to catalyze ethylene polymerization in the catalyst **4** system. The molecular weight increases gradually in the case of catalyst **3**.

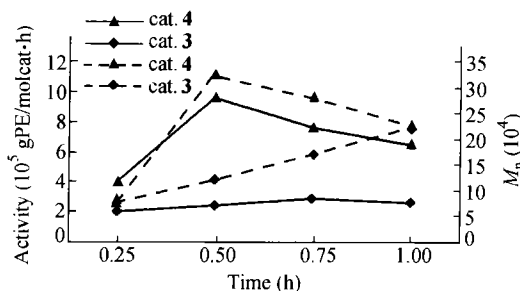


Fig. 2 Influences of polymerization time on catalytic activity and molecular weight of polyethylene
Solid line denotes activity and dotted line denotes molecular weight of polyethylene.

Polymerization conditions: $[\text{Cat.}] = 1 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$, MAO/Cat = 1000, $T = 40^\circ\text{C}$, 10^5 Pa , $V(\text{toluene}) = 25 \text{ mL}$

Figure 3 demonstrates the influences of polymerization temperature on activity and polymer molecular weight. It can be found that both catalysts **3** and **4** have an optimum polymerization temperature, at 60 and 40°C, respectively. This may results from a decreasing ethylene solubility in toluene at higher temperature in combination with a deactivation process due to the poor thermal stability of the cationic methyl complex^[18]. The molecular weight of the polymer also significantly depends upon the polymerization temperature because there is a competition between the chain transfer and chain propagation. Higher temperature favors the β -hydrogen chain transfer and forms lower molecular weight polymer in hence.

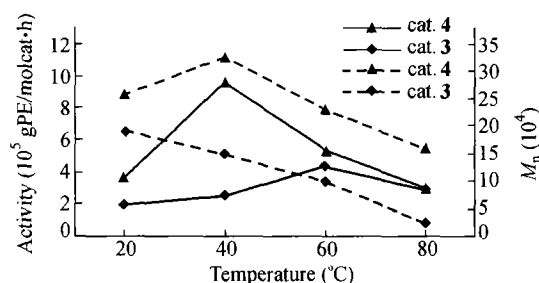


Fig. 3 Influences of polymerization temperature on catalytic activity and molecular weight of polyethylene

Solid line denotes activity and dotted line denotes molecular weight of polyethylene.

Polymerization conditions: [Cat.] = 1×10^{-4} mol $\cdot$ L $^{-1}$, MAO/Cat = 1000, t = 0.5 h, 10^5 Pa, V (toluene) = 25 mL

Figure 4 shows the results of the effects of catalyst concentration on polymerization. It is clear that the activity of catalyst **4** increases with catalyst concentration and reaches a maximum value at 1.0×10^{-4} mol/L, then declines. Moreover, the molecular weight of the polymer obtained by catalysts **4** has an almost same trend. However, the catalytic activity of catalyst **3** does not change obviously, while the molecular weight of the polymer decreases monotonously.

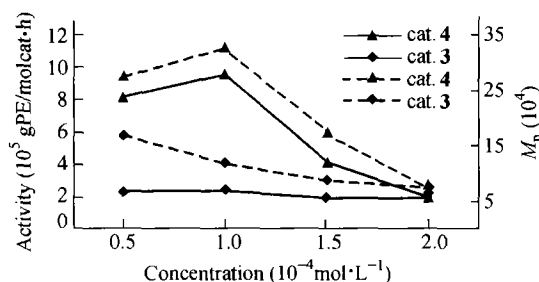


Fig. 4 Influences of catalyst concentration on catalytic activity and molecular weight of polyethylene

Solid line denotes activity and dotted line denotes molecular weight of polyethylene.

Polymerization conditions: MAO/Cat = 1000, T = 40°C, t = 0.5 h, 10^5 Pa, V (toluene) = 25 mL

Comparison of Catalytic Behaviors of Complexes **3**, **4**, **5**, **6** and Mononuclear Metallocene

From the polymerization results listed in Table 1, we observed that the thiophenedimethylene bridged binuclear metallocene catalysts are more active than the phenylenedimethyl bridged binuclear metallocene catalysts (**3** > **5**, **4** > **6**). Generally speaking, the activity increases with increasing of electron density at the metal atom^[19], because increasing of electron density lowers the stability of the η^2 -alkene-metal bond resulting in a more weakly coordinated monomer, facilitating insertion into the growing polymer chain. Alternatively, or, in addition, a higher electron density at the metal atom may weaken the metal-carbon σ -bond of the growing polymer chain, which could also facilitate the insertion of the monomer and hence lead to an increased rate of polymerization. In the case of catalysts **3** and **4**, hyperconjugative effect of thiophene ring is better than that of phenylene, so they are more active than catalysts **5** and **6**, respectively. It also can be found that the binuclear zirconium catalysts are more active than the binuclear titanium catalysts. It is in good agreement with the general concepts of catalytic

behaviors of metallocene catalysts. The difference may be attributed to the larger number of active centers present in zirconium catalysts^[19]. In addition, Table 1 also indicates that the activity of binuclear metallocene is higher than that of mononuclear metallocene catalyst. It agrees with our expectation, rigid bridges might decrease the rate of deactivation reaction.

Table 1. The results of GPC and DSC

Catalyst	[Cat.] ($10^{-4} \text{ mol} \cdot \text{L}^{-1}$)	$n(\text{Al})/$ $n(\text{Cat.})$	Temp. ($^{\circ}\text{C}$)	Time (h)	Activity (10^5 gPE $\text{mol}^{-1} \cdot \text{cat}^{-1} \cdot \text{h}^{-1}$)	$M_n (10^5)$	T_m ($^{\circ}\text{C}$)	MWD
Cat.3	1.0	1000	40	0.50	2.44	1.21	132.2	4.74
Cat.4	1.0	1000	40	0.50	9.61	3.26	131.0	3.48
Cat.5	1.0	1000	40	0.50	1.18	3.94	130.7	4.23
Cat.6	1.0	1000	40	0.50	6.40	3.16	132.0	4.88
Cp_2TiCl_2	2.0	1000	40	0.50	0.80	2.03	131.6	2.15
Cp_2ZrCl_2	2.0	1000	40	0.50	3.52	2.30	131.0	2.02

Polymerization conditions: $V(\text{toluene}) = 25 \text{ mL}$, 10^5 Pa

The molecular weight distributions (M_w/M_n) of some polymers were measured by gel permeation chromatography (GPC) and the results are shown in Table 1. The molecular weight distributions of the polyethylene produced by catalysts **3** and **4** are broader than that produced by mononuclear metallocene catalyst. This fact was reported by others as well^[20]. Although there are two metals in one binuclear metallocene catalyst, there is no direct evidence for a bimodal distribution (Figs. 5 and 6). These results may indicate that the interaction between two metals creates more than one kind of active species during the polymerization^[21], but the difference between two active species is not enough to produce polyethylene with bimodal distribution. The melting points of polyethylene are $130\text{--}133^{\circ}\text{C}$, which means that the polymers are highly linear and highly crystalline^[22].

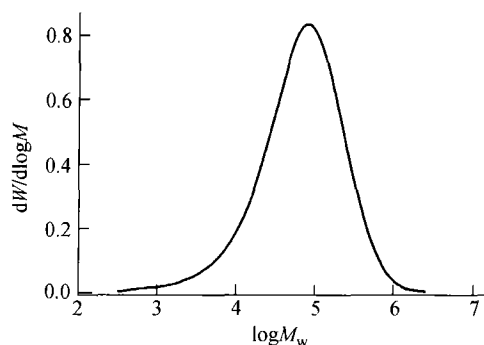


Fig. 5 GPC curve of polyethylene produced by complex **3** ($MWD = 4.74$)

Polymerization conditions: $[\text{cat}] = 1.0 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$, $\text{MAO/Cat} = 1000$, $T = 40^{\circ}\text{C}$, $t = 0.5 \text{ h}$, 10^5 Pa , $V(\text{toluene}) = 25 \text{ mL}$

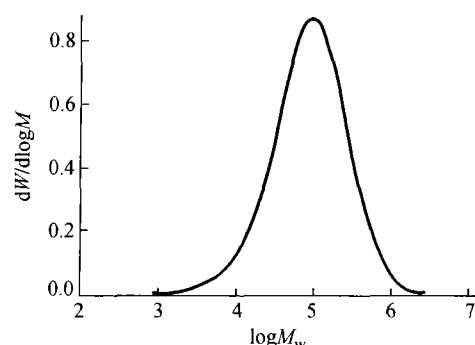


Fig. 6 GPC curve of polyethylene produced by complex **4** ($MWD = 3.48$)

Polymerization conditions: $[\text{cat}] = 1.0 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$, $\text{MAO/Cat} = 1000$, $T = 40^{\circ}\text{C}$, $t = 0.5 \text{ h}$, 10^5 Pa , $V(\text{toluene}) = 25 \text{ mL}$

CONCLUSIONS

The novel thiophenedimethylene and phenylenedimethylene bridged homobinuclear metallocenes **3**, **4**, **5** and **6** were synthesized and studied as catalysts for ethylene polymerization in the presence of MAO. The catalytic activity of thiophenedimethylene bridged binuclear metallocene catalysts are higher than that of phenyldimethylene bridged analogous. The GPC spectra of the polymers produced by the binuclear metallocene catalyst show obviously broader molecular weight distributions than that of polyethylene produced by mononuclear metallocene catalyst.

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