

Immobilization and activation of 2,6-bis(imino)pyridyl Fe, Cr and V precatalysts using a $\text{MgCl}_2/\text{AlR}_n(\text{OEt})_{3-n}$ support: Effects on polyethylene molecular weight and molecular weight distribution

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Received 24 April 2006; received in revised form 13 June 2006; accepted 12 July 2006

Available online 22 August 2006

Abstract

Ethylene polymerizations carried out with various bis(imino)pyridyl iron, chromium and vanadium complexes immobilized on a $\text{MgCl}_2/\text{AlR}_n(\text{OEt})_{3-n}$ support gave relatively broad polyethylene molecular weight distributions in the case of iron, but high molecular weight and a very narrow molecular weight distribution with vanadium, indicative of a single active species. The narrow MWD was confirmed by melt rheometry. Similar results were obtained after reaction of the bis(imino)pyridyl complex LVCl_3 (**6**) with MeLi or AlEt_3 , where alkylation of the pyridine ring gives a complex $\text{L}'\text{VCl}_2$ (**7**). In the case of chromium, a bimodal distribution was obtained, with evidence of incomplete catalyst immobilization. The polyethylene molecular weights obtained with the iron complexes were strongly dependent on the substituents in the bis(imino)pyridyl ligand, and were somewhat higher than have been obtained in homogeneous polymerization. In contrast, the molecular weights obtained with the bis(imino)pyridyl chromium and vanadium complexes were much higher than those previously obtained under homogeneous conditions. In all cases, the activities of the immobilized catalysts were higher than those found in homogeneous polymerization.

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Keywords: Catalysis; Ethylene; Immobilization; Magnesium chloride; Polymerization

1. Introduction

Bis(imino)pyridyl iron complexes of type $\{\text{ArN}=\text{C}(\text{Me})\}_2\text{C}_5\text{H}_3\text{N}\}\text{FeCl}_2$ have been shown to be very active precatalysts for ethylene polymerization [1,2]. However, in contrast to the great majority of homogeneous olefin precatalysts, these systems typically give polyethylene with relatively broad molecular weight distribution. In many cases a bimodal molecular weight distribution is obtained and evidence has been presented that, for systems activated with methylaluminoxane (MAO), this is caused by the formation of a low molecular weight fraction resulting from chain transfer to aluminium, particularly in the early stages of polymerization [3]. The question remains as to whether chain transfer to aluminium is the only reason for the broad polydispersities obtained with these systems, or whether more than one type

of active species is operative [4]. Strong evidence for the presence of different active species has recently been provided by Barabanov et al. [5], who used ^{14}C radiotagging to determine the numbers of active centres and propagation rate constants in homogeneous polymerization. The results obtained indicated the presence of highly reactive but unstable active centres producing a low molecular weight polymer fraction, as well as less active but more stable species producing higher molecular weight polymer. Iron-based precatalysts can be activated by both MAO and aluminium trialkyls and it has been reported that narrow molecular weight distribution can be obtained using Al/Bu_3 [6,7] or $i\text{Bu}_2\text{AlOAl}/\text{Bu}_2$ [8]. Following these studies, carried out under homogeneous polymerization conditions, several groups investigated the immobilization and activation of bis(imino)pyridyl iron precatalysts on various supports, including silica [9–11] and magnesium chloride [12,13]. The MgCl_2 -supported systems consistently gave broad polyethylene molecular weight distribution, irrespective of the type of aluminium trialkyl used as cocatalyst.

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Recently, we and others have investigated the immobilization of a range of early- and late-transition metal precatalysts using supports of type $\text{MgCl}_2/\text{AlR}_n(\text{OR})_{3-n}$, prepared by reaction of AlR_3 with either solid, spherical adducts of MgCl_2 and ethanol [12,14] or adducts of MgCl_2 and 2-ethylhexanol in hydrocarbon solution [15]. Widespread implementation of homogeneous and single-site catalysts in polyolefin production, especially in gas-phase and slurry processes, is dependent on the development of effective techniques for catalyst immobilization and considerable research is being carried out in this field [16]. Our own studies have concentrated on the use of supports typically prepared by the reaction of AlEt_3 with spherical, partially dealcoholated adducts of MgCl_2 and EtOH [17]. The spherical particle morphology of the support is retained and replicated during catalyst immobilization and polymerization, leading to the formation of spherical polymer particles without reactor fouling.

In the present work, we have investigated the immobilization and activation of different bis(imino)pyridyl iron(II) precatalysts, including the effect of cocatalyst type and concentration. In order to assess whether with these systems the polyethylene polydispersity is dependent on the transition metal, the ligand or the metal/ligand combination, bis(imino)pyridyl chromium(II) and vanadium(III) precatalysts have also been immobilized and activated using the same $\text{MgCl}_2/\text{AlR}_n(\text{OEt})_{3-n}$ support.

2. Experimental

2.1. Materials

All manipulations were performed under an argon atmosphere using glove box (Braun MB-150 G1 or LM-130) and Schlenk techniques. Light petroleum (b.p. 40–60 °C) and dichloromethane were passed over a column containing Al_2O_3 and stored over 4 Å molecular sieves. All the solvents were freeze-thaw degassed at least twice prior to use.

Precatalysts **1–4** (structures shown in Scheme 1) were prepared according to various literature procedures [3,18,19]. {2,6-[ArN=C(Me)]₂C₅H₃N}CrCl₂ (**5**; Ar = 2,6-diisopropylphenyl) and {2,6-[ArN=C(Me)]₂C₅H₃N}VCl₃ (**6**; Ar = 2,6-diisopropylphenyl) were prepared following procedures similar to those described by Devore et al. [20] and by Gambarotta and coworkers

[21]. {2,6-[ArN=C(Me)]₂(2-MeC₅H₃N)}VCl₂ (**7**; Ar = 2,6-diisopropylphenyl) was prepared by the reaction of **6** with MeLi in toluene as described by Gambarotta and coworkers [21]; after solvent removal under vacuum, the residue was redissolved in ether and after filtration the ether was removed under vacuum to yield a dark green solid.

AlEt_3 (25 wt.% solution in toluene) and ZnEt_2 (1.0 M solution in hexane) were purchased from Aldrich. $\text{Al}i\text{Bu}_3$ (1 M solution in hexane) and MAO (25 wt.% solution in toluene) were purchased from Fluka and Akzo Nobel, respectively.

Ethylene (3.5 grade supplied by Air Liquide) was purified by passing over columns of 4 Å molecular sieves and BTS copper catalyst.

2.2. Support preparation and catalyst immobilization

Support preparation was performed by the addition of AlEt_3 to a slurry of an adduct $\text{MgCl}_2 \cdot 1.1\text{EtOH}$ (average particle size d_{50} 82 μm) in light petroleum ($\text{AlEt}_3/\text{EtOH} = 2$) at 0 °C, after which the mixture was kept at room temperature for 2 days with occasional agitation. The resultant support was washed with light petroleum three times and dried under argon flow and subsequently under vacuum until free flowing. The Al contents of the support were determined by the H. Kolbe Microanalytisches Laboratorium, Mülheim an der Ruhr, Germany. The ethoxide content in $\text{MgCl}_2/\text{AlEt}_n(\text{OEt})_{3-n}$ support was determined by gas chromatography (GC) analysis of the ethanol content of a solution obtained by dissolving 100 mg of support in 5 mL of BuOH containing a known quantity of PrOH as an internal standard. The Al and OEt contents of the support were 3.89 and 4.89 wt.%, respectively, indicating an overall support composition $\text{MgCl}_2 \cdot 0.17\text{AlEt}_{2.25}(\text{OEt})_{0.75}$.

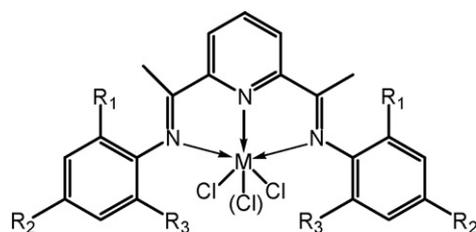
Catalyst immobilization was effected by mixing the support (50–100 mg) with a precatalyst solution in dichloromethane (2 mL, containing 0.5–1.0 μmol of precatalyst) and keeping at room temperature overnight. The slurry of the immobilized catalyst in dichloromethane was diluted with light petroleum and used directly in ethylene polymerization.

2.3. Polymerization procedure

Polymerization was carried out in a 1L Premex autoclave by charging the immobilized catalyst (50–100 mg, containing 0.5–1.0 μmol precatalyst), slurried in approximately 100 mL light petroleum, to 400 mL light petroleum containing the desired amount of cocatalyst, at 50 °C and an ethylene pressure of 5 bar. After catalyst injection, polymerization was continued at constant pressure for 1 h and with a stirring rate of around 1000 rpm. After venting the reactor, 20 mL of acidified ethanol were added and stirring was continued for 30 min. The polymer was recovered by filtration, washed with water and ethanol and dried in vacuo overnight at 60 °C.

2.4. Polymer characterization

Molecular weights and molecular weight distributions of the resulting polymers were determined by means of gel perme-



Cat.	M	R ₁	R ₂	R ₃
1	Fe	Me	Me	Me
2	Fe	<i>i</i> Pr	H	<i>i</i> Pr
3	Fe	Cl	Me	Me
4	Fe	Me	H	H
5	Cr	<i>i</i> Pr	H	<i>i</i> Pr
6	V	<i>i</i> Pr	H	<i>i</i> Pr

Scheme 1. Structure of bis(imino)pyridyl metal (Fe, Cr and V) precatalysts.

ation chromatography on a PL-GPC210 at 135 °C using 1,2,4-trichlorobenzene as solvent. Melting points of the polymers were obtained on a Q100 (TA Instruments) DSC in the standard DSC run mode. The particle morphologies of the polymers were examined using a Philips S-250MK3 SEM-EDX.

Oscillatory shear measurements were performed on a Rheometrics ARES melt rheometer. Strain controlled frequency sweep tests were carried out at 180 °C over an angular frequency range from 0.01 to 100 rad s⁻¹. The constant dynamic strain applied on a compressed PE plate of diameter 8 mm was 0.5%. The measurements were performed using parallel plate geometry, maintaining a distance between the plates of about 0.5 mm. All measurements were carried out under nitrogen atmosphere on polymers stabilized with 0.1 wt.% Irganox 1010 (added as a solution in acetone, after which the polymer was dried under reduced pressure).

3. Results and discussion

3.1. Bis(imino)pyridyl iron precatalysts

Our first studies were directed at the immobilization and activation of the bis(imino)pyridyl iron complexes **1–3**. Previous results have shown that high polymerization activity and good polymer particle morphology could be obtained with precatalysts **1** and **2**, using MgCl₂-based supports similar to those used in the present work [12]. Precatalyst **3** was selected in order to investigate the effect on polyethylene molecular weight of chloro substitution in the aryl rings of the ligand, it having been reported that the electron-withdrawing effect of halogen-containing ligands leads to a lowering of product molecular weight in ethylene polymerization and oligomerization [22]. The immobilization of these precatalysts was carried out using a support of composition MgCl₂·0.17AlEt_{2.25}(OEt)_{0.75}, prepared by reaction of AlEt₃ with a slurry of an adduct MgCl₂·1.1EtOH

in light petroleum. Because of the limited solubility of the precatalysts in hydrocarbon solvents, immobilization was carried out at ambient temperature by contact of the support with a dichloromethane solution of the precatalyst. A relatively low precatalyst loading of 10 μmol/g support was used, our previous studies with other catalysts having shown that particularly high catalyst activities can be obtained at low loadings [14b]. Quantitative catalyst immobilization was indicated by complete discoloration of the liquid phase after contacting overnight, to give sand-coloured supported catalysts. We found that it was not necessary to remove the dichloromethane from the immobilized catalyst slurry prior to polymerization. The slurry was simply diluted with light petroleum and injected as such into a polymerization reactor containing light petroleum and different amounts of cocatalyst.

In order to determine the effect of cocatalyst type and concentration on catalyst performance and in particular on the molecular weight and molecular weight distribution of the polymers obtained, polymerizations were carried out in the presence of AlEt₃, Al*i*Bu₃ or ZnEt₂. It has been reported by Gibson and coworkers that, under homogeneous polymerization conditions, low molecular weight polymers having very narrow polydispersity could be obtained in the presence of diethyl zinc [23]. Under such conditions, the chain growth process is characterized by an exceptionally rapid and reversible exchange of the growing polymer chains between iron and zinc. We were interested to see whether this effect could take place in a heterogeneous system, or whether limited molecular mobility would restrict the reversibility of chain transfer between iron and zinc.

The results of the ethylene polymerizations carried out are given in Tables 1–3. In order to ensure effective scavenging of impurities, a cocatalyst concentration of at least 1 mmol/L was used. These polymerizations were carried out at low catalyst concentration (2 μmol/L), resulting in Al/Fe (or Zn/Fe) molar ratios ≥500. It is apparent that very high catalyst activities

Table 1

Effect of cocatalyst in ethylene polymerization with {2,6-[ArN=C(Me)]₂C₅H₃N}FeCl₂ (**1**; Ar = 2,4,6-trimethylphenyl) immobilized on a MgCl₂/AlR_{*n*}(OEt)_{3-*n*} support

Experiment	Cocatalyst	Al/Fe (mol/mol)	Zn/Fe (mol/mol)	Activity (kg mol ⁻¹ Fe bar ⁻¹ h ⁻¹)	\bar{M}_w (g/mol)	\bar{M}_n (g/mol)	\bar{M}_w/\bar{M}_n
1	AlEt ₃	500	0	17400	435800	44400	9.8
2	AlEt ₃	1000	0	15090	425600	38500	11.1
3	Al <i>i</i> Bu ₃	500	0	4840	425800	38500	11.1
4	Al <i>i</i> Bu ₃	1000	0	10000	418900	36100	11.6
5	ZnEt ₂	0	500	1470	163300	30100	5.4
6	ZnEt ₂	0	1000	1800	144900	24700	5.9

Table 2

Effect of cocatalyst in ethylene polymerization with {2,6-[ArN=C(Me)]₂C₅H₃N}FeCl₂ (**2**; Ar = 2,6-diisopropylphenyl) immobilized on a MgCl₂/AlR_{*n*}(OEt)_{3-*n*} support

Experiment	Cocatalyst	Al/Fe (mol/mol)	Zn/Fe (mol/mol)	Activity (kg mol ⁻¹ Fe bar ⁻¹ h ⁻¹)	\bar{M}_w (g/mol)	\bar{M}_n (g/mol)	\bar{M}_w/\bar{M}_n
1	AlEt ₃	500	0	4620	748600	133100	5.6
2	AlEt ₃	1000	0	5200	771400	146000	5.3
3	Al <i>i</i> Bu ₃	500	0	1040	403600	103700	3.9
4	Al <i>i</i> Bu ₃	1000	0	2600	458400	123400	3.7
5	ZnEt ₂	0	500	960	275200	41500	6.6
6	ZnEt ₂	0	1000	2200	320900	46400	6.9

Table 3
Effect of cocatalyst in ethylene polymerization with $\{2,6\text{-[ArN=C(Me)]}_2\text{C}_5\text{H}_3\text{N}\}\text{FeCl}_2$ (**3**; Ar=2-chloro-4,6-dimethylphenyl) immobilized on a $\text{MgCl}_2/\text{AlR}_n(\text{OEt})_{3-n}$ support

Experiment	Cocatalyst	Al/Fe (mol/mol)	Zn/Fe (mol/mol)	Activity ($\text{kg mol}^{-1} \text{Fe bar}^{-1} \text{h}^{-1}$)	\bar{M}_w	\bar{M}_n	\bar{M}_w/\bar{M}_n
1	AlEt ₃	500	0	8200	102100	17900	5.7
2	AlEt ₃	1000	0	7480	103600	13400	7.7
3	Al <i>i</i> Bu ₃	500	0	2320	108800	13100	8.3
4	Al <i>i</i> Bu ₃	1000	0	4320	103200	17100	6.0
5	ZnEt ₂	0	500	1120	84300	13100	6.4
6	ZnEt ₂	0	1000	1920	80500	12300	6.5

were obtained, most notably with precatalyst **1** in combination with AlEt₃. This precatalyst also gave relatively broad molecular weight distribution, with a polydispersity of around 10–12, but no narrowing in molecular weight distribution was observed when Al*i*Bu₃ rather than AlEt₃ was used as cocatalyst. It is also seen that a doubling in AlR₃ concentration had relatively little effect on polyethylene molecular weight, an indication that chain transfer to aluminium was not the reason for the broad polydispersity in this system. There was also no indication of the bimodality typically observed in homogeneous, MAO-activated polymerization, in which the formation of the low molecular weight peak is ascribed to chain transfer to aluminium [1,3]. Ethylene polymerization with precatalyst **1** in combination with diethyl zinc gave lower but still very appreciable activity and also significantly lower molecular weights, confirming the effectiveness of ZnEt₂ as chain transfer agent with the immobilized catalyst. However, polydispersities in the range 5–6 indicate that, in contrast to homogeneous polymerization [23], the reversibility of chain transfer between iron and zinc is limited, no doubt as a result of restricted chain mobility in this heterogeneous system.

The results with precatalyst **2** show similar trends, but in this case somewhat narrower molecular weight distributions were obtained, with AlEt₃ and Al*i*Bu₃ giving polydispersities of 5.3–5.6 and 3.7–3.9, respectively. Precatalyst **3** gave relatively low molecular weights in comparison to precatalysts **1** and **2**, comparison of catalysts **1** and **3** indeed showing that the replacement of a 2-methyl by a 2-chloro substituent in each aryl ring of the ligand leads to a significant molecular weight reduction. Again, no significant effect of cocatalyst concentration on molecular weight or molecular weight distribution is apparent. However, the results in Tables 1–3 indicate that, for most of the systems investigated and particularly when using Al*i*Bu₃ or ZnEt₂, an increase in metal alkyl concentration led to increased catalyst activity. This could indicate that with these alkyls the generation of the catalytically active species was less efficient than was the case with AlEt₃. Al*i*Bu₃ has been reported to be a less efficient activator than AlEt₃ for precatalyst **2** in homogeneous polymerization [7]. It is likely that, in the MgCl₂-immobilized system, the different activities are due to differences in the alkylating capacity of the cocatalyst. The AlEt_n(OEt)_{3-n} present in the support is not likely to play a significant role, although in previous work we have observed that Cp₂TiCl₂ could be activated using MgCl₂/AlEt_n(OEt)_{3-n} in the absence of any additional cocatalyst [14a]. The precise role of magnesium chloride in the immobilization and activation of early- and late-transition metal catalysts is as yet unresolved but

will depend on the nature of the catalyst. In the case of metallocenes which are not easily activated using AlR₃, Lewis acidic sites on the support surface may participate in the formation of cationic active species, as has been described by Marks [24]. This may be less important for the bis(imino)pyridyl iron catalysts, which can be activated with simple aluminium alkyls, but a general advantage of the use of a MgCl₂ support for both early- and late-transition metal systems is stabilization of the active species (vide infra), preventing the rapid decay often observed in homogeneous polymerization.

Comparison of the results obtained with precatalysts **1** and **2** shows that the presence of *isopropyl* as opposed to methyl substituents in the 2,6-positions of the aryl groups in the ligand leads, as has been noted previously [3,12b], to somewhat lower activities. However, at the same time a significant narrowing in polyethylene molecular weight distribution is obtained, using either AlEt₃ or Al*i*Bu₃ as cocatalyst. Comparison of precatalysts **1** and **3** shows that the replacement of a methyl by a chloro substituent leads to somewhat lower activity as well as to the large decrease in polymer molecular weight. Lower activity following the substitution of a methyl group by a chlorine atom on the *ortho* position of the aryl groups has also been noted in homogeneous polymerization [25]. The steric bulk of a chloro substituent is very similar to that of a methyl group, so the different behaviours of catalyst **3** must arise from the electron-withdrawing nature of the halogen substituent, which should diminish the electron density on the metal. The DSC melting temperatures (T_{m2}) of the polymers prepared as in Tables 1–3 were all above 133 °C, indicating the formation of linear, high-density polyethylene. The melting enthalpies of the polymers prepared with precatalysts **1**, **2** and **3** were in the ranges 196–212, 176–188 and 206–231 J/g, respectively, indicating an increase in crystallinity with decreasing molecular weight. Relatively stable activity was observed in all of the above polymerizations. Typical plots are shown in Fig. 1, from which only a moderate decay in activity is apparent from changes in monomer mass flow and the temperature difference between the reactor contents and the cooling mantle. This result is a further illustration of the stabilizing effect of a MgCl₂ support [12,13] and is in striking contrast to the rapid decay typically observed with these catalysts under homogeneous polymerization conditions [3,5,6].

The polymer molecular weights obtained with the MgCl₂-immobilized systems listed in Table 1 are higher than the molecular weights obtained with these precatalysts under homogeneous conditions [3], but the difference is relatively small in comparison to the very large increases in molecular weight fre-

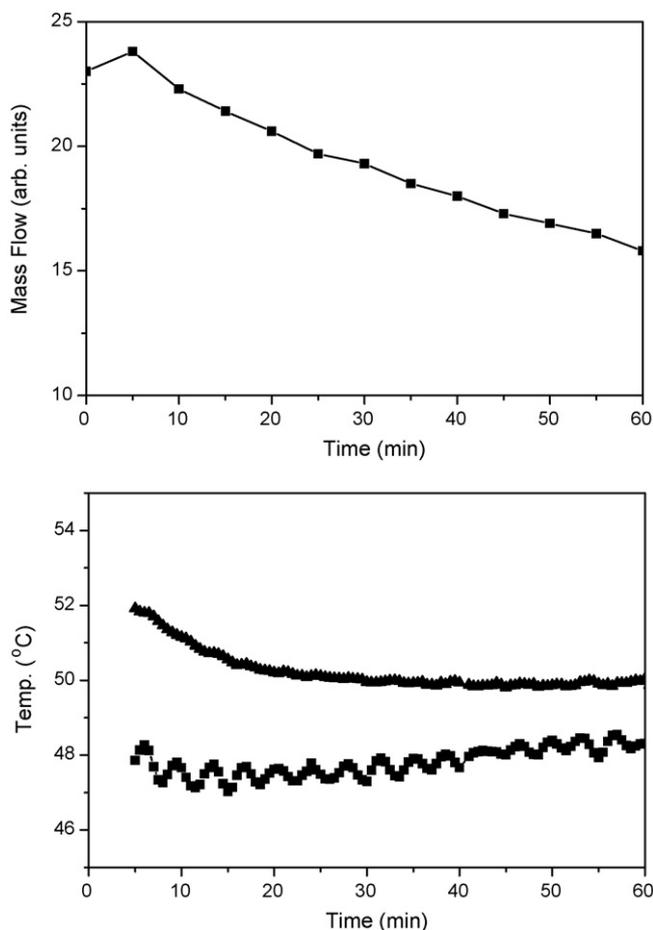


Fig. 1. Mass flow and temperature profiles in ethylene polymerization using complex **1** immobilized on a $\text{MgCl}_2/\text{AlEt}_n(\text{OEt})_{3-n}$ support and activated with AlEt_3 (▲: internal temperature; ●: cooling mantle temperature).

quently observed when immobilizing various early-transition metal precatalysts on similar supports [14a,b]. In order to further assess the effect of precatalyst immobilization on product molecular weight, an additional experiment was carried out with precatalyst **4**, which represents a new generation of ethylene oligomerization catalysts, illustrating the very important role that ligand steric effects play in transition metal-catalyzed olefin polymerization and oligomerization [19]. In this experiment AlEt_3 ($\text{Al}/\text{Fe}=2000$) was used as cocatalyst, resulting in the formation of an oligomeric (light petroleum-soluble) fraction and a solid, polymeric fraction, in the proportions 8.7:1, with an overall catalyst activity of $36\,720\text{ kg mol}^{-1}\text{ Fe bar}^{-1}\text{ h}^{-1}$. ^1H NMR analysis of the oligomeric fraction indicated that the product comprised mainly (91%) vinyl-terminated chains, with \bar{M}_n approximately 250. This result shows that precatalyst **4** remains predominantly an oligomerization catalyst when immobilized on magnesium chloride, a further indication that the effect on product molecular weight of immobilizing a bis(imino)pyridyl iron catalyst on a MgCl_2 -based support is relatively small. The formation of oligomeric and polymeric fractions in MAO-activated homogeneous polymerization with the closely related catalyst $\{2,6\text{-[ArN=C(Me)]}_2\text{C}_5\text{H}_3\text{N}\}\text{FeCl}_2$ ($\text{Ar}=2\text{-ethylphenyl}$) has been reported by Quijada et al. [26].

3.2. Bis(imino)pyridyl chromium and vanadium precatalysts

Tridentate bis(imino)pyridyl ligands have been widely used in the preparation of highly active iron- and cobalt-based catalysts for olefin polymerization, but there are fewer examples of their use in the preparation of early-transition metal precatalysts. However, bis(imino)pyridyl chromium [20,27,28] and vanadium [21,29] complexes have been synthesized and have been shown to be active ethylene oligomerization and polymerization catalysts when activated by methylaluminoxanes under homogeneous conditions. Esteruelas et al. [27] reported the formation of waxes and low molecular weight polyethylene using $\{2,6\text{-[ArN=C(Me)]}_2\text{C}_5\text{H}_3\text{N}\}\text{CrCl}_2$ or $\{2,6\text{-[ArN=C(Me)]}_2\text{C}_5\text{H}_3\text{N}\}\text{CrCl}_3$ ($\text{Ar}=2,6\text{-diisopropylphenyl}$). Small et al. [28] reported the formation of mixtures of oligomers and polymers using a range of bis(imino)pyridyl chromium complexes and provided evidence that the active species derived from Cr(II) and Cr(III) complexes were identical. Gambarotta and coworkers [21] investigated the preparation of $\{2,6\text{-[ArN=C(Me)]}_2\text{C}_5\text{H}_3\text{N}\}\text{VCl}_3$ ($\text{Ar}=2,6\text{-diisopropylphenyl}$), which after activation with MAO produced polyethylenes having high polydispersities. GPC analysis revealed bimodal distributions, indicating the formation of different active species. Schmidt et al. [29] prepared a series of bis(imino)pyridyl V(III) complexes, most of which gave low molecular weight oligomers.

In order to determine whether bis(imino)pyridyl chromium and vanadium precatalysts could be effectively immobilized and activated using a $\text{MgCl}_2/\text{AlR}_n(\text{OEt})_{3-n}$ support, and to determine whether or not single-site catalyst characteristics and narrow polymer molecular weight distribution could be obtained, the Cr(II) and V(III) complexes **5** and **6** were synthesized. Precatalyst immobilization was carried out in dichloromethane under conditions similar to those used for the bis(imino)pyridyl iron precatalysts. The ethylene polymerization results obtained using the Cr(II) precatalyst **5** are summarized in Table 4. The catalyst activities are much lower than those achieved with the corresponding iron catalyst **2**, and reveal little effect of the cocatalyst. GPC analysis of the polymers obtained revealed broad, bimodal molecular weight distributions, irrespective of the cocatalyst used. The \bar{M}_w values are, however, one to two orders of magnitude higher than those reported for homogeneous polymerization using this complex [27], indicating a significant effect of immobilization on MgCl_2 . The formation of a low molecular weight fraction, in addition to the main (high molecular weight) polymer fraction, could arise from the presence of more than one active species, possibly as a result of incomplete immobilization of the catalyst on the support. In order to test this possibility, we carried out a polymerization in toluene rather than light petroleum, taking into account that leaching of the catalyst into solution should be more prevalent in toluene. The GPC traces of polymers prepared in light petroleum and in toluene are given in Fig. 2, which indeed shows that polymerization in toluene increased the proportion of the low molecular weight component.

The polymerization results obtained using the vanadium(III) precatalyst **6** are given in Table 5. It is immediately obvious

Table 4
Effect of cocatalyst in ethylene polymerization with $\{2,6\text{-[ArN=C(Me)]}_2\text{C}_5\text{H}_3\text{N}\}\text{CrCl}_2$ (**5**; Ar = 2,6-diisopropylphenyl) immobilized on a $\text{MgCl}_2/\text{AlR}_n(\text{OEt})_{3-n}$ support

Experiment	Cocatalyst	Al/Cr (mol/mol)	Activity ($\text{kg mol}^{-1} \text{Cr bar}^{-1} \text{h}^{-1}$)	\bar{M}_w (g/mol)	\bar{M}_n (g/mol)	\bar{M}_w/\bar{M}_n
1	AlEt_3	500	220	690000	48000	14.4
2	AlEt_3	1000	220	1111000	38700	28.7
3	AlEt_3	2000	240	635000	56300	11.3
4	$\text{Al}i\text{Bu}_3$	1000	160	967000	43200	22.4
5	MAO	1000	140	1070000	30700	34.9
6 ^a	AlEt_3	500	320	637000	30000	21.2

^a Polymerization in toluene.

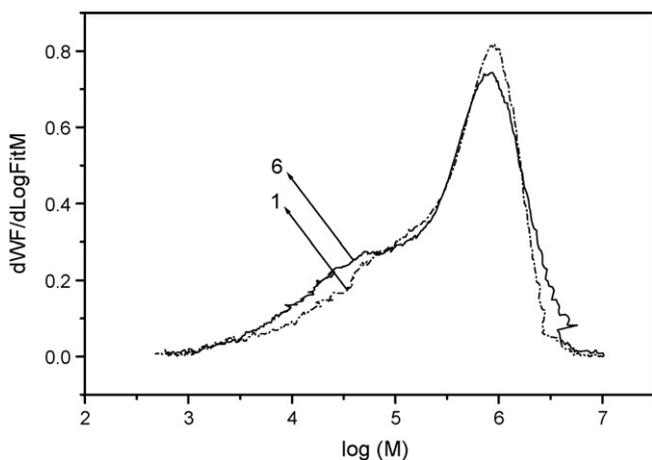


Fig. 2. Effect of polymerization solvent on the MWD of PE produced with complex (**5**) immobilized on a $\text{MgCl}_2/\text{AlEt}_n(\text{OEt})_{3-n}$ support and activated with AlEt_3 (the curve numbers correspond to the experiment numbers in Table 4).

that immobilization of this catalyst on the MgCl_2 support gives, in contrast to the iron- and chromium-based systems, not only high polyethylene molecular weight but also very narrow molecular weight distribution. The presence of a single active species is indicated by the narrow (Schulz–Flory) distributions, with \bar{M}_w/\bar{M}_n close to 2. In order to obtain further confirmation of the narrow molecular weight distributions of the polyethylenes synthesized with the MgCl_2 -immobilized bis(imino)pyridyl vanadium precatalyst, the melt rheological properties of polymers prepared using either AlEt_3 or $\text{Al}i\text{Bu}_3$ as cocatalyst were compared with those of a polymer having $\bar{M}_w/\bar{M}_n = 5.6$, prepared (Table 2, experiment 1) using the related bis(imino)pyridyl iron catalyst **2**. Oscillatory shear measurements were carried out at 180 °C to determine the dependence of the storage modulus, G' , on shear. As we have shown in previous studies, melt rheome-

Table 5
Effect of cocatalyst in ethylene polymerization with $\{2,6\text{-[ArN=C(Me)]}_2\text{C}_5\text{H}_3\text{N}\}\text{VCl}_3$ (**6**; Ar = 2,6-diisopropylphenyl) and $\{2,6\text{-[ArN=C(Me)]}_2(2\text{-MeC}_5\text{H}_3\text{N})\}\text{VCl}_2$ (**7**; Ar = 2,6-diisopropylphenyl) immobilized on a $\text{MgCl}_2/\text{AlR}_n(\text{OEt})_{3-n}$ support

Experiment	Catalyst	Cocatalyst ^a	Temperature (°C)	Activity ($\text{kg mol}^{-1} \text{V bar}^{-1} \text{h}^{-1}$)	\bar{M}_w (g/mol)	\bar{M}_n (g/mol)	\bar{M}_w/\bar{M}_n
1	6	AlEt_3	50	560	1770000	848000	2.1
2	6	AlEt_3	70	2140	1961000	1205000	1.6
3	6	$\text{Al}i\text{Bu}_3$	50	500	1090000	590000	1.8
4	6	MAO	50	560	1050000	534000	2.0
5	7	AlEt_3	50	320	1531000	1053000	1.5
6	7	AlEt_3	70	907	2040000	1363000	1.5

^a Al/V molar ratio = 1000.

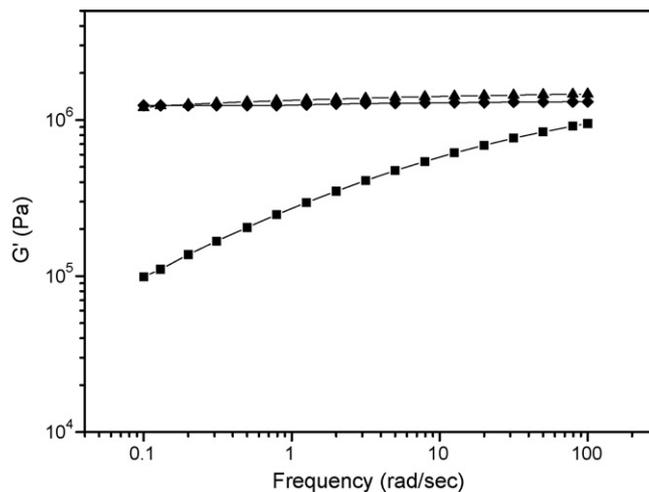


Fig. 3. Shear frequency dependence of storage modulus (G') at constant strain of (\blacklozenge and \blacktriangle) polyethylene ($\bar{M}_w/\bar{M}_n = 1.8\text{--}2.1$) prepared using an immobilized V catalyst, compared to (\blacksquare) a reference polyethylene ($\bar{M}_w/\bar{M}_n = 5.6$) prepared using an immobilized iron catalyst.

try is a very effective tool for the qualitative comparison of the molecular weight distributions in high molecular weight polymers [14d]. The results in Fig. 3 show a constant storage modulus over the entire frequency range for the V-derived polymers, characteristic of polyethylene having narrow molecular weight distribution [30]. In contrast, the decrease in storage modulus with decreasing frequency for the Fe-derived polymer illustrates the much broader molecular weight distribution of this polymer.

The successful immobilization and activation of precatalyst **6** contrasts with previous, unsuccessful attempts to heterogenize this and related V(III) precatalysts on a silica support, which resulted in little or no activity [29]. The activities of 500–560 $\text{kg mol}^{-1} \text{V bar}^{-1} \text{h}^{-1}$ obtained with MgCl_2 -

immobilized precatalyst **6** at 50 °C are higher than those reported [21] for homogeneous polymerizations with MAO activation, where it was also noted that rapid deactivation took place when the temperature was increased to 140 °C. Rapid deactivation during polymerization is a characteristic feature of many homogeneous vanadium catalysts [31], but very effective stabilization can be achieved by immobilization on magnesium chloride. This has been demonstrated by Nakayama et al. [15b], who obtained very stable polymerization kinetics even at 75 °C using a MgCl₂-based support/activator in combination with an FI–V complex, and recently we have observed stable polymerization activity with an immobilized vanadium(III) amidinate catalyst [14e]. In the present work, we carried out a polymerization with MgCl₂-immobilized precatalyst **6** at 70 °C. No deactivation was apparent during the course of polymerization and the activity (Table 5) was significantly higher than that obtained at 50 °C.

The above polymerization studies consistently gave spherical polymer particle morphology, with no evidence of reactor fouling. Scanning electron micrographs of polymers produced with immobilized bis(imino)pyridyl Fe(II), Cr(II) and V(III) precatalysts are shown in Fig. 4, demonstrating that the spherical morphology of the original support had been retained and replicated throughout catalyst immobilization and polymerization. It is, however, apparent that the particle morphology of the Cr-PE is inferior to that of the polymers obtained with the iron and vanadium catalysts, which may be a further indication of incomplete catalyst immobilization in the case of the chromium catalyst.

It is evident from the above studies that MgCl₂-immobilized bis(imino)pyridyl iron, chromium and vanadium precatalysts exhibit very different characteristics in ethylene polymerization. The iron systems give polyethylenes with molecular weight distributions (\bar{M}_w/\bar{M}_n) in the range 3–12, dependent on the steric bulk of the bis(imino)pyridyl ligand. However, there was no evidence of the low molecular weight peak typically observed in polymers prepared under homogeneous conditions with MAO, which has been ascribed to chain transfer to aluminium [3], or when AlMe₃ is used as cocatalyst with a MgCl₂-supported iron catalyst [13]. Changes in cocatalyst concentration had little effect on molecular weight or molecular weight distribution and it therefore appears that these systems contain more than one active species. The mode of coordination of the iron species LFeCl₂ to the support is likely to involve bridged chloride species, Mikenas et al. having determined that the

maximum amount of precatalyst that can be immobilized on MgCl₂ is similar to the amount of TiCl₄ that can be adsorbed, suggesting that these components adsorb on the same surface acidic sites [13]. However, in this system good polymer particle morphology and absence of fouling do not necessarily provide proof of strong anchoring of the precatalyst to the support during polymerization, as the limited hydrocarbon solubility of the catalyst would tend to prevent leaching from the support.

The possibility of side reactions involving the bis(imino)pyridine ligand when attached to different metals has been investigated by several groups and is a complex issue [32], although Gibson and coworkers have reported that the ligand could be recovered intact after MAO-activated ethylene polymerizations with the bis(imino)pyridyl iron complex **2** [3]. Reactions between the free ligand and various lithium, magnesium and zinc alkyls have been shown to give *N*-alkylated products arising from attack of the metal alkyl at the pyridine nitrogen atom [33]. Very recent work by Budzelaar and coworkers [34] has revealed that reactions of the free ligand with aluminium alkyls are unexpectedly complex, alkyl additions to the imine carbon and at the 2- and 4-positions of the pyridine ring being observed. It has also been shown that the iron atom in a bis(imino)pyridyl iron complex can be displaced by reaction with an aluminium alkyl, but the resulting Al complex was catalytically inactive, indicating that this reaction represents a deactivation pathway [35]. Gambarotta and coworkers have investigated reactions of various other bis(imino)pyridyl transition metal complexes with alkylating agents. Ligand coupling via deprotonation of a methyl group attached to the imino function was observed for a manganese complex, while reaction of LCrCl₃ with AlMe₃ resulted in reduction to LCr(μ-ClAlMe₃)₂ [36]. An unusual result was obtained when the corresponding vanadium complex LVCl₃ (**6**) was reacted with excess MAO or MeLi. In this case, alkylation of the pyridine ring took place, leading to the formation of species **7**, as illustrated in Scheme 2 [21]. This reaction, leading to a decrease in the metal coordination number, was suggested to be a key factor contributing to the polymerization activity obtained using complex **6** in combination with MAO and it was found that complex **7** indeed gave activities and polymer characteristics that were very similar to those obtained using complex **6** [21].

In order to compare the active species formed from complexes **6** and **7** on a MgCl₂-based support, we synthesized and immo-

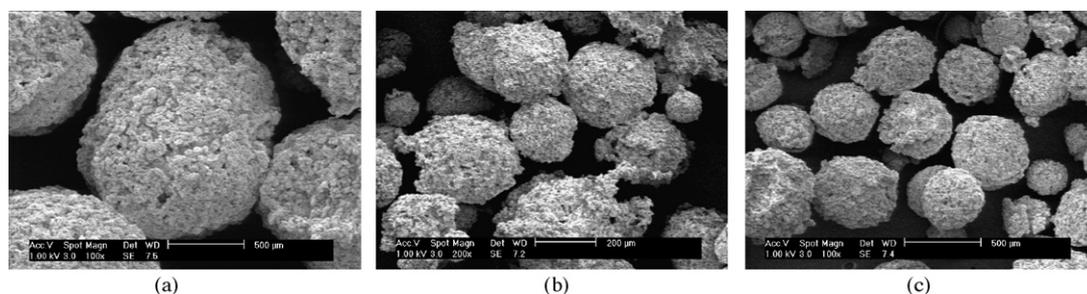
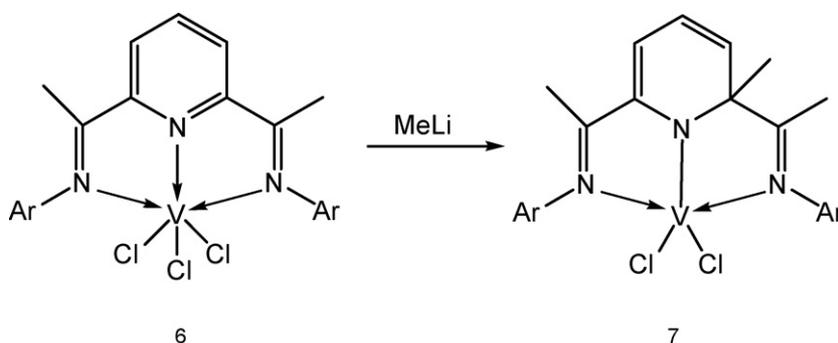
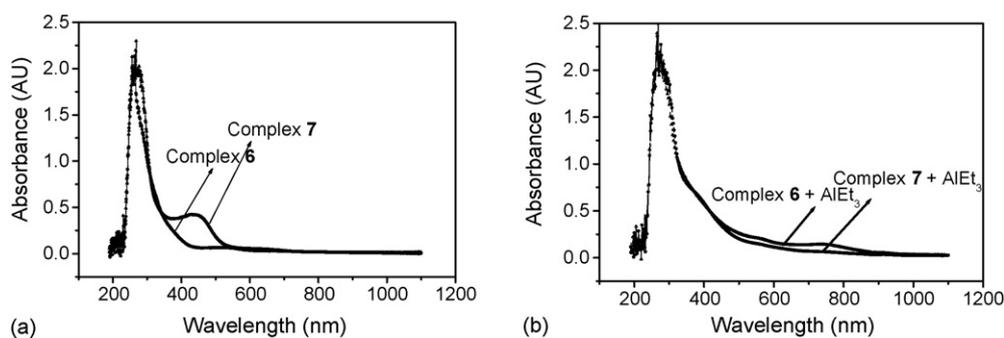


Fig. 4. Scanning electron micrographs of polyethylene prepared using bis(imino)pyridyl iron, chromium and vanadium catalysts immobilized on a MgCl₂/AlEt₃(OEt)_{3–n} support: (a) Fe complex **3**; (b) Cr complex **5**; (c) V complex **6**.

Scheme 2. Reaction of precatalyst **6** with MeLi [21].Fig. 5. UV-vis spectra of complexes **6** and **7** in dichloromethane (a) before and (b) after contact with AlEt₃.

bilized complex **7**. During the immobilization of complexes **6** and **7** it was observed that the colour changed from light red (**6**) or light green (**7**) in the starting solutions to give the same sand colour in the final supported catalysts. Comparison of the results of ethylene polymerizations carried out with each complex (Table 5) reveals somewhat lower activities for complex **7**, but the polyethylene molecular weights were very similar to those obtained with complex **6**, an indication that very similar types of active species were present in each system. Further evidence for the formation of similar active species was obtained by comparing the UV spectra of complexes **6** and **7** in solution in dichloromethane, before and after contact with AlEt₃ (Al/V = 100). Fig. 5a reveals a significant difference between the spectra of complexes **6** and **7**, but the similarity of the spectra in Fig. 5b indicates that similar species are generated on contact with triethylaluminium. It is therefore likely that, in the polymerizations carried out with MgCl₂-immobilized complex **6** in the presence of AlEt₃, alkylation takes place to give a complex very similar to **7**, but with an ethyl rather than a methyl group at the 2-position of the pyridine ring.

4. Conclusions

The molecular weight and polydispersity of polyethylene prepared with bis(imino)pyridyl complexes of iron, chromium and vanadium immobilized on supports of type MgCl₂/AlR_n(OEt)_{3-n} is strongly dependent on the nature of the transition metal. Iron-based catalysts give polymers with molecular weight distributions ranging from 3 to 12, depending on the substituents in the bis(imino)pyridyl ligand. The

molecular weights obtained with the iron catalysts are somewhat higher than those reported for homogeneous polymerization. In contrast, immobilization of bis(imino)pyridyl chromium and vanadium complexes on magnesium chloride gives much higher molecular weights than have been obtained under homogeneous conditions and furthermore, in the case of vanadium, a very narrow molecular weight distribution which can be ascribed to the presence of a single active species formed via alkylation of the pyridine ring.

Acknowledgements

We thank Drs. A.P. Jekel of the Center for Catalytic Olefin Polymerization at the Rijksuniversiteit Groningen for GPC analysis and Dr. X. Zheng of Eindhoven University of Technology for SEM characterization of polymer particle morphology. This work is part of the Research Programme of the Dutch Polymer Institute (DPI), under project number #495.

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