Synthesis, structures and ethylene polymerization behavior of half-metallocene chromium(III) catalysts bearing salicylaldiminato ligands†

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A series of half-metallocene chromium(III) complexes bearing a salicylaldiminato ligand, Cp′[2-R^1-4-R^2-6-(CH = NR^3)C_6H_2O]CrCl [Cp′ = Cp (**1**, **5**), Cp* (**2**, **3**, **4**, **6**, **7**, **8**); R^1 = Ph (**1**, **2**, **3**, **5**, **6**, **8**), ^{i}Pr (**4**), ^{t}Bu (**7**); R^2 = H (**1**, **2**, **3**), Br (**4**), NO_2 (**5**, **6**, **7**, **8**); R^3 = ^{i}Pr (**1**, **2**, **5**, **6**, **7**), ^{t}Bu (**3**, **4**, **8**)], were synthesized. The structures of complexes **1**, **3–5**, **7–8** were determined by single crystal X-ray diffraction analysis. The X-ray crystallographic analysis indicates that these complexes adopt a pseudo-octahedral coordination environment with a three-legged piano stool geometry. Upon activation with a small amount of $AlEt_3$, complexes **1–8** exhibit good to high catalytic activity for ethylene polymerization and produce ultra-high molecular weight polyethylene (PE) under mild conditions. The productivity of these complexes is relatively low when activated with $AlMe_3$ and Al^iBu_3. Both the productivity of these catalyst systems and the molecular weight of the produced PE can be tuned in a broad range by changing the ligands and the AlR_3 co-catalyst.

Introduction

Chromium-based olefin polymerization catalysts hold a quite interesting position among transition metal olefin polymerization catalysts. The chromium-based heterogeneous catalysts of Phillips and Union Carbide systems (Cr/SiO_2) have been commercially applied for the production of high density polyethylene. In recent years, homogeneous single-site Cr-based catalyst systems[1] both for ethylene oligomerization and polymerization,[2–19] as well as for ethylene trimerization[20] and tetramerization[21] have been reported. We are interested in developing alkylaluminium activated homogeneous Cr-based olefin polymerization catalyst systems with high catalytic activity. In the literature, non-metallocene type chromium complexes bearing salicylaldimine and β-diketiminate ligands were reported to be active catalysts in the presence of alkylaluminium chlorides.[2] A number of alkylaluminium activated half-metallocene chromium(III) catalyst systems for ethylene polymerization, including $[Cp^*CrL_2R]^+A^-$ (L = py, 1/2dppe, MeCN, THF; R = Me, Et; A = PF_6, BPh_4),[3] Cp*Cr(acac)Cl/Et_3Al,[5b] Cp*Cr(C_6F_5)(η^3-Bz)/Et_3Al (Bz = benzyl),[12] have been reported. Recently, half-metallocene chromium(III) complexes bearing *β*-ketoiminato, *β*-diketiminate,[13a] hydroxyindanimine[13b] and salicylaldiminato ligands[14] were also reported to show good catalytic activity for ethylene polymerization upon activation with alkylaluminium. Of these reported half-metallocene chromium(III) complexes bearing varied ligands, the complexes with a salicylaldiminato ligand developed by our group[14] exhibit high catalytic activity for ethylene polymerization and produce high molecular weight polyethylene in the presence of a small amount of AlR_3. In these complexes, both the cyclopentadienyl and salicylaldiminato[22] ligands have been found to be excellent for constructing olefin polymerization catalysts, the catalytic performance of which can be tuned in a broad range by ligand modification. In our recent work, we have systematically screened these types of complexes for ethylene polymerization and found that some salicylaldiminato ligands with electron-withdrawing substituent(s) exhibit a special influence on the catalytic performance of their complexes. Herein, we wish to report the synthesis, structural characterization of a number of new half-metallocene chromium(III) complexes bearing a salicylaldiminato ligand with electron-withdrawing substituent(s), Cp′[2-R^1-4-R^2-6-(CH=NR^3)C_6H_2O]CrCl [Cp′ = Cp (**1**, **5**), Cp* (**2**, **3**, **4**, **6**, **7**, **8**); R^1 = Ph (**1**, **2**, **3**, **5**, **6**, **8**), ^{i}Pr (**4**), ^{t}Bu (**7**); R^2 = H (**1**, **2**, **3**), Br (**4**), NO_2 (**5**, **6**, **7**, **8**); R^3 = ^{i}Pr (**1**, **2**, **5**, **6**, **7**), ^{t}Bu (**3**, **4**, **8**)], and their catalytic properties for ethylene polymerization in the presence of AlR_3.

Results and discussion

Synthesis and characterization

The new half-metallocene chromium(III) complexes **1–8** were synthesized in good yields (60–70%) *via* the reaction of *in situ* produced Cp′$CrCl_2$(THF) with the sodium salts (Na$\mathbf{L_1}$–Na$\mathbf{L_6}$) of a corresponding salicylaldiminato ligand in THF as shown in Scheme 1. The free salicylaldimine ligands $\mathbf{HL_1}$-$\mathbf{HL_6}$ were synthesized in high yields by the condensation reaction of a substituted salicylaldehyde with 2 equiv. of a corresponding amine in hexane following a published procedure.[23] Of these free ligands, $\mathbf{HL_1}$ and $\mathbf{HL_2}$ are known compounds.

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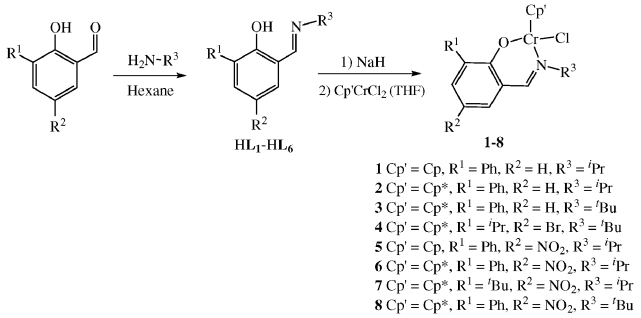

Scheme 1 The synthetic procedure for complexes **1–8**

The salicylaldehyde derivatives (R = Ph, ^{t}Bu, ^{i}Pr) were synthesized in high yields by treatment of the corresponding phenol derivatives with paraformaldehyde in the presence of magnesium chloride and triethylamine according to a literature procedure.[24] The 5-nitrosalicylaldehyde derivatives were obtained in 75–85% yields from the nitration reaction of 3-R^1-salicylaldehyde (R^1 = Ph, ^{t}Bu) with nitric acid in glacial acetic acid following a literature procedure.[25] The sodium salts of the corresponding salicylaldiminato ligands were prepared from the reaction of the free ligands with NaH at 0 °C. These half-metallocene chromium(III) complexes were found to be thermally stable even heated to melting temperature under inert atmosphere, but being air and moisture sensitive. They are well soluble in CH_2Cl_2, toluene, THF and Et_2O, but less soluble in common alkanes such as pentane and hexane. All complexes **1–8** were characterized with elemental analyses and the structures of complexes **1**, **3–5**, **7–8** were determined by single crystal X-ray diffraction analysis. The free salicylaldimine ligands **HL$_1$-HL$_6$** were all characterized with elemental analysis and ^{1}H NMR spectroscopy.

Crystal structures

Single crystals of complexes **1**, **3–5**, **7–8** suitable for X-ray diffraction studies were obtained from either *n*-hexane–dichloromethane or *n*-hexane–chloroform mixed solvent. The crystal structures of these complexes have been determined by X-ray diffraction analysis. The ORTEP drawings of these complexes are shown in Fig. 1–6, respectively. Selected bond lengths, angles and dihedral angles for these complexes are given in Table 1. The X-ray crystallographic analysis reveals that all these complexes have a pseudo-octahedral coordination environment in their solid state structures and adopt a three-legged piano stool geometry with the O, N, Cl atoms being the three legs and the Cp or Cp* ring being the seat. There are two independent molecules with minor structural differences in the unit cell of complex **3**, which are labelled as **3A** and **3B**. Selected bond lengths and angles of **3A** are given in Table 1 and will be used in subsequent discussions. In the unit cells of complexes **4**, **7** and **8**, there is a $CHCl_3$ (for **4**) or CH_2Cl_2 (for **7** and **8**) solvent molecule per Cr(III) complex. In these complexes, the Cr–C bond lengths are in line with those observed in related monocyclopentadienyl chromium(III) complexes.[3,4d] It should be noted that the complexes with a NO_2 group on the salicylaldiminato ligand have shorter Cr(1)-Cp′(centroid) and Cr(1)–C(average) distances by comparing the data in Table 1 (**1** > **5**; **3A** > **8**), which may be caused by the strong electron withdrawing effect of the NO_2 group. The Cr–Cl (2.301–2.336 Å) and Cr–O (1.903–1.939 Å) bond lengths in these complexes are close to those reported for known *β*-ketoiminato[13] and salicylaldiminato[14,17] chromium(III) complexes. They do not change very much with the variation in R^1–R^3 groups. However, the Cr–N bond length is obviously affected by the R^3 group on the imine N atom, being shorter (2.013, 2.033 and 2.045 Å, respectively) for complexes **1**, **5** and **7** with R^3 = ^{i}Pr, and longer (2.098, 2.097 and 2.093 Å, respectively) for complexes **3**, **4** and **8** with R^3 = ^{t}Bu. The short imine C=N bond lengths (1.270–1.302 Å) demonstrate the retention of C=N double bond character in these complexes as indicated by Gibson *et al.* for bis(salicylaldiminato) chromium(III) complexes (1.283–1.308 Å).[17] In addition, the O–C bond length is slightly affected by the substituent group on the salicylaldiminato ligands as seen from the data for complexes **1** (1.309(2) Å), **3A** (1.308(7) Å), **5** (1.294(6) Å), and **8** (1.283(7) Å).

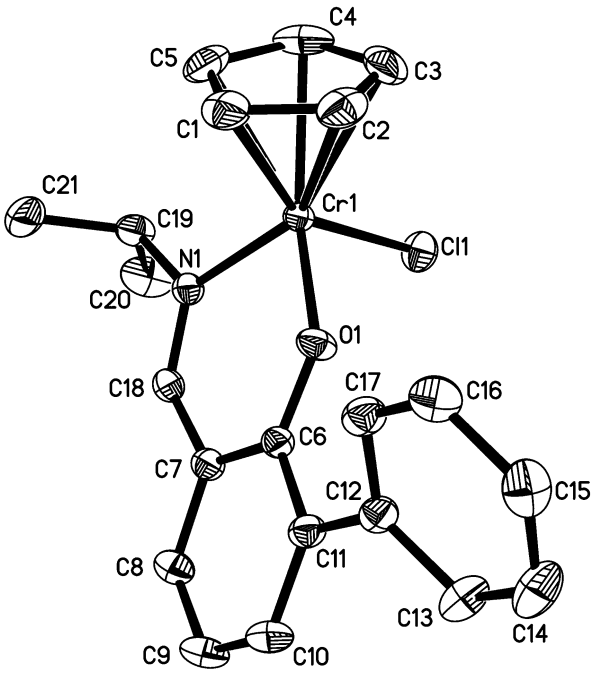

Fig. 1 Plot of a molecule of **1** with thermal ellipsoids drawn at the 30% probability level. Hydrogens are omitted for clarity.

The O–Cr–N, O–Cr–Cl and N–Cr–Cl bond angles in these complexes occur in the ranges of 86.67–90.25°, 92.14–98.65° and 92.15–100.40°, respectively, with the variation in R^1, R^3 and Cp′ groups. It was noted that complexes with a Cp ligand (**1** and **5**) have larger O–Cr–Cl bond angles (97.05–98.65°) and smaller N–Cr–Cl bond angles (92.15–93.16°) than complexes with a bulkier Cp* ligand (92.14–95.69° and 96.24–100.40°, respectively). For most of these complexes, a bulkier R^1 and a less bulky R^3 groups would result in a larger O–Cr–Cl bond angle and a smaller N–Cr–Cl bond angle, while a bulkier R^3 and a less bulky R^1 groups correspond to a smaller O–Cr–Cl bond angle and a larger N–Cr–Cl bond angle as indicated by the corresponding data of complexes **4** (R^1 ↓, R^3 ↑, O–Cr–Cl = 94.67(8) Å, N–Cr–Cl = 100.14(9) and **7** (R^1 ↑, R^3 ↓, O–Cr–Cl = 95.69(13) Å, N–Cr–Cl = 96.24(14)) in

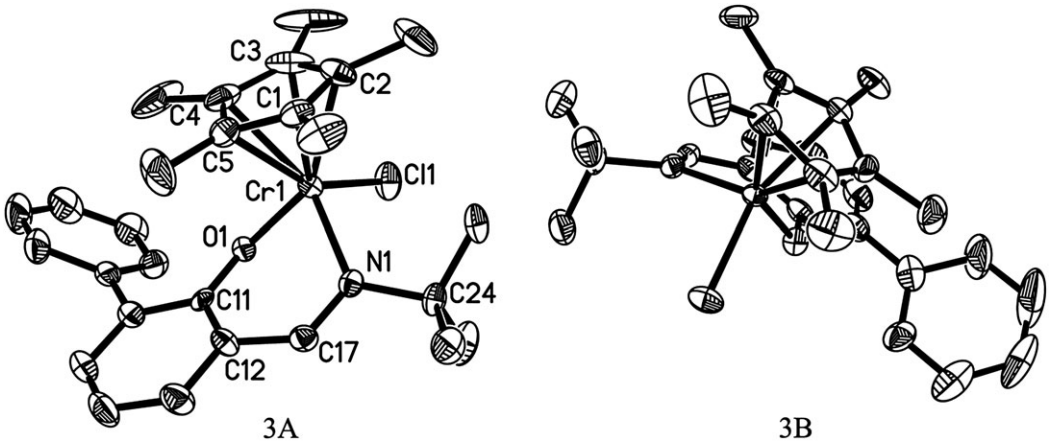

Fig. 2 Plot of independent molecules of **3** with thermal ellipsoids drawn at the 30% probability level. Hydrogens are omitted for clarity.

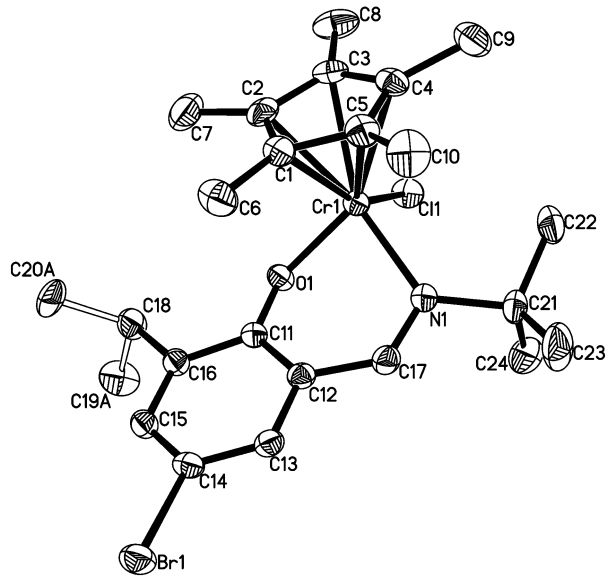

Fig. 3 Plot of a molecule of **4** with thermal ellipsoids drawn at the 30% probability level. Hydrogens and solvent $CHCl_3$ are omitted for clarity.

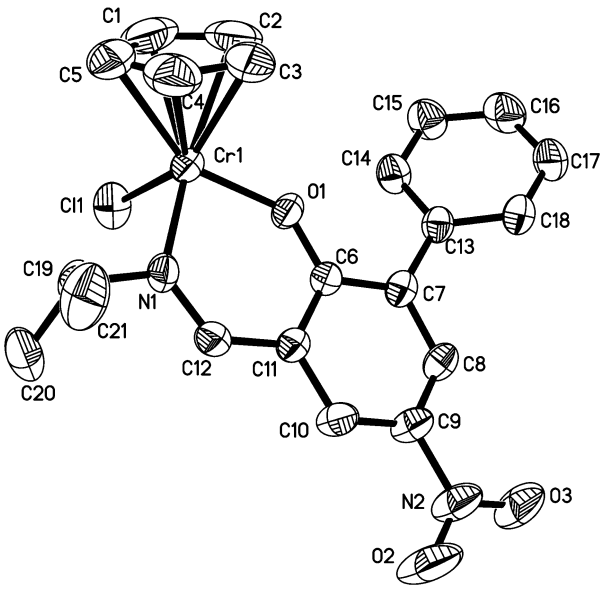

Fig. 4 Plot of a molecule of **5** with thermal ellipsoids drawn at the 30% probability level. Hydrogens and solvent CH_2Cl_2 are omitted for clarity.

Table 1. These complexes have similar dihedral angles between the Cp′ ring and the plane through Cr, O and N atoms in the range of 46.2–51.4°. In comparison, the impact of the R^1 and R^3 groups on the dihedral angle between the Cp′ ring and the phenyl ring in the salicylaldiminato ligand is much more remarkable for these complexes, which makes the Cp′-phenyl ring dihedral angle changes in a large range from 9.4 to 61.2°. In addition to the steric effect of the substituents, the packing force in some cases may also be an important factor to affect the bond parameters.

Ethylene polymerization studies

The half-metallocene chromium (III) complexes **1–8** have been studied as ethylene polymerization catalysts activated with $AlMe_3$, $AlEt_3$ and Al^iBu_3. The experimental results are summarized in Table 2. Upon activation with a small amount of $AlEt_3$ (Al/Cr molar ratio = 25), complexes **1–8** all show reasonable to high catalytic activity for ethylene polymerization

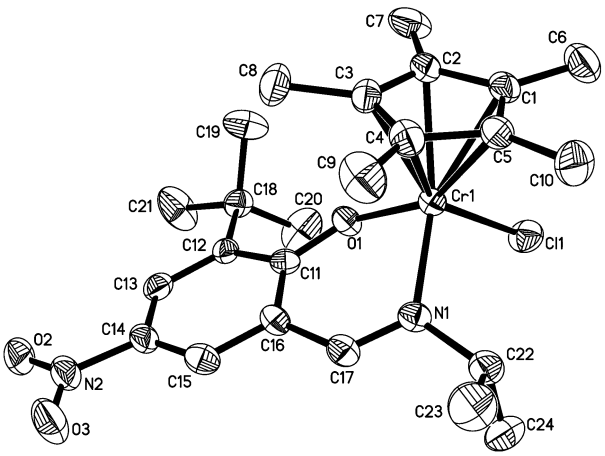

Fig. 5 Plot of a molecule of **7** with thermal ellipsoids drawn at the 30% probability level. Hydrogens and solvent CH_2Cl_2 are omitted for clarity.

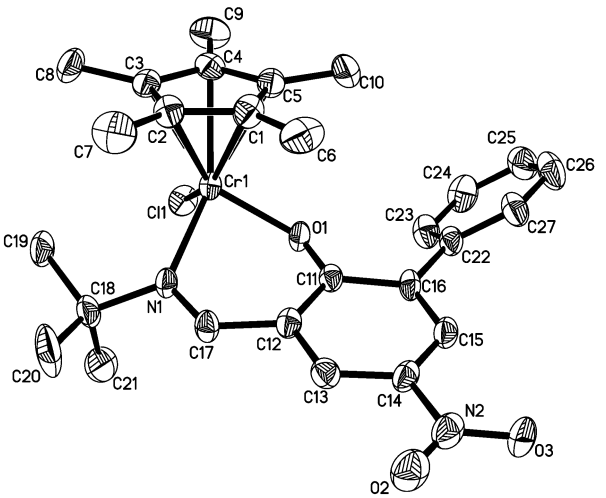

Fig. 6 Plot of a molecule of **8** with thermal ellipsoids drawn at the 30% probability level. Hydrogens and solvent CH_2Cl_2 are omitted for clarity.

to produce high or ultra-high molecular weight polyethylene. It is well known that the catalytic activity or productivity of metallocene catalysts can be tuned by steric and electronic effects of the substituents on their ligands. By examining the results in Table 2, it can be found that the productivity of complexes with R^3 = ^{i}Pr increases with the increase in the steric bulk of R^1 group (comparing the results for **6** and **7**). It is possible that a bulky R^1 in the *ortho*-position of the oxygen atom in the salicylaldiminato ligand could prevent the coordinated oxygen atom from further coordinating to a AlR_3 or another chromium complex molecule, and therefore keep the active catalyst molecule from inactivation by forming inactive binuclear species. Similarly, the productivity of complexes with R^1 = Ph increases with the increase in the size of R^3 group at the imine nitrogen atom (comparing the results for **2** and **3**, **6** and **8**), which may also be attributed to a bulky R^3 group weakening the interaction between the active catalyst and AlR_3 molecules. It should be noted that reverse results have been observed for complexes with R^1 = ^{t}Bu[14] and related half-metallocene chromium(III) complexes.[13] These results demonstrate the importance of matching the ligand substituent size to the likely coordination geometry of the active species.[17] To investigate the electronic effect of R^2 group at the *para*-position of the oxygen atom in the salicylaldiminato ligand, an electron withdrawing R^2 group has been introduced in complexes **4** (R^2 = Br), **5**, **6**, **7** and **8** (R^2 = NO_2) and their catalytic performance has been examined. It was found that the productivity of complex **4** with R^2 = Br is remarkably lower than that of complex **3** with R^2 = H, while the complexes with R^2 = NO_2 show only slightly lower productivity in comparison to the corresponding complexes with R^2 = H (comparing the data for **1** and **5**, **2** and **6**, **3** and **8**) under similar conditions. The complex **7** exhibits even higher productivity (2260 kg PE molCr^{-1} h^{-1}) than its analog Cp*Cr[2-^{t}Bu-6-(CH=N^{i}Pr)C_6H_3O]Cl with R^2 = H (2108 kg PE molCr^{-1} h^{-1}) upon activation with $AlEt_3$. The reason for the very low productivity of complex **4** is not clear. Based on previous knowledge, it is reasonable to assume that the electron withdrawing R^2 group in these complexes could reduce the negative charge on the coordinating atoms of the salicylaldiminato ligand and therefore increase the positive charge on the metal centre, which would favor the coordination of ethylene to the metal centre and also enhance the interaction between the catalyst and the AlR_3 co-catalyst. Therefore, the productivity of a specific complex could be enhanced or weakened by an electron withdrawing R^2 group depending on which factor is the predominant one. One more interesting thing worth mentioning is that complexes **1** and **5** with a Cp ligand have lower productivity in comparison with that with a Cp* ligand. These results might be attributed to that the bulky and electron-donating methyl groups on the cyclopentadienyl ring could weaken the interaction between the catalyst and the AlR_3 co-catalyst and stabilize the catalytically active species,[18] and thus improve the productivity.

As can be seen from the data in Table 2, the productivity of these half-sandwich chromium(III) catalysts is sensitive to the alkylaluminium co-catalysts. It was found that these complexes show reasonable productivity when activated with $AlEt_3$, while their productivity is very low upon activation with $AlMe_3$ and Al^iBu_3. The complicated effect of the alkylaluminium co-catalysts on the productivity of these chromium(III) catalysts should be attributed to the interaction between the catalyst and co-catalyst molecules as discussed previously.[21]

Table 1 Selected structural data for complexes **1**, **3–5** and **7–8**

Complex	**1**	**5**	Complex	**3A**	**4**	**7**	**8**
Cr(1)–O(1)	1.9099(12)	1.903(4)	Cr(1)–O(1)	1.919(4)	1.928(2)	1.939(4)	1.922(4)
Cr(1)–N(1)	2.0334(15)	2.013(4)	Cr(1)–N(1)	2.098(5)	2.097(3)	2.045(5)	2.093(5)
Cr(1)–Cl(1)	2.3035(6)	2.3034(17)	Cr(1)–Cl(1)	2.310(2)	2.3359(12)	2.3005(18)	2.303(2)
Cr(1)–Cp(centroid)	1.915	1.881	Cr(1)–Cp*(centroid)	1.914	1.918	1.895	1.900
Cr(1)–C_{av}	2.249	2.214	Cr(1)–C_{av}	2.256	2.264	2.245	2.242
O(1)–C(6)	1.309(2)	1.294(6)	O(1)–C(11)	1.308(7)	1.303(4)	1.294(7)	1.283(7)
N(1)–C(12)	1.287(2)	1.297(6)	N(1)–C(17)	1.297(7)	1.302(5)	1.289(7)	1.270(7)
O(1)–Cr(1)–N(1)	90.25(5)	90.05(15)	O(1)–Cr(1)–N(1)	87.27(18)	87.78(11)	88.17(18)	86.67(18)
O(1)–Cr(1)–Cl(1)	98.65(4)	97.05(13)	O(1)–Cr(1)–Cl(1)	92.14(15)	94.67(8)	95.69(13)	94.66(14)
N(1)–Cr(1)–Cl(1)	92.15(5)	93.16(12)	N(1)–Cr(1)–Cl(1)	100.40(16)	100.14(9)	96.24(14)	100.01(15)
Cp–Cr(1)–O(1)	119.5	120.1	Cp*–Cr(1)–O(1)	120.3	120.1	122.2	118.9
Cp–Cr(1)–N(1)	128.1	125.9	Cp*–Cr(1)–N(1)	126.7	125.1	124.0	126.7
Cp–Cr(1)–Cl(1)	120.5	122.4	Cp*–Cr(1)–Cl(1)	120.8	120.9	122.2	121.1
Cp-phenyl ring	61.2	49.1	Cp*-phenyl ring	17.1	9.4	21.4	13.7
Cp–[O–Cr–N]	51.0	51.4	Cp*–[O–Cr–N]	49.6	46.2	48.0	47.4

Table 2 Summary of ethylene polymerization catalyzed by complexes 1–7 activated with AlR_3[a]

Entry	Complex	AlR_3	T/°C	Time/min	Yield/g	Activity[b]	Mη[c] ($\times 10^4$)	Tm[d]/°C	Xc[e] (%)
1	**1**	$AlMe_3$	20	30	trace	—	—	—	—
2	**1**	$AlEt_3$	20	30	1.32	528	69	138.6	56.6
3	**1**	Al^iBu_3	20	30	0.19	76	72	138.5	57.2
4	**2**	$AlMe_3$	20	30	0.21	84	86	138.9	59.3
5	**2**	$AlEt_3$	20	30	2.18	872	108	139.2	60.3
6	**2**	Al^iBu_3	20	30	0.32	128	93	139.1	59.6
7	**3**	$AlMe_3$	20	30	0.26	104	106	138.7	58.1
8	**3**	$AlEt_3$	20	30	2.94	1176	133	139.1	64.7
9	**3**	Al^iBu_3	20	30	0.44	176	109	138.5	61.6
10	**4**	$AlMe_3$	20	30	Trace	—	—	—	—
11	**4**	$AlEt_3$	20	30	0.74	296	136	138.4	60.6
12	**4**	Al^iBu_3	20	30	0.15	60	120	138.8	61.2
13	**5**	$AlMe_3$	20	30	0.18	72	78	138.6	58.9
14	**5**	$AlEt_3$	20	30	1.24	496	87	139.1	63.8
15	**5**	Al^iBu_3	20	30	Trace	—	—	—	—
16	**6**	$AlMe_3$	20	30	0.19	76	103	138.4	59.4
17	**6**	$AlEt_3$	20	30	2.05	820	126	139.3	61.5
18	**6**	Al^iBu_3	20	30	0.28	112	114	139.1	60.8
19	**7**	$AlMe_3$	0	30	2.85	1140	92	137.6	65.8
20	**7**	$AlMe_3$	20	30	2.11	844	108	138.3	61.1
21	**7**	$AlMe_3$	40	30	0.98	392	116	138.6	62.4
22	**7**	$AlEt_3$	20	5	1.72	4128	108	137.2	61.2
23	**7**	$AlEt_3$	20	10	2.94	3528	114	137.3	63.1
24	**7**	AlEt3	20	15	3.78	3024	126	138.6	62.2
25	**7**	$AlEt_3$	20	20	4.35	2610	136	139.1	64.4
26	**7**	$AlEt_3$	20	30	5.65	2260	141	140.1	65.6
27	**7**	Al^iBu_3	20	30	0.67	268	117	138.6	54.2
28	**8**	$AlMe_3$	20	30	0.17	68	103	138.4	57.3
29	**8**	$AlEt_3$	20	30	2.83	1132	138	138.8	60.5
30	**8**	Al^iBu_3	20	30	0.22	88	124	138.5	58.6

[a] Polymerization conditions: solvent 60 ml of toluene, catalyst 5 umol, Al/Cr 25, time 30 min, ethylene pressure 5 bar. [b] Kg PE mol Cr^{-1} h^{-1}. [c] Measured in decahydronaphthalene at 135 °C. [d] Determined by DSC at a heating rate of 10 k min^{-1}. [e] Crystallinity Xc = $\Delta H_f/\Delta H_f^\circ$, ΔH_f° = 273 J g^{-1} for completely crystalline PE.

For the catalyst systems studied in this work, the interaction between the catalyst and co-catalyst molecules may be quite different for different alkylaluminium co-catalysts. For the $AlMe_3$ activated catalyst systems, the interaction between the catalyst and co-catalyst molecules might be too strong for $AlMe_3$ being replaced by ethylene, which gives rise to these catalyst systems showing low productivity. The fact that the productivity of these catalysts is also very low when activated with Al^iBu_3 may be due to the Al^iBu_3 molecule being so bulky that there is not enough space available for an ethylene molecule to approach the metal center and replace the Al^iBu_3 molecule, although the interaction between the catalyst and Al^iBu_3 molecules is not very strong. To investigate the effect of polymerization temperature on the productivity of these catalyst systems, ethylene polymerization experiments with typical complex **7** were carried out at 0, 20, and 40 °C, and the results were listed in Table 2 (entries 19–21). It was found that the productivity of complex **7** increases with the decrease in polymerization temperature from 40 °C to 0 °C. This result seems to be indicative of that the thermal stability of the catalytically active species formed during the polymerization is improved with the decrease in polymerization temperature, which leads to the increase in the productivity. Otherwise, the productivity would decrease with the decrease in polymerization temperature since the polymerization reaction rate would be expected to decrease from 40 °C to 0 °C. The variation in the productivity of the complexes of this type with polymerization time was also examined with complex 7 (entries 22–26 in Table 2). As can be seen from these results, though the productivity decreases with the polymerization time from 5 to 30 min, the lifetime of the catalyst is relatively long and the polymerization reaction can last for at least 30 min.

The polyethylenes produced by these catalysts with an Al/Cr molar ratio of 25 possess high molecular weight (0.7–1.4 $\times$ 10^6 Dalton). Their viscosity-average molecular weight (Mη) was measured in decahydronaphthalene at 135 °C and the Mη data are given in Table 2. By examining the Mη data, it can be seen that the molecular weight of the polyethylene is affected by several factors. In general, catalysts with bulky Cp′, R^1 and R^3 groups seem to produce polyethylenes with relatively high molecular weight, which can be attributed to a catalyst with bulkier coordination environment would slow down the rate of the chain transfer reaction. These results are normal for metallocene catalyst systems[26] and similar results were also observed for related half-sandwich chromium(III) catalysts bearing hydroxyindanimine ligands.[13b] The obtained polyethylene samples were all analyzed by differential scanning calorimetry (DSC), and the melting transition temperature and crystallinity data are summarized in Table 2. Most of the samples show a sharp endothermic melting peak in the range of 138.4–139.2° in their DSC diagrams with the crystallinity in the range of 54.2–66.9%. The high melting transition temperature implies the obtained

polyethylenes are linear,[24] and the sharp melting peak is indicative of that the molecular weight distribution of these polyethylenes is narrow. ^{13}C NMR spectra of the polyethylene samples obtained at 130 °C in $C_6D_4Cl_2$ show no signals for branches,[27] which confirms that the polyethylenes are linear.

Conclusion

A number of half-metallocene chromium(III) complexes bearing a salicylaldiminato ligand, Cp′[2-R^1-4-R^2-6-(CH=NR^3)C$_6$H$_2$O]CrCl (**1–8**) were synthesized in good yields. X-Ray crystallographic analysis indicates that these half-metallocene chromium(III) complexes adopt a pseudo-octahedral coordination environment with a three-legged piano stool geometry. When activated with a small amount of AlR_3, these complexes exhibit good to high productivity for ethylene polymerization and produce high molecular weight polyethylene under mild conditions. These complexes show higher productivity upon activation with $AlEt_3$ than with $AlMe_3$ and Al^{t}Bu$_3$ co-catalysts. The complexes with R^2 = NO$_2$ show slightly lower productivity in comparison to the corresponding complexes with R^2 = H under similar conditions.

Experimental

General considerations

All manipulations for air- and water-sensitive compounds were performed under an inert atmosphere of nitrogen using standard Schlenk or glovebox techniques. Solvents were dried and purified by known procedures and distilled under nitrogen prior to use. $CrCl_3(THF)_3$[28] and Cp*Li[29] were prepared according to the literature procedures. All other reagents were purchased from Aldrich or Acros and used as received. ^{1}H NMR spectra were measured using a Varian Mercury-300 NMR spectrometer and the elemental analysis was performed on a Perkin-Elmer 2400 analyzer. The intrinsic viscosity [η] was measured in decahydronaphthalene at 135 °C using an Ubbelohde viscometer. Viscosity average molecular weight (Mη) values of polyethylenes were calculated by the following equation[30]: [η] = 6.77 × 10^{-4} M$\eta^{0.67}$. Melting transition temperature (Tm) and crsytallinity (Xc) of the polymers were measured with a 204 differential scanning calorimeter (DSC). The samples (5–10 mg) were heated from 30 °C to 180 °C at a rate of 10 °C min^{-1} and the data from the second heating cycle were used. ^{13}C NMR spectra of polyethylene samples were measured on a Varian Unity 400-MHz spectrometer at 130 °C in *O*–$C_6D_4Cl_2$.

2-^{i}Pr-6-(CH=N^{i}Pr)C$_6$H$_3$OH (HL$_3$). To a stirred mixture of 3-bromyl-5-isopropylsalicylaldehyde (2.43 g, 10.0 mmol) and anhydrous $MgSO_4$ (~1 g) in *n*-hexane (15 mL) was added *tert*-butylamine (1.46 g, 20.0 mmol) under nitrogen. After the mixture was heated at reflux temperature for 8 h, the solvent was removed under reduced pressure to give the crude imine product. The crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (95 : 5) as the eluent to afford pure HL$_3$ (2.74 g, 9.21 mmol, 92.1%) as an orange oil. ^{1}H NMR ($CDCl_3$): δ 1.25 (s, *J* = 2.4 Hz, 6H, CH*Me*$_2$), 1.47 (s, 9H, C*Me*$_3$), 3.55 (h, *J* = 2.4 Hz, 1H, C*H*Me$_2$), 7.47 (s, 1H, Ph*H*), 7.62 (s, 1H, Ph*H*), 8.38 (s, 1H, C*H* = N), 14.38 (s, 1H, O*H*).

2-Ph-4-NO$_2$-6-(CH=N^{i}Pr)C$_6$H$_2$OH (HL$_4$). To a solution of 5-phenylsalicylaldehyde (6.94 g, 35 mmol) in 25 mL of glacial acetic acid was added a nitric acid (2.20 ml, 16 M, 35.2 mmol) solution in 10 mL of glacial acetic acid at room temperature, and the reaction solution was stirred for 6 h. To the reaction mixture was added 100 mL of saturated Na_2CO_3 aqueous solution and the product was extracted with 100 mL of ethyl ether. The organic phase was separated and washed with water (2 × 100 mL), dried over $MgSO_4$, and filtered. The solvent was removed by rotatory evaporation to leave the crude product which was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (90 : 10) as the eluent. Pure 3-phenyl-5-nitrosalicylaldehyde (7.65 g, 31.5 mmol, 90%) was obtained as an orange oil. ^{1}H NMR ($CDCl_3$): δ 7.24 (m, 3H, *s*-Ph*H*), 7.37 (d, *J* = 6.9 Hz, 2H, *s*-Ph*H*), 8.26 (s, 1H, Ph*H*), 8.30 (s, 1H, Ph*H*), 9.80 (s, 1H, C*H*O), 11.92 (s, 1H, O*H*). Compound HL$_4$ was synthesized in the same manner as HL$_3$ with 3-phenyl-5-nitrosalicylaldehyde (2.43 g, 10.0 mmol) and isopropylamine (1.20 g, 20.0 mmol) as starting materials. Pure product (2.82 g, 97.5%, 9.75 mmol) was obtained as yellow crystals. ^{1}H NMR ($CDCl_3$): δ 1.31 (d, *J* = 6.0 Hz, 6H, CH*Me*$_2$), 3.59 (m, *J* = 6.3 Hz, 1H, C*H*Me$_2$), 6.96 (t, *J* = 7.2 Hz, 1H, aromatic-H),7.28 (d, *J* = 7.2 Hz, 2H, aromatic-H), 7.35 (d, *J* = 7.2 Hz, 2H, aromatic-H), 7.48 (t, *J* = 7.2 Hz, 1H, Ph*H*), 7.64 (d, 2H, Ph*H*), 8.42 (s, 1H, CH = N), 14.47 (s, 1H, O*H*).

2-^{t}Bu-4-NO$_2$-6-(CH=N^{i}Pr)C$_6$H$_2$OH (HL$_5$). 3-tertbutyl-5-nitrosalicylaldehyde (6.69 g, 30.0 mmol, 86%) was obtained as an orange oil. ^{1}H NMR ($CDCl_3$): δ 1.46 (s, 9H, C*Me*$_3$), 8.41 (s, 2H, Ph*H*), 9.97 (s, 1H, C*H*O), 12.44 (s, 1H, O*H*). Compound HL$_5$ was synthesized in the same manner as HL$_4$ with 3-*tert*-butyl-5-nitrosalicylaldehyde (2.23 g, 10.0 mmol) and isopropylamine (1.20 g, 20.0 mmol) as starting materials. Pure product (2.54 g, 9.61 mmol, 96.1%) was obtained as yellow crystals. ^{1}H NMR ($CDCl_3$): δ 1.38 (d, *J* = 6.3 Hz, 6H, CH*Me*$_2$), 1.44(s, 9H, C*Me*$_3$), 3.73 (m, *J* = 6.3 Hz, 1H, C*H*Me$_2$), 7.86 (s, 1H, Ph*H*), 7.94 (s, 1H, Ph*H*), 8.07 (s, 1H, C*H*=N), 15.10 (s, 1H, O*H*).

2-Ph-4-NO$_2$-6-(CH=N^{t}Bu)C$_6$H$_2$OH (HL$_6$). Compound HL$_6$ was synthesized in the same manner as HL$_4$ with 3-phenyl-5-nitrosalicylaldehyde (2.43 g, 10.0 mmol) and *tert*-butylamine (1.46 g, 20.0 mmol) as starting materials. Pure product (2.84 g, 9.5 mmol, 95.2%) was obtained as yellow crystals. ^{1}H NMR ($CDCl_3$): δ 1.48 (s, 9H, C*Me*$_3$), 7.36 (t, *J* = 7.2 Hz, 1H, aromatic-H),7.45 (t, *J* = 7.2 Hz, 2H, aromatic-H), 7.45 (d, *J* = 7.2 Hz, 2H, aromatic-H), 7.62 (d, *J* = 7.2 Hz, 1H, Ph*H*), 8.26 (s, 1H, Ph*H*), 8.28 (s, 1H, CH = N), 14.68 (s, 1H, O*H*).

CpCr[2-Ph-6-(CH=N^{i}Pr)C$_6$H$_3$O]Cl (1). A suspension of CpLi (0.144 g, 2.00 mmol) in THF (10 mL) was slowly added to a purple suspension of $CrCl_3(THF)_3$ (0.750 g, 2.00 mmol) in THF (20 mL) at 0 °C. The mixture was allowed to warm to room temperature and stirred overnight to get a blue solution. In another flask, to a solution of 2-Ph-6-(CH=N^{i}Pr)C$_6$H$_3$OH

(HL_1) (0.477 g, 2.00 mmol) in THF (15 mL) was added NaH (60% purity, 0.820 g, 2.05 mmol) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 1 h, then added slowly to the above reaction mixture at −15 °C. The obtained reaction mixture was allowed to warm to room temperature and stirred overnight. During the reaction, the color of the reaction mixture changes from blue to green. Removal of the solvents under reduced pressure to give a dark-green residue, followed by extraction with toluene (20 mL) to remove the insoluble impurities. Pure product **1** was obtained by recrystallization from CH_2Cl_2/*n*-hexane (v/v = 1∼2 : 10) as green crystals (0.545 g, 1.39 mmol, 69.5%). Mp: 143 °C. Anal. Calcd for $C_{21}H_{21}ClCrNO$ (390.85): C 64.53; H 5.42; N 3.58. Found: C 64.26; H 5.30; N 3.51.

Cp*Cr[2-Ph-6-(CH=N^{i}Pr)C_6H_3O]Cl (2). Complex **2** was synthesized in the same manner as **1** with HL_1 (0.477 g, 2.00 mmol), NaH (60% purity, 0.820 g, 2.05 mmol), Cp*Li (0.284 g, 2.00 mmol) and $CrCl_3(THF)_3$ (0.750 g, 2.00 mmol) as starting materials. Pure **2** (0.650 g, 1.41 mmol, 70.5%) was obtained as green powder. Mp: 153 °C. Anal. Calcd for $C_{26}H_{31}ClCrNO$ (460.98): C 67.74; H 6.78; N, 3.04; Found: C 67.66; H 6.71; N 3.08.

Cp*Cr[2-Ph-6-(CH=N^{t}Bu)C_6H_3O]Cl (3). Complex **3** was synthesized in the same manner as **1** with 2-Ph-6-(CH=N^{t}Bu)-C_6H_3OH (HL_2) (0.507 g, 2.00 mmol), NaH (60% purity, 0.820 g, 2.05 mmol), Cp*Li (0.284 g, 2.00 mmol) and $CrCl_3(THF)_3$ (0.750 g, 2.00 mmol) as starting materials. Pure **3** (0.641 g, 1.35 mmol, 67.5%) was obtained as green powder. Mp: 161 °C. Anal. Calcd for $C_{27}H_{33}ClCrNO$ (475.01): C 68.27; H 7.00; N 2.95. Found: C 68.39; H 6.92; N 2.96.

Cp*Cr[2-^{i}Pr-4-Br-6-(CH=N^{t}Bu)C_6H_2O]Cl (4). Complex **4** was synthesized in the same manner as **1** with HL_3 (0.596 g, 2.00 mmol), NaH (60% purity, 0.820 g, 2.05 mmol), Cp*Li (0.284 g, 2.00 mmol) and $CrCl_3(THF)_3$ (0.750 g, 2.00 mmol) as starting materials. Pure **4** (0.504 g, 1.04 mmol, 52.0%) was obtained as green crystals. Mp: 166 °C.Anal. Calcd for $C_{24}H_{34}BrNOCrCl$ (484.43): C 59.70; H 7.07; N 2.89. Found: C 59.52; H 7.00; N 2.81.

CpCr[2-Ph-4-NO_2-6-(CH=N^{i}Pr)C_6H_2O]Cl (5). Complex **5** was synthesized in the same manner as **1** with HL_4 (0.568 g, 2.00 mmol), NaH (60% purity, 0.820 g, 2.05 mmol), CpLi (0.144 g, 2.00 mmol) and $CrCl_3(THF)_3$ (0.750 g, 2.00 mmol) as starting materials. Pure **5** (0.532 g, 1.22 mmol, 61.1%) was obtained as green crystals. Mp: 149 °C. Anal. Calcd for $C_{21}H_{20}ClCrN_2O_3$ (435.84): C 57.87; H 4.63; N 6.43. Found: C 57.76; H 4.55; N 6.40.

Cp*Cr[2-Ph-4-NO_2-6-(CH=N^{i}Pr)C_6H_2O]Cl (6). Complex **6** was synthesized in the same manner as **1** with HL_4 (0.568 g, 2.00 mmol), NaH (60% purity, 0.820 g, 2.05 mmol), Cp*Li (0.284 g, 2.00 mmol) and $CrCl_3(THF)_3$ (0.750 g, 2.00 mmol) as starting materials. Pure **6** (0.643 g, 1.27 mmol, 63.3%) was obtained as green crystals. Mp: 158 °C. Anal. Calcd for $C_{26}H_{30}ClCrN_2O_3$ (505.98): C 61.72; H 5.98; N 5.54. Found: C 61.56; H 5.89; N 5.52.

Cp*Cr[2-^{t}Bu-4-NO_2-6-(CH=N^{i}Pr)C_6H_2O]Cl (7). Complex **7** was synthesized in the same manner as **1** with HL_5 (0.529 g, 2.00 mmol) with Cp*Li (0.284 g, 2.00 mmol), $CrCl_3(THF)_3$ (0.750 g, 2.00 mmol) and NaH (60% purity, 0.820 g, 2.05 mmol) as starting materials. Pure **7** (0.637 g, 1.31 mmol, 65.5%) was obtained as green crystals. Mp: 163 °C. Anal. Calcd for $C_{24}H_{34}ClCrN_2O_3$ (485.99): C 59.31; H 7.05; N 5.76. Found: C 59.24; H 7.08; N 5.78.

Cp*Cr[2-Ph-4-NO_2-6-(CH=N^{t}Bu)C_6H_2O]Cl (8). Complex **8** was synthesized in the same manner as **1** with HL_6 (0.507 g, 2.00 mmol), NaH (60% purity, 0.820 g, 2.05 mmol), Cp*Li (0.284 g, 2.00 mmol) and $CrCl_3(THF)_3$ (0.750 g, 2.00 mmol) as starting materials. Pure **8** (0.671 mg, 1.29 mmol, 64.5%) was obtained as green crystals. Mp: 167 °C. Anal. Calcd for $C_{27}H_{32}ClCrN_2O_3$ (520.00): C 62.36; H 6.20; N 5.39. Found: C 62.25; H 6.16; N 5.31.

Table 3 Crystal data and structural refinements details for complexes **1**, **3–5** and **7–8**.

Complexes	**1**	**3**	**4**·$CHCl_3$	**5**·CH_2Cl_2	**7**·CH_2Cl_2	**8**·CH_2Cl_2
Formula	$C_{21}H_{21}ClCrNO$	$C_{27}H_{33}ClCrNO$	$C_{25}H_{35}BrClCrNO\cdot CHCl_3$	$C_{21}H_{20}ClCrN_2O_3\cdot CH_2Cl_2$	$C_{24}H_{34}ClCrN_2O_3\cdot CH_2Cl_2$	$C_{27}H_{32}ClCrN_2O_3\cdot CH_2Cl_2$
Fw	390.84	474.99	639.25	520.77	570.91	604.92
Cryst syst	Orthorhombic	Triclinic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	*Pbca*	$P\bar{1}$	$P2_12_12$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a/Å	12.378(3)	7.7239(15)	12.321(3)	11.365(2)	9.839(2)	9.0986(18)
b/Å	16.829(3)	16.784(3)	25.157(5)	18.149(4)	11.779(2)	12.398(3)
c/Å	17.805(4)	20.079(4)	9.3501(19)	12.4745(3)	25.013(5)	26.249(5)
α (°)	90	80.09(3)	90	90	90	90
β (°)	90	80.03(3)	90	110.76(3)	99.29(3)	94.29(3)
γ (°)	90	85.18(3)	90	90	90	90
V/Å^3	3709.1(13)	2521.5(9)	2898.2(11)	2400.3(8)	2860.9(10)	2952.6(10)
Z	8	4	4	4	4	4
F(000)	1624	1004	1308	1068	1196	1260
M mm^{-1}	1.400	0.578	2.160	0.836	0.708	0.690
R_{int}	0.0328	0.1368	0.0573	0.0654	0.1476	0.1961
R_1	0.0319	0.0951	0.0414	0.0741	0.1015	0.1000
WR_2	0.0831	0.1901	0.0880	0.2262	0.1957	0.2035
GooF	1.077	1.011	1.023	1.037	1.062	1.022

X-Ray crystallographic studies

Single crystals of complexes **1**, **3–5**, **7–8** suitable for X-ray crystal structural analysis were obtained from CH_2Cl_2–*n*-hexane or $CHCl_3$–*n*-hexane (v/v = 1 ~ 2 : 10) mixed solvent system. The data were collected on the Siemens P4 four-circle diffractometer at 293 K. All structures were solved by direct methods[31] and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were included in idealized positions. All calculations were performed using the SHELXTL crystallographic software packages.[32] Details of the crystal data, data collections, and structure refinements are summarized in Table 3.

Ethylene polymerization experiments

A dry 250 ml steel autoclave with a magnetic stirrer was charged with 60 ml of toluene, and saturated with ethylene (1.0 bar) at 20 °C. The autoclave was kept in a water bath at the corresponding temperature. The polymerization reaction was started by injection of a mixture of AlR_3 and a catalyst in toluene (10 ml). The vessel was repressurized to the required pressure with ethylene immediately and the pressure was kept by continuously feeding ethylene. After 30 min, the polymerization was quenched by injecting acidified methanol [HCl (3M)/methanol = 1 : 1], and the polymer was collected by filtration, washed with water, methanol, and dried at 60 °C in vacuo to a constant weight.

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