Ethylene Polymerization by Phenylenedimethylene-Bridged Homobinuclear Zirconocene/Methylaluminoxane Systems

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ABSTRACT: In the presence of methylaluminoxane (MAO), ethylene polymerization was successfully performed with homobinuclear zirconocene complexes {[(C$_5$H$_5$)ZrCl$_2$](C$_5$H$_4$CH$_2$C$_6$H$_4$CH$_2$C$_5$H$_4$)[(C$_5$H$_5$)ZrCl$_2$]; **3o**, **4m**, and **5p**}, which were prepared conveniently by the reaction of disodium(phenylenedimethylene)dicyclopentadienide [C$_6$H$_4$(CH$_2$C$_5$H$_4$Na)$_2$] with 2 equiv of (N^5-Cyclopentadienyl)trichlorozirconium dimethoxyethane (CpZrCl$_3$(DME)) in tetrahydrofuran and characterized by ^{1}H-NMR and elemental analysis. The effects of the polymerization parameters, such as the temperature, time, concentration of the catalyst, MAO/catalyst molar ratio, and isomeric difference of the homobinuclear metallocene complexes **3o**, **4m**, and **5p** were studied in detail. The results showed that all three catalytic systems had moderate activities in ethylene polymerization and afforded polyethylene with relatively broad polydispersities. The catalytic activity of **4m** was somewhat higher than that of **3o** and **5p** but lower than that of 4,4′-bis(methylene)biphenylene-bridged zirconocene catalysts; this indicated that the distance between the two metal centers was too short in comparison with a 4,4′-bis(methylene)biphenylene bridge to increase the catalytic activity. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 2193–2198, 2006

Key words: metallocene catalysts; molecular weight distribution/molar mass distribution; polyethylene (PE)

INTRODUCTION

Binuclear metallocenes possessing a unique synergism[1] of two metal centers have received much attention because of their special catalytic behavior, such as high catalytic activity, producing polymers with high molecular weights and broad or even bimodal molecular weight distributions (MWDs),[2–8] high incorporation of styrene,[9] hexene, and pentene in copolymers of ethylene, and significant importance in polymer microstructures.[2] These interesting catalytic properties are the results of cooperative effects between two metals, the ligand structures, and the nature of the bridge. Until now, bridges used to link two cyclopentadienyl rings or their derivatives could be divided roughly into two classes: flexible bridges such as polymethylene[10] and polysiloxane[11,12] and rigid bridges containing a phenyl ring[13] or double linkages.[14,15] In flexible bridged binuclear metallocene complexes, the two active metal centers have little restriction to being held in close proximity because of the free movement of the bridge, as shown by Noh and coworkers.[14,15] They studied doubly bridged binuclear titanocenes and found that the second bridging bialkoxy-terminated ligands likely exerted a more pronounced influence than the first polymethylene bridges on the catalytic activity and the stereochemistry of the polymers produced. Obviously, the introduction of the second bridge, which provides more rigidity to the whole molecule, is one of the important reasons for improving the catalytic activity. In other words, from the perspective of bimolecular deactivation,[16] the rigidified double bridges limit the free movement of both moieties, and this helps to increase the catalytic lifetime. In addition, the rigidified double bridges avoid overcrowding of the active centers and benefit the coordination of the monomers to the metals. In consideration of increasing the rigidity of the bridge, binuclear metallocenes containing a phenylene bridge are worthy of study. Moreover, some other advantages, such as relatively simple synthesis, convenient modification, clear electronic and steric effects, and easy tuning of the distance between two active centers, have attracted our interest in the application of phenylene-bridged binuclear metallocenes in ethylene po-

lymerization. Similar phenylenedimethylene-bridged homobinuclear titanocenes have been reported in the literature, however, they have never been used as catalysts for olefin polymerization[17] or studied systematically in ethylene polymerization.[18]

This article presents the preparation of three isomers of homobinuclear zirconocenes and their application as catalysts activated by methylaluminoxane (MAO) in ethylene polymerization.

EXPERIMENTAL

All manipulations of air-sensitive materials were performed with rigorous exclusion of oxygen and moisture in thoroughly dried Schlenk-type glassware on a high-vacuum line.

Materials

Tetrahydrofuran (THF) and toluene were distilled under argon from sodium benzophenone ketyl before use, and methylene chloride was distilled under argon from CaH_2. Other solvents were dried and distilled according to standard methods and were collected before use. MAO (10 wt % in toluene) was provided by Witco (Milwaukee, WI). Ethylene (polymer-grade) was purified via bubbling through triisobutylaluminum in toluene.

Measurements

^{1}H-NMR spectra were recorded on a Bruker Avance DMX500 spectrometer (Madison, WI) at the ambient temperature, and the chemical shifts were referenced with respect to tetramethylsilane. Electron impact mass spectra were measured on an HP 6890/5973 gas chromatography/mass spectrometry instrument (70 eV, 50–270°C) (Miami, FL), mass spectra used for measuring metal complex were performed on Varian MAT 311 A spectrometer, electron impact ionization (El.70 eV) and elemental analysis was conducted on a PerkinElmer 240 elemental analyzer (Shelton, CT). The molecular weight of polyethylene was measured in decahydronaphthalene at 135°C with a modified Ubbelohde-type viscometer according to $[\eta] = 6.67 \times 10^{-4} M_\eta^{0.67}$ (mL/g). MWDs of some polymers were determined by gel permeation chromatography (GPC; model 150, Waters; 135°C) with polystyrene columns as a standard. The melting temperatures (T_m's) of the polymers were measured with differential scanning calorimetry (DSC; DSC-7, PerkinElmer).

Synthesis

Synthesis of the starting materials

$CpZrCl_3(DME)$[19] and $C_6H_4(CH_2Br)_2$[20] were synthesized according to literature methods.

CpZrCl₃(DME) ^{1}H-NMR (500 MHz, CDCl$_3$, δ, ppm): 3.88 (brs, 6H, 2 × OCH$_3$), 4.10 (brs, 4H, 2 × OCH$_2$), 6.69 (s, 5H, C$_5$H$_5$) 1,2-Bis(bromomethyl)benzene *m/z*: m$^+$, 264. mp: 96–97°c. 1,3-bis(bromomethyl)benzene *m/z*: m$^+$, 264. mp: 71–72°c. 1,4-bis(bromomethyl)benzene *m/z*: m$^+$, 264. mp: 144–146°c.

Synthesis of bis(cyclopentadienylmethyl)benzenes [$C_6H_4(CH_2C_5H_5)_2$; **1o, 1m,** and **1p**]

1,2-Bis(bromomethyl)benzene (1.5 g, 5.68 mmol) in 30 mL of THF was added to a solution of cyclopentadienylsodium (11.37 mmol) in 20 mL of 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 NaBr that formed was washed with 7 mL of THF twice, and the filtered solution was added to the filtrate. The remaining NaBr was dried in vacuo (95–98% yield).The same procedure was used to prepare **1m** and **1p**.

Synthesis of disodium(phenylenedimethylene) dicyclopentadienides [$C_6H_4(CH_2C_5H_4Na)_2$; **2o, 2m,** and **2p**]

Yellow filtrates containing **1o, 1m**, and **1p** were 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 mixtures were allowed to warm to room temperature after the completion of the addition and were stirred for an additional 45 min until no gas evolved. The mixtures were then filtered, and the clear, orange filtrates were used in situ for further reactions. Like other cyclopentadienide salts, **2o, 2m**, and **2p** were very air-sensitive, and the color of the solutions varied from faint orange to reddish brown.

Synthesis of [$(C_5H_5)ZrCl_2$]($C_5H_4CH_2C_6H_4CH_2C_5H_4$)[$(C_5H_5)ZrCl_2$] (**3o, 4m,** and **5p**)

To a solution of CpZrCl$_3$(DME) (4.01 g, 11.37 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 in vacuo, and the residues were extracted with methylene chloride. The solution was concentrated and cooled to −15°C, and this yielded the products as white solids.

Compound **3o** Yield: 1.76 g (45.2%). ANAL. Calcd for C$_{28}$H$_{26}$Cl$_4$Zr$_2$: C, 48.97%; H, 3.82%. Found: C, 48.68%; H, 4.18%. ^{1}H-NMR (CDCl$_3$, 20°C, δ, ppm): 4.01 (s, 4H, 2 × CH$_2$), 6.18 (t, *J* = 2.6 Hz, 4H, C$_5$H$_4$), 6.32 (t, *J* = 2.6 Hz, 4H, C$_5$H$_4$), 6.46 (s, 10H, 2 × C$_5$H$_5$), 7.15 (m, 4H, C$_6$H$_4$). Mass spectrometry: [*m/z* (%)]: 686.9 (5.4) [M]$^+$, 421.9 (9.1), 385.6 (6.6), 356.8 (100), 354.8 (10.2), 321.0
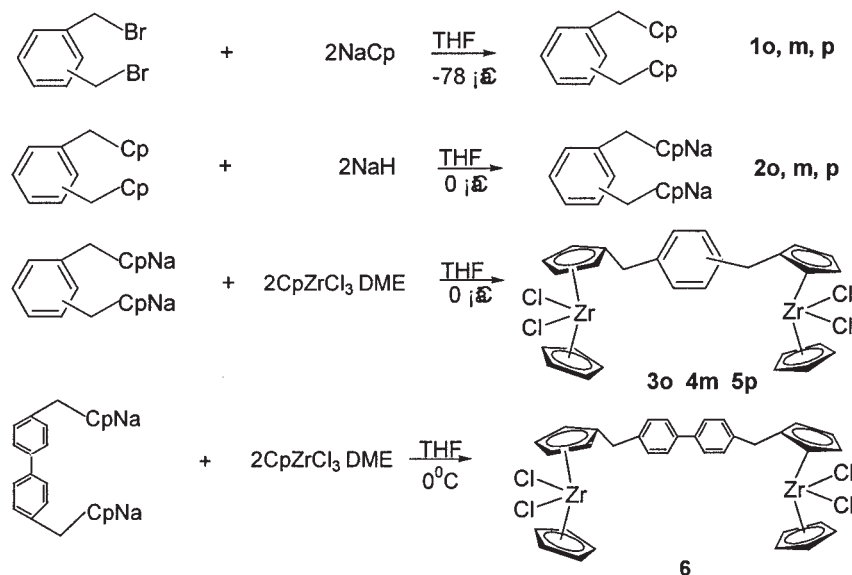
Scheme 1

(62.1), 278.9 (15.7), 252.7 (12.1), 226.8 (14.5), 192.9 (7.2), 165.0 (6.0), 159.9 (8.4), 65 (12.6), 38.9 (10.8).

Compound **4m** Yield: 1.58 g (40.5%). ANAL. Calcd for $C_{28}H_{26}Cl_4Zr_2$: C, 48.97%; H, 3.82%. Found: C, 48.71%; H, 4.05%. ^{1}H-NMR (CDCl$_3$, 20°C, δ, ppm): 3.97 (s, 4H, 2 × CH$_2$), 6.22 (t, J = 2.6 Hz, 4H, C$_5$H$_4$), 6.34 (t, J = 2.7 Hz, 4H, C$_5$H$_4$), 6.42 (s, 10H, 2 × C$_5$H$_5$),7.06 (m, 4H, C$_6$H$_4$). Mass spectrometry [m/z (%)]: 686.9 (6.5) [M]$^+$, 649.8 (6), 620.7 (25.7), 421.9 (75.4), 385.9 (13.2), 356.8 (98.2), 320.9 (100), 354.8 (6.0), 291.8 (15), 254.8 (6.6), 226.8 (27.5), 65.0 (4.8), 38.9 (7.2).

Compound **5p** Yield: 1.94 g (49.7%). ANAL. Calcd for $C_{28}H_{26}Cl_4Zr_2$: C, 48.97%; H, 3.82%. Found: C, 48.60%;

H, 4.10%. ^{1}H-NMR (CDCl$_3$, 20°C, δ, ppm): 3.97 (s, 4H, 2 × CH$_2$), 6.22 (t, J = 2.6 Hz, 4H, C$_5$H$_4$), 6.33 (t, J = 2.6 Hz, 4H, C$_5$H$_4$), 6.49 (s, 10H, 2 × C$_5$H$_5$), 7.13 (m, 4H, C$_6$H$_4$). Mass spectrometry [m/z (%)]: 686.9 (7.2) [M]$^+$, 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).

Compound **6** With the procedure in analogy to **3p**, compound **6** was synthesized from CpZrCl$_3$(DME) (5.64 g, 16 mmol)) in THF (30 mL) and NaC$_5$H$_4$CH$_2$–C$_6$H$_4$-p-C$_6$H$_4$–CH$_2$C$_5$H$_4$Na (8 mmol).

ANAL. Calcd: C, 53.53%; H, 3.96%. Found: C, 53.42%; H, 4.03%. ^{1}H-NMR (CDCl$_3$, 20°C, δ, ppm): 7.50
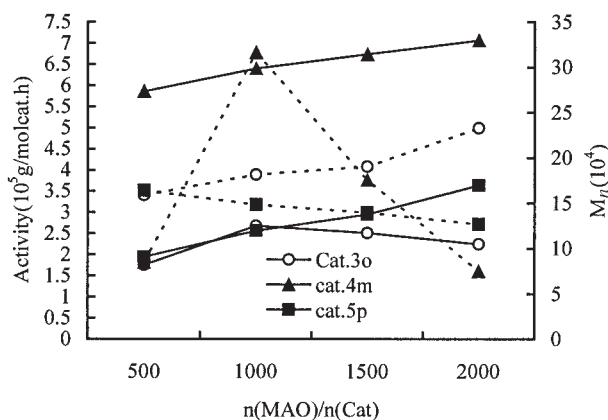

Figure 1 Influence of the MAO/catalyst molar ratio [n(MAO)/n(Cat)] on the catalytic activity and number-average molecular weight (M_n) of polyethylene. The solid lines show the activity, and the dashed lines show the molecular weight of polyethylene {polymerization conditions: [catalyst] = 1 × 10^{-4} mol/L, temperature = 40°C, time = 0.5 h, pressure = 1 bar, volume (toluene) = 25 mL}.
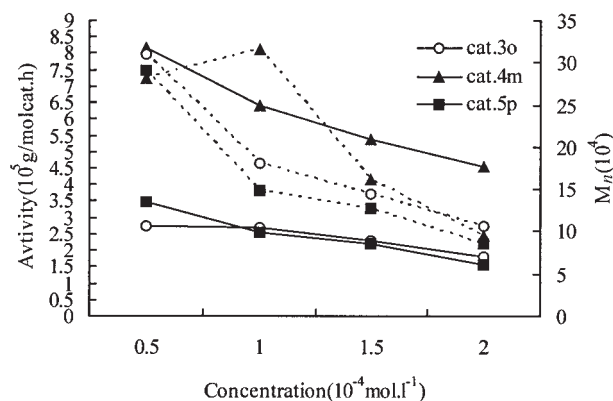

Figure 2 Influence of the catalyst concentration on the catalytic activity and number-average molecular weight (M_n) of polyethylene. The solid lines show the activity, and the dashed lines show the molecular weight of polyethylene {polymerization conditions: MAO/catalyst = 1000, temperature = 40°C, time = 0.5 h, pressure = 1 bar, volume (toluene) = 25 mL}.
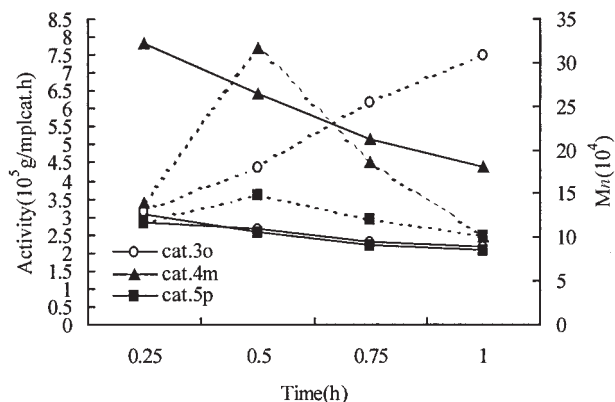
Figure 3 Influence of the polymerization time on the catalytic activity and number-average molecular weight (M_n) of polyethylene. The solid lines show the activity, and the dashed lines show the molecular weight of polyethylene {polymerization conditions: [catalyst] = 1×10^{-4} mol/L, MAO/catalyst = 1000, temperature = 40°C, pressure = 1 bar, volume (toluene) = 25 mL}.
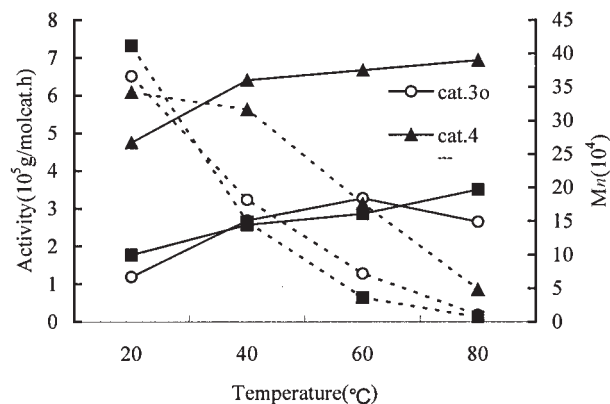

Figure 4 Influence of the polymerization temperature on the catalytic activity and viscosity-average molecular weight (M_n) of polyethylene. The solid lines show the activity, and the dashed lines show the molecular weight of polyethylene {polymerization conditions: [catalyst] = 1×10^{-4} mol/L, MAO/catalyst = 1000, time = 0.5 h pressure = 1 bar, volume (toluene) = 25 mL}.

(d, J = 7.8 Hz, 4H, Ar—H), 7.25 (d, J = 7.8 Hz, 4H, Ar—H), 6.49 (s, 10H, C_5H_5), 6.35 (t, J = 2.1 Hz, 4H, C_5H_4), 6.26 (t, J = 2.1 Hz, 4H, C_5H_4), 4.04 (s, 4H 2 $\times$ CH_2).

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 a constant temperature was reached, an MAO solution was injected into the reaction system. Ethylene was introduced into the flask, which was stirred with a magnetic bar. The polymerization mixture was quenched by the careful addition of acidic ethanol (containing 10% HCl), filtered, washed with excess ethanol, and dried at 60°C *in vacuo* to a constant weight.

RESULTS AND DISCUSSION

Preparation of the binuclear catalysts 3o, 4m, and 5p

The bridged binuclear catalysts **3o**, **4m**, and **5p** were prepared according to the reaction routes described in

Scheme 1. The yield of the ligands **1o**, **1m**, and **1p** depended on the order of addition of the starting materials and the reaction temperature. When cyclopentadienyl sodium was added to bis(bromomethyl)-benzene in a THF solution above 0°C, the yield of ligand **1** decreased because of competitive intramolecular cyclization.[21] However, when the reaction was carried out between −78 and 0°C with the addition of bis(bromomethyl)benzene to cyclopentadienyl sodium in THF, the yield was satisfyingly high, around 95 and 98%. The compounds were not isolated. They were used directly for the next reaction step. The ^{1}H-NMR data obtained for the isomeric complexes **3o**, **4m**, and **5p** were very similar, showing one broad singlet for CH_2, one singlet for C_5H_5, and two pseudo triplets belonging to the pseudo-A_2B_2 splitting pattern for the bridging C_5H_4 groups.[22]

Ethylene polymerization

All three binuclear zirconocenes were expected to be efficient catalysts for ethylene polymerization because they were quite similar in structure in comparison with mononuclear Cp_2ZrCl_2. The preliminary results

TABLE I
GPC and DSC Results

Catalyst	[Catalyst] (10^{-4}mol/L)	MAO/ catalyst	Temperature (°C)	Time (h)	Activity (10^5 g of polyethylene mol^{-1} catalyst^{-1} h^{-1})	M_n (10^4)	T_m (°C)	MWD
3o	1.0	1000	40	1	2.17	30.86	129.6	4.72
4m	1.0	1000	40	1	4.37	10.12	132.0	4.88
5p	1.0	1000	40	1	2.09	10.17	133.4	3.90
6	1.0	1000	40	1	6.06	27.33	131.8	3.18
Cp_2ZrCl_2	2.0	500	40	1	1.83	30.18	130.6	1.69

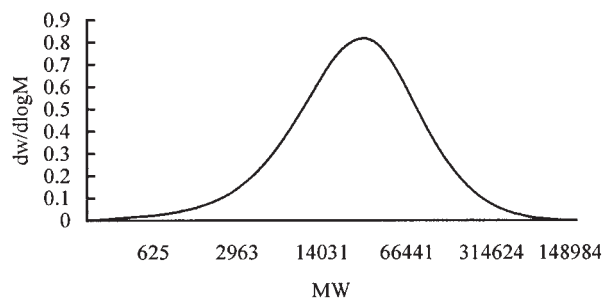Polymerization conditions: volume (toluene) = 25 mL pressure = 1 bar.

Figure 5 GPC curve for polyethylene produced by complex **3o** {MWD = 4.72; MW = molecular weight; conditions: [catalyst] = 1.0×10^{-4} mol/L, Al/catalyst = 1000, temperature = 40°C, time = 1.0 h, pressure = 1 bar, volume (toluene) = 25 mL; dw/dlog M = the differential method}.

Figure 7 GPC curve for polyethylene produced by complex **5p** {MWD = 3.90; MW = molecular weight; conditions: [catalyst] = 1.0×10^{-4} mol/L, Al/catalyst = 1000, temperature = 40°C, time = 1.0 h, pressure = 1 bar, volume (toluene) = 25 mL; dw/dlog M = the differential method}.

proved some similarities in their catalytic behavior. As shown in Figure 1, an increase in the MAO/catalyst molar ratio was favorable for raising the catalytic activity for all three zirconocenes. Figure 2 shows that an increase in the catalyst concentration reduced both the catalytic activity and molecular weight of polyethylene gradually. This could be explained by more bimolecular deactivation and less monomer available for every inserting site. Figure 3 shows that with the prolongation of the polymerization time, all catalytic activities decreased, and this was in agreement with the common sense of homogeneous polymerization by metallocene/MAO. Figure 4 illustrates the effect of the temperature on polymerization. A high temperature was favorable for reaching a high catalytic activity. However, a high temperature could also cause the acceleration of a β-hydrogen transfer reaction, which led to a decrease in the molecular weight of polyethylene.

The variation of the polymerization conditions indicated in Figures 1 and 2 does not demonstrate a great influence on the catalytic activity. The reason might be that these binuclear zirconocenes were not very sensitive to changes in the polymerization con-
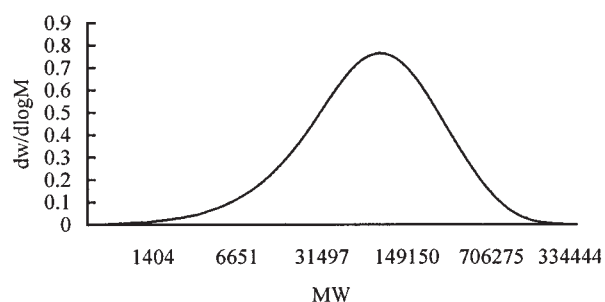

Figure 6 GPC curve for polyethylene produced by complex **4m** {MWD = 4.88; MW = molecular weight; conditions: [catalyst] = 1.0×10^{-4} mol/L, Al/catalyst = 1000, temperature = 40°C, time = 1.0 h, pressure = 1 bar, volume (toluene) = 25 mL; dw/dlog M = the differential method}.
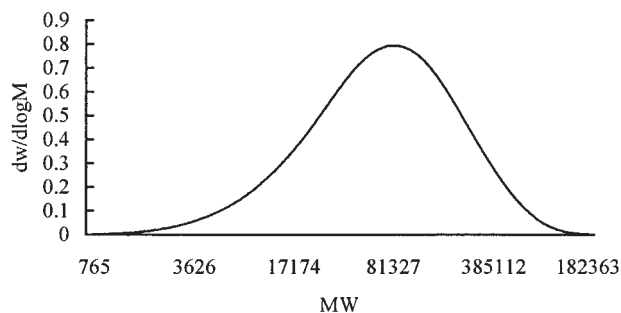
ditions. It could be attributed to the combination of two metals in one molecule, which averaged the change. Jüngling and Mülhaupt[23] proposed that only one metal was catalytically active in their phenylene-bridged binuclear catalyst system at a given time.[23] In our case, the binuclear zirconocenes did not have such a conjugated linkage. Therefore, they were not efficient for transferring an electron-deficient character from one metal to the other. As shown in Table I, all three catalyst systems demonstrated a higher catalytic activity than Cp_2ZrCl_2; the catalytic activity of **4m** was twice as high as that of Cp_2ZrCl_2. Huang et al.[24] also reported that the catalytic activity of bimetallic metallocene complexes was higher than that of the corresponding monocyclopentadienyl analogues. Therefore, it was reasonable to suppose that there was more than one metal effective in the polymerization at a given time. The catalytic activity of **3o** was only slightly higher than that of Cp_2ZrCl_2. That might be due to the steric congestion around the zirconium center, which hindered the coordination of ethylene to the second metal. The reason for the low catalytic activity of **5p** cannot be interpreted.

The MWDs of polyethylene obtained from all three isomers were broader than that obtained with Cp_2ZrCl_2. However, the GPC spectra showed only one peak (Fig. 5–7).

Noh et al.[11] reported that binuclear catalysts with more [CH_2] units in the spacing group represent higher activities. In other words, a longer bridging distance helps to increase the catalytic activity. However, complex **5p** showed almost the same activity as **3o**; probably in such a rigid molecule, a slight variation in structure is not sufficient to cause a difference in the catalytic activity. When two zirconium metals were linked by 4,4'-bis(methylene)biphenylene, the catalytic activity (as shown in Table I) increased dramatically. This indicates that the distance between two metals is an important factor influencing the catalytic activity.

The melting points of polyethylenes obtained from these binuclear zirconocenes were all around 130°C and were similar to that of polyethylene obtained by Cp$_2$ZrCl$_2$; this indicated that they were highly crystalline linear polymers.[25]

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