

Syntheses of chromium(III) complexes with Schiff-base ligands and their catalytic behaviors for ethylene polymerization

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Received 1 October 2004; received in revised form 20 July 2005; accepted 30 August 2005

Available online 10 October 2005

Abstract

A series of chromium(III) complexes LCrCl_3 (**4a–c**) bearing chelating 2,2'-iminodiphenylsulfide ligands [$\text{L} = (2\text{-ArMeC}=\text{NAr})_2\text{S}$] was synthesized in good yields from the corresponding ligands and $\text{CrCl}_3 \cdot (\text{THF})$. Using modified methylaluminoxane (MMAO) as a cocatalyst, these complexes display moderate activities towards ethylene polymerization, and produce highly linear polyethylenes with broad molecular weight distribution. Polymer yields, catalyst activities and the molecular weights, as well as the molecular weight distributions of the polymers can be controlled over a wide range by the variation of the structures of the chromium(III) complexes and the polymerization parameters, such as Al/Cr molar ratio, reaction temperature and ethylene pressure.

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Keywords: Chromium complex; Catalysts; Ziegler–Natta polymerization; Ethylene

1. Introduction

Numerous catalysts have been developed for the production of polyolefins since the late 1950s. A large fraction of the catalysts, especially the industrially relevant ones, are heterogeneous systems prepared by the deposition of soluble Ti-, Zr- or Cr-containing precursors on high surface area supports, such as silica, alumina or magnesium chloride. Among these transition metals that catalyze the polymerization of olefins, chromium occupies a prominent position [1–17].

In general, two classes of chromium-based catalysts are used commercially, namely the so-called Phillips catalyst [18] and the Union Carbide catalyst [19,20]. The Phillips catalyst is essentially composed of a chromium oxide and an inorganic carrier like SiO_2 , $\text{SiO}_2\text{–Al}_2\text{O}_3$, etc., while the Union Carbide catalyst is formed by treatment of silica with low-valent organometallic compound, most notably chromocene (Cp_2Cr).

There is an increasing interest in the development of the novel non-metallocene chromium catalysts for ethylene poly-

merization since they may allow an even greater control over the properties of the resultant polymers. Several new chromium catalyst families have been described in the recent literatures [21–30]. For example, the di(organoimido)chromium(VI) complexes $(\text{RN})_2\text{CrX}_2$ ($\text{X} = \text{Cl}$, Me, CH_2Ph) have been proved to be excellent precatalysts for ethylene polymerization [21–23]. This prompts us to search new chromium catalysts for olefin polymerization. Here, we describe the synthesis, characterization and ethylene polymerization behavior of a series of novel chromium(III) complexes [LCrCl_3] bearing chelating 2,2'-iminodiphenylsulfide ligands. We also report the effects of the reaction conditions, such as cocatalyst, Al/Cr molar ratio, the temperature and pressure of the polymerization on the catalytic behaviors of the chromium(III) precatalysts towards ethylene polymerization.

2. Experimental

All manipulations of water- and/or moisture-sensitive compounds were performed by means of standard high vacuum Schlenk and cannula techniques under a N_2 atmosphere. Toluene was refluxed and distilled from sodium/benzophenone under

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dry nitrogen. Modified methylaluminoxane (MMAO) (7% aluminum in heptane solution), diethylaluminum chloride, ethylaluminum dichloride, triisobutylaluminum, triethylaluminum and trimethylaluminum were purchased from Akzo Nobel Chemical Inc.

The NMR data of the ligands were obtained on a Bruker 300 MHz spectrometer at ambient temperature, CDCl₃ or DMSO as solvent. The NMR data of the polymers were obtained on a Varian Unity-400 MHz spectrometer at 110 °C with *o*-C₆D₄Cl₂ as the solvent. Mass spectra were obtained using electron impact (EI-MS). Elemental analyses were obtained using Carlo Erba 1106 and ST02 apparatus. The IR spectra were recorded on a Bio-Rad FTS-135 spectrophotometer. The DSC measurements were performed on a Perkin-Elmer Pyris 1 differential scanning calorimeter at a rate of 10 °C/min. The molecular weights and the molecular weight distributions of the polymer samples were determined at 150 °C by a PL-GPC 220 type high-temperature chromatograph equipped with three PLgel 10 μm Mixed-B LS type columns. 1,2,4-Trichlorobenzene (TCB) was employed as the solvent at a flow rate of 1.0 mL/min. The calibration was made by polystyrene standard EasiCal PS-1 (PL Ltd.).

2.1. Synthesis of ligands and complexes

2.1.1. 2,2'-Dinitro diphenyl thioether **1**

To a solution of 42 mmol of *o*-chloronitrobenzene in toluene, 10 mL of aqueous Na₂S (2 M) and a catalytic amount of tetrabutylammonium bromide were given. The mixture was refluxed overnight. Upon cooling to room temperature, the product crystallized from solution. The solid was recrystallized from ethanol to yield 3.48 g of **1** as yellow crystals (63%). ¹H NMR (DMSO-d₆): δ 8.12 (dd, 2H, Ar-H), 7.51 (m, 4H, Ar-H), 7.30 (dd, 2H, Ar-H).

2.1.2. 2,2'-Diamino diphenyl thioether **2**

A 250 mL Schlenk flask containing 150 mL of degassed ethanol was charged with 1.38 g (5 mmol) of **1**, 1 g of Pd-C catalyst (5% Pd), and hydrogen. After the mixture was stirred at 35 °C for 2 days, Pd-C was removed by filtration, and the solvent was evaporated. The residue was recrystallized in ethanol to give 2,2'-diamino diphenyl thioether **2** as a white crystal in 92% yield (9.96 g). ¹H NMR (DMSO-d₆): δ 7.20 (dd, 2H, Ar-H), 7.11 (m, 2H, Ar-H), 6.70 (m, 4H, Ar-H), 4.19 (s, 2H, -NH₂).

2.1.3. 2,2'-Iminodiphenylsulfide ligand **3a**

Two equivalents of phenyl methyl ketone (6 g, 0.05 mol) with one equivalent of **2** (5.4 g, 0.025 mol) were dissolved in 50 mL methyl alcohol. After the addition of a few drops of glacial acetic acid, the solution was refluxed overnight. Upon cooling to room temperature, the mixture was poured into petroleum ether. The crude product was recrystallized in ethanol to give 2,2'-iminodiphenylsulfide ligand **3a** as a yellow crystal in 75% yield (7.9 g). The other ligands **3b** and **3c** were prepared by the same procedure with similar yields. ¹H NMR (CDCl₃): δ 7.82 (d, 2H, Ar-H), 7.40 (m, 6H, Ar-H), 6.96 (t, 4H, Ar-H), 6.68 (m,

6H, Ar-H), 1.99 (s, 6H, -CH₃). EI-MS: *m/z* = 420 [M⁺]. Anal. Calcd for C₂₈H₂₄N₂S: C, 79.96; H, 5.75; N, 6.66%. Found: C, 80.06; H, 5.71; N, 6.60%.

2.1.4. 2,2'-Iminodiphenylsulfide ligand **3b**

Using the procedure described above, we obtained ligand **3b** in 70% yield. ¹H NMR (CDCl₃): δ 7.83 (d, 2H, Ar-H), 7.49 (d, 6H, Ar-H), 7.04 (m, 8H, Ar-H), 2.35 (s, 6H, Ar-CH₃), 2.23 (s, 6H, -CH₃). EI-MS: *m/z* = 448 [M⁺]. Anal. Calcd for C₂₈H₂₄N₂S: C, 80.32; H, 6.29; N, 6.24%. Found: C, 80.38; H, 6.34; N, 6.19%.

2.1.5. 2,2'-Iminodiphenylsulfide ligand **3c**

Using the procedure described above, we obtained ligand **3c** in 62% yield. ¹H NMR (CDCl₃): δ 7.82 (d, 2H, Ar-H), 7.46 (d, 6H, Ar-H), 7.02 (m, 8H, Ar-H), 2.33 (s, 6H, Ar-CH₃), 2.20 (s, 6H, -CH₃). EI-MS: *m/z* = 448 [M⁺]. Anal. Calcd for C₂₈H₂₄N₂S: C, 80.32; H, 6.29; N, 6.24%. Found: C, 80.26; H, 6.27; N, 6.26%.

2.1.6. 2,2'-Iminodiphenylsulfide Cr(III) complex **4a**

Ligand **3a** 0.72 g (1.72 mmol) and CrCl₃(THF)₃ 0.27 g (1.72 mmol) were combined in a Schlenk flask under an Argon atmosphere. Then 50 mL of THF was added with a syringe. The mixture was stirred at room temperature for 10 h. **4a** was isolated as a green powder in 84% yield. The chromium complexes **4b** and **4c** were prepared by the same procedure with similar yields. EI-MS (70 eV): *m/z* = 578 [M⁺]. Anal. Calcd for C₂₈H₂₄Cl₃CrN₂S: C, 58.09; H, 4.18; N, 4.84%. Found: C, 58.16; H, 4.11; N, 4.89%.

2.1.7. 2,2'-Iminodiphenylsulfide Cr(III) complex **4b**

Yield, 87%. EI-MS (70 eV): *m/z* = 606 [M⁺]. Anal. Calcd for C₃₀H₂₈Cl₃CrN₂S: C, 59.36; H, 4.65; N, 4.62%. Found: C, 59.31; H, 4.62; N, 4.65%.

2.1.8. 2,2'-Iminodiphenylsulfide Cr(III) complex **4c**

Yield, 89%. EI-MS (70 eV): *m/z* = 606 [M⁺]. Anal. Calcd for C₃₀H₂₈Cl₃CrN₂S: C, 59.36; H, 4.65; N, 4.62%. Found: C, 59.40; H, 4.60; N, 4.58%.

2.2. General procedures for ethylene polymerization

The polymerization was carried out in a 200 mL Schlenk flask equipped with a magnetic stirrer. The flask was repeatedly evacuated and refilled with nitrogen, and finally filled with ethylene gas (ambient pressure) from Schlenk line. MMAO and toluene were added via a gastight syringe. The catalyst, dissolved in toluene under a dry nitrogen atmosphere, was transferred into the Schlenk flask to initiate the polymerization. After polymerization for 30 min at given temperature, all the polymerization experiments were stopped by a large excess of methanol containing a small amount of hydrochloric acid. The coagulated polymer was washed with methanol, filtered and dried under vacuum.

High-pressure polymerization experiments were carried out in a mechanically stirred 200 mL stainless steel reactor, equipped

with an electric heating mantle controlled by a thermocouple dipping into the reaction mixture. The reactor was baked under nitrogen flow for 24 h at 150 °C and subsequently cooled to the temperature of polymerization. The reagents were transferred via a gastight syringe to the evacuated reactor. Ethylene was introduced into the reactor, and the reactor pressure was maintained at given pressure throughout the polymerization run by continuously feeding the ethylene gas. After proceeding for 30 min, the polymerization was stopped by turning the ethylene off and relieving the pressure. The reaction mixture was poured into a solution of HCl/ethanol (10 vol%) to precipitate the polymer. The polymer was isolated by filtration, washed with ethanol, and dried under vacuum.

3. Results and discussion

3.1. Synthesis and characterization of complexes

A general synthetic route for chromium complexes **4a–c** bearing chelating 2,2'-iminodiphenylsulfide ligands used in this study is shown in Scheme 1. The tridentate ligands **3a–c** were prepared via the condensation reaction of two equivalents of the corresponding methyl aryl ketone with one equivalent of 2,2'-iminodiphenylsulfide (yields: **3a**, 75%; **3b**, 70%; **3c**, 62%). The chromium complexes **4a–c** were synthesized in good yield (yields: **4a**, 84%; **4b**, 87%; **4c**, 89%) via the complexation reaction of CrCl₃·(THF) with corresponding ligands **3a–c** in tetrahydrofuran (THF) at room temperature. All the chromium complexes are green in color.

The characterization of these complexes was difficult because of their poor solubility in organic solvents and the fact that they are paramagnetic, thus high-resolution NMR spectroscopic analysis is impossible. We predict theoretically the molecular model of **4a** using Becke's nonlocal-exchange functional with the nonlocal correlation functional of Lee–Yang–Parr (BLYP) functional with DND basis set. The density functional theory

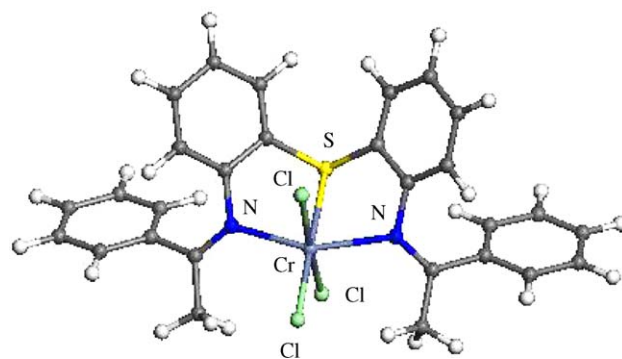
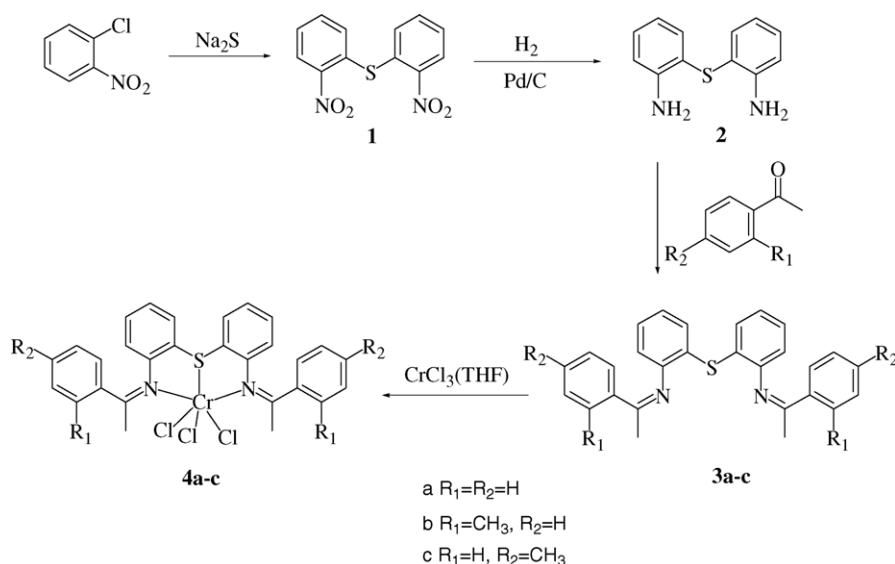


Fig. 1. Molecular structure of complex **4a**.

(DFT) calculations are performed on Origin 3900 workstation by DMol³ module of the Material Studio Modeling software package, which prove to obtain high accuracy while keeping the computational cost fairly low for an ab initio method. The structure optimized at the BLYP/DND level is shown in Fig. 1. The geometry of the six-member around the chromium atom could be described as a distorted octahedron. In order to characterize the nature of the optimum structure, we also calculate the harmonic vibrational frequencies by normal-mode analysis at the same level. The optimum complex corresponds to all real frequencies, indicative of a stationary point. The total energy, binding energy, and zero-point energy for the optimum complex **4a** are -3056.8182408 , -10.5471239 and 0.435 au, respectively.

3.2. Catalysis

The initial attempts to polymerize ethylene with chromium complexes **4a–c** were unsuccessful. These complexes were not active as a single component catalyst, and only low catalytic activities (less than 10 kg PE/mol_{Cr}·h) were observed when diethylaluminum chloride or ethylaluminum dichloride was used as a cocatalyst. However, there were remarkable increases



Scheme 1. Synthesis of chromium(III) 2,2'-iminodiphenylsulfide complexes.

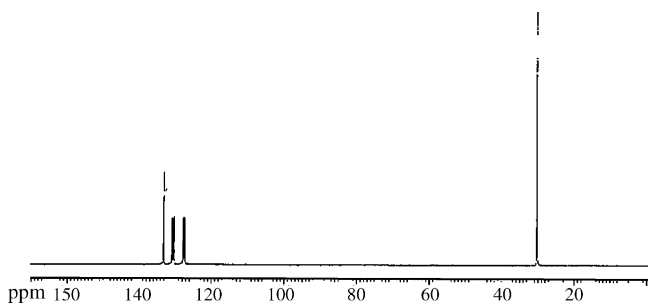


Fig. 2. ^{13}C NMR spectrum of polyethylene prepared with complex **4a**.

in catalytic activities (in the range 30–50 kg PE/mol_{Cr}·h) while triisobutylaluminum, triethylaluminum or trimethylaluminum was used as a cocatalyst. It is interesting that chromium complexes **4a–c** displayed moderate activities towards ethylene polymerization (more than 70 kg PE/mol_{Cr}·h) upon activation with MMAO, and converted ethylene into highly linear polyethylene (Fig. 2).

The conditions of the polymerizations will influence the catalyst activities and the properties of the polymers. To examine these effects, we undertook a series of polymerization experiments under various conditions. The effect of the Al/Cr molar ratio on the polymerization reaction was firstly investigated. The polymerizations of ethylene were performed with complexes **4a–c** at 25 °C, varying the Al/Cr molar ratio from 800 to 2400. As shown in Fig. 3, the catalyst activities increase with an increase in the Al/Cr molar ratio from 800 to 1200, nevertheless, further increase of the Al/Cr molar ratio leads to only a slight improvement of catalyst activities.

The strong temperature dependence of activity is a common characteristic of Ziegler–Natta catalysts due to the high activation energy required for polymerization process. For the different kinds of catalysts, however, we would observe maximum values at different temperatures. For chromium complexes **4a–c**, the catalytic activities towards ethylene polymerization increase

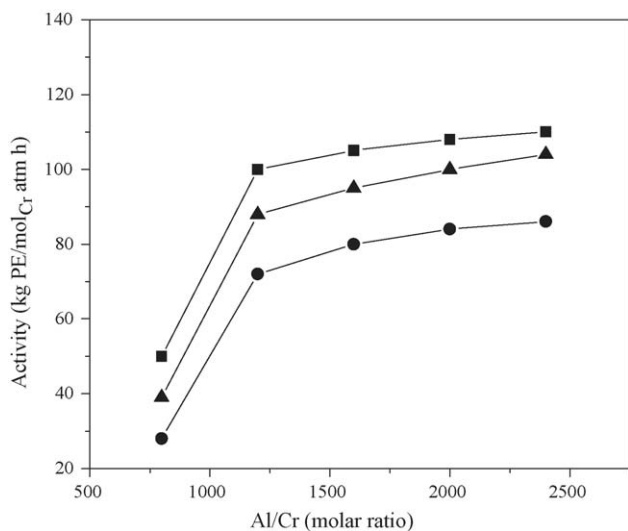


Fig. 3. Effect of Al/Cr molar ratio on the catalytic activity of complexes **4a** (●), **4b** (■) and **4c** (▲). Pressure of ethylene, 1 atm; time of polymerization, 30 min; temperature, 25 °C; cocatalyst, MMAO.

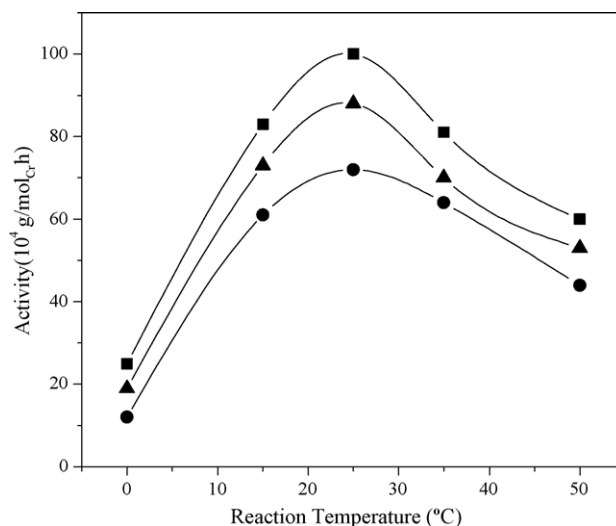


Fig. 4. Effect of temperature on the catalytic activity of complexes **4a** (●), **4b** (■) and **4c** (▲). Pressure of ethylene, 1 atm; time of polymerization, 30 min; Al/Cr = 1200 (molar ratio); cocatalyst, MMAO.

gradually to maximum values and then decrease gradually with the increase of reaction temperature. Under atmospheric pressure of ethylene, the optimum reaction temperature is ca. 25 °C, as shown in Fig. 4. This behavior is intrinsically related to the unstability of the catalyst at higher polymerization temperatures.

The results of polymerizations performed under different pressures (1, 5 and 10 atm) employing complexes **4a–c** are summarized in Table 1. The data listed in Table 1 indicate that the ethylene pressure considerably influences the yields and the molecular weights (MWs) as well as the molecular weight distributions (MWDs) of the resultant polymers. First, significant increases in the productivities of the catalysts were observed (**4a**: from 72 kg PE/mol_{Cr}·h at 1 atm to 146 kg PE/mol_{Cr}·h at 5 atm; **4b**: from 100 kg PE/mol_{Cr}·h at 1 atm to 188 kg PE/mol_{Cr}·h at 5 atm; **4c**: and from 88 kg PE/mol_{Cr}·h at 1 atm to 162 kg PE/mol_{Cr}·h at 5 atm). Second, changes in MWs and MWDs of the resulted polymers could be observed in Fig. 5, which shows two GPC traces for the polymerization tests with **4a**/MMAO catalytic system under different pressures. Employing precatalyst **4a** at 1 atm ethylene with 1200 equiv MMAO (Entry 1), the MWD of PE displays clearly bimodal distribution and the low molecular weight fraction is dominant. On increasing the pressure to 5 atm (Entry 4), a unimodal distribution is observed. The similar trends can be observed using complexes **4b** and **4c**. This indicates that increasing ethylene pressure could control β -H elimination reaction during the polymerization of ethylene with **4a–c**/MMAO systems.

It is noteworthy that the **4a–c**/MMAO systems also exhibit high catalytic activities towards ethylene polymerization at high temperature (50 °C) in the case of high pressure (5 atm). Moreover, high molecular weight polyethylenes can be easily obtained under this condition (Entries 10–12).

The data listed in Table 1 show that the structure of the ligands considerably affects the performances of the precatalysts and the properties of the polymer produced. For example, the replacement of the proton at R₁ position (**4a**) with methyl (**4b**)

Table 1
Results of ethylene polymerization by complexes **4a–c** activated with MMAO^a

Entry	Catalyst	Temperature (°C)	Pressure (atm)	Yield (g)	Activity (kg PE/mol _{Cr} ·h atm)	\overline{M}_w^b (kg/mol)	$\overline{M}_w/\overline{M}_n^b$	T_m^c (°C)
1	4a	25	1	0.18	72	60.5	61	127.3
2	4b	25	1	0.25	100	72.7	67	128.6
3	4c	25	1	0.22	88	70.1	66	128.1
4	4a	25	5	1.83	146	234	12.8	135.6
5	4b	25	5	2.35	188	268	13.5	136.9
6	4c	25	5	2.03	162	261	13.0	136.2
7	4a	25	10	2.52	101	339	9.6	138.3
8	4b	25	10	3.58	143	389	10.1	139.8
9	4c	25	10	3.24	130	378	9.8	139.5
10	4a	50	10	2.54	102	288	9.3	137.3
11	4b	50	10	3.51	140	346	9.8	138.6
12	4c	50	10	3.11	124	317	9.6	138.1

^a Polymerization conditions: 5 μ mol catalyst, Al/Cr = 1200 (molar ratio), polymerization for 30 min.

^b \overline{M}_w and $\overline{M}_w/\overline{M}_n$ were determined by GPC vs. polystyrene standards, uncorrected.

^c T_m , melting temperatures were determined by means of DSC with a heating rate of 10 °C/min in nitrogen.

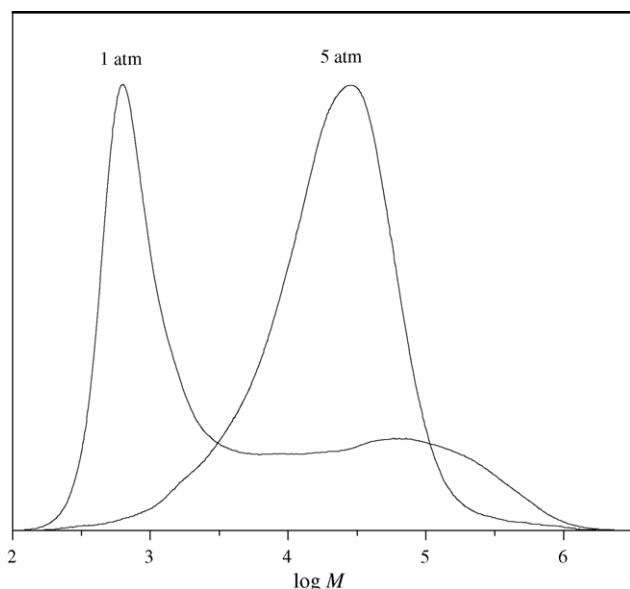


Fig. 5. GPC curves of the polyethylene prepared with the precatalysts **4a**. **4a**/MMAO: Entry 1 in Table 1, **4a**/MMAO: Entry 4 in Table 1.

results in the increase of catalyst activity and the weight-average molecular weight (\overline{M}_w) of the polyethylene obtained (the catalyst activity from 146 to 188 kg PE/mol_{Cr}·h, \overline{M}_w from 234 to 268 kg/mol) in the case of 5 atm of ethylene pressure. In general, the catalyst activities were found to decrease in the order **4b** > **4c** > **4a**. Clearly, steric protection of the metal center is also a crucial factor in controlling chain transfer reaction.

4. Conclusion

A new family of homogeneous chromium catalysts for ethylene polymerization, derived from chelating 2,2'-iminodiphenylsulfide ligands has been developed. Activated with MMAO, they display moderate activities, and produce high linear polyethylene with broad molecular weight distribution. Ligand structure and polymerization conditions influence dramatically the catalyst activities and polymer properties. The

increase of the steric hindrance of the ligand can result in the enhancement of catalyst activity and the molecular weight of the polymer prepared. The polyethylenes obtained under an atmospheric pressure display relatively low T_m (less than 129 °C) and bimodal distributions. The increase of ethylene pressure not only increases the molecular weight and T_m (up to 140 °C), but also decreases the molecular weight distribution of the polymers by controlling chain transfer reaction.

Acknowledgements

The authors are grateful for the financial support by the National Natural Science Foundation of China and SINOPEC (No. 20334030).

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