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Synergetic Effect of a Nickel Diimine in Ethylene Polymerization with Immobilized Fe-, Cr-, and Ti-Based Catalysts on $MgCl_2$ Supports

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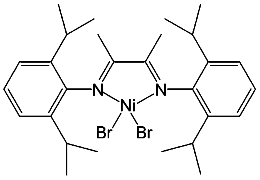
ABSTRACT: Significant increases in the productivity of iron-, chromium-, and titanium-based $MgCl_2$-supported catalysts for ethylene polymerization have been obtained by incorporation of a limited amount of a nickel diimine catalyst giving branched polyethylene. Formation of the latter during the early stages of polymerization reduces the monomer diffusion limitation inherent in ethylene homopolymerization, thereby increasing the productivity of the main catalyst component. The final products are essentially linear, high-density polyethylenes containing very small amounts of branched polymer. As well being effective for catalysts prepared by coimmobilization of the Ni and Fe, Cr, or Ti component on the $MgCl_2$ support, it is also shown that the productivity of preformed Ziegler−Natta catalysts can be improved significantly by impregnation with the nickel diimine component. In the latter case, more rapid increases in rate throughout the polymerization indicated easier fragmentation of the support in the presence of the nickel complex.

Introduction

It is well-known that, in ethylene homopolymerization using a heterogeneous catalyst, the rate of polymerization can be impeded by relatively slow diffusion of the monomer through the crystalline polyethylene formed on the particle surface[1,2] and by difficult polymer particle growth in the case of catalyst supports having low friability.[3] The diffusion limitation can be alleviated by introducing a comonomer, which leads to easier monomer diffusion through the less crystalline copolymer formed, or by carrying out a prepolymerization with propylene or other α-olefin prior to an ethylene homopolymerization.[4−6] In each case, significant increases in catalyst activity can be obtained, and the increased activity observed in copolymerization is generally referred to as the comonomer activation effect. It has recently been demonstrated by Hammawa and Wanke that comonomer activation in ethylene polymerization is a physical rather than a chemical effect and is particularly prevalent in systems in which low friability of the support impedes effective particle fragmentation and growth.[3] In such cases, ethylene homopolymerization leads to the pores of an unfragmented catalyst becoming filled with polymer, resulting in limited monomer diffusion into the particle.

The above-mentioned effects are observed with both heterogeneous Ziegler−Natta catalysts and immobilized early transition metal complexes such as metallocenes and related single-site catalysts which polymerize ethylene to linear (high-density) polyethylene. Recently, however, there has been increasing interest in late-transition metal catalysts for olefin polymerization, following the discovery by Brookhart and co-workers of aryl-substituted α-diimine nickel(II) and palladium(II) complexes able to polymerize ethylene to give polyolefins with substantial chain branching.[7,8] Subsequently, the Brookhart and Gibson groups independently discovered that bis(imino)pyridyl iron(II) complexes can be activated with methylaluminoxane (MAO) to afford highly active catalysts for ethylene polymerization, giving essentially linear polyethylene.[9,10] However, the practical use of homogeneous catalyst systems in current slurry and gas-phase polymerization processes for polyolefins is limited by relatively short catalyst lifetimes, and in particular by a lack of control over polymer particle morphology, leading to serious reactor fouling. For this reason, considerable efforts have been made to develop effective routes for the immobilization of such catalysts on suitable supports.[11] The most commonly used support is silica, but in recent years increasing attention has been paid to the potential use of magnesium chloride as support material for the immobilization and activation of a range of early- and late-transition metal complexes. Particularly effective routes involve the use of supports of composition $MgCl_2/AlR_n(OR')_{3-n}$, prepared by reaction of either an aluminum alkyl with a solid $MgCl_2$/ethanol adduct[12] or a hydrocarbon solution of a $MgCl_2$/2-ethylhexanol adduct.[13] The latter approach has been used by Fujita and co-workers, who immobilized and activated various phenoxyimine (FI) catalysts and achieved catalyst activities comparable with those obtained using MAO.[14]

Scheme 1. Catalyst Structures



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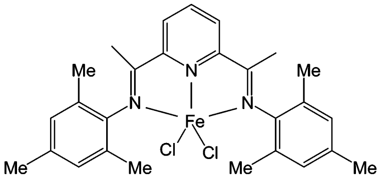

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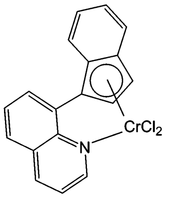

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Our own work in this area has concentrated on the use of $MgCl_2/AlR_n(OEt)_{3-n}$ supports, prepared via the reaction of AlR_3 with spherical, partially dealcoholated[12] adducts $MgCl_2 \cdot n$EtOH. We have found that a wide range of titanium,[15] vanadium,[16]

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Table 1. Ethylene Polymerization Using Binary Iron and Nickel Catalysts on a $MgCl_2$-Based Support[a]

	catalyst loading on support				
entry	Fe complex **2** (μmol/g)	Ni complex **1** (μmol/g)	cocatalyst	temp (°C)	activity (kg/mol of Fe·h·bar)
1	5		$AlEt_3$	50	10600
2	5	5	$AlEt_3$	50	13840
3		5	$AlEt_3$	50	560[b]
4	5		$Al\textit{i}Bu_3$	50	3040
5	5	5	$Al\textit{i}Bu_3$	50	6080
6	5		$AlEt_3$	60	11720
7	5	5	$AlEt_3$	60	14680
8		5	$AlEt_3$	60	400[b]
9	5		$AlEt_3$	70	15280
10	5	5	$AlEt_3$	70	19520
11		5	$AlEt_3$	70	640[b]

[a] Polymerization conditions: 500 mL of light petroleum, immobilized catalyst 100 mg, $AlEt_3$ or $Al\textit{i}Bu_3$ 1 mmol, ethylene pressure 5 bar, time 1 h. [b] Activity in kg/mol of Ni·h·bar.

Table 2. Effect of Ni Loading on Binary Catalyst (1 + 2) Activity[a]

	catalyst loading on support		
entry	Fe complex **2** (μmol/g)	Ni complex **1** (μmol/g)	activity (kg/mol of Fe·h·bar)
1	5	0	10 600
2	5	1	16 480
3	5	3	15 160
4	5	5	13 840

[a] Polymerization conditions: 500 mL of light petroleum, immobilized catalyst 100 mg, $AlEt_3$ 1 mmol, temperature 50 °C, ethylene pressure 5 bar, time 1 h.

Table 3. Effect of Coimmobilization on Catalyst Activity[a]

entry	catalyst(s)	loading on support (μmol/g)	activity (kg/mol of Fe·h·bar)
1	Fe (**1**)	5	20 440
2	Ni (**2**)	5	960[b]
3[c]	[Fe (**1**) + Ni (**2**)]	5 + 5	27 600
4[d]	Fe (**1**) and Ni (**2**)	5 and 5	21 200
5[e]	Ni (**2**) and Fe (**1**)	5 and 5	19 500

[a] Polymerization conditions: 500 mL of light petroleum, $AlEt_3$ 1 mmol, temperature 50 °C, ethylene pressure 5 bar, time 1 h. [b] Activity in kg/mol of Ni·h·bar. [c] Fe and Ni catalysts coimmobilized on the support. [d] Fe and Ni catalysts immobilized on separate portions of support and then charged successively to the polymerization reactor in the order (1) Fe and (2) Ni. [e] Fe and Ni catalysts immobilized on separate portions of support and then charged successively to the polymerization reactor in the order (1) Ni and (2) Fe.

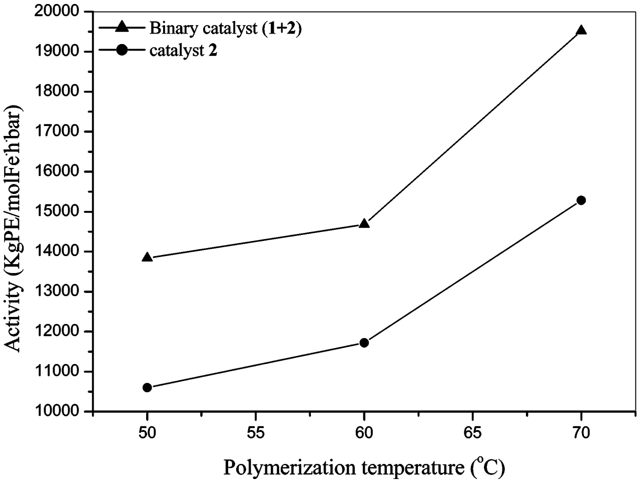

Figure 1. Polymerization activities obtained with single (Fe) and binary (Fe + Ni) catalyst systems.

and chromium[17] single-site catalysts for ethylene polymerization can be easily and effectively immobilized and activated using supports of this type. These supports have also been shown, by ourselves and others, to be effective for the immobilization and activation of the late-transition metal nickel[18] and iron[19,20] catalysts. A particular advantage of the use of magnesium chloride supports in catalyst immobilization is that in most cases stable catalyst activity is obtained, in contrast to the rapid decay in activity frequently observed in homogeneous polymerization. For example, we have observed stable activities in ethylene polymerization at 50 °C with various titanium complexes,[15b] while Nakayama et al. obtained high stability even at 75 °C with a vanadium-based FI complex.[14a] Stable polymerization kinetics with a $MgCl_2$-supported iron catalyst have been reported by Mikenas et al.[21] An exception to this trend was the significant decay observed with a α-diimine nickel catalyst immobilized on a $MgCl_2/AlEt_n(OEt)_{3-n}$ support, where the productivity in the second half-hour of a polymerization at 50 °C was only about a quarter of that obtained in the first half-hour.[18]

The $MgCl_2$-immobilized Brookhart-type Ni-based systems gave, as is the case in homogeneous polymerization, polyethylenes with significant chain branching as a result of the “chain-walking” process, involving migration of the metal along the alkyl chain.[7,22] The degree of chain branching is determined by the steric characteristics of the α-diimine ligand and increases with increasing steric bulk around the metal atom, although this also leads to a decrease in catalyst activity. Taking into account the limited activity (and decay characteristics) of the α-diimine catalysts giving high levels of chain branching, compared to the very high activities that can be obtained with 2,6-bis(imino)-pyridyl iron catalysts on similar supports,[19,20] it occurred to us that, by incorporating a nickel catalyst into an $MgCl_2$-immobilized iron-based system, the formation of Ni-catalyzed branched polyethylene in the early stage of polymerization may lead to a significant decrease in the monomer diffusion limitation, and thereby to further increases in the productivity of the iron catalyst, with which negligible chain branching is obtained. Combinations of nickel and other catalysts have been used previously in MAO-activated homogeneous polymerization for the preparation of reactor blends of different types of polyethylene.[23] In contrast, our target in this work was not to produce a branched/linear polyethylene blend, but to produce in still higher yield an iron-catalyzed high-density polyethylene containing a minimal amount of branched polymer. We report here on the beneficial effects obtained by the coimmobilization of 2,3-bis(2,6-diisopropylphenylimino)butane nickel(II) dibromide (**1**) and 2,6-bis(1-(2,4,6-trimethylphenylimino)ethyl)pyridine iron(II) dichloride (**2**) on a $MgCl_2$-based support and on the extension of these studies to coimmobilization of the nickel complex together with 1-(8-quinolyl)indenylchromium(III) dichloride (**3**) and with $TiCl_4$.

Experimental Section

Materials. All manipulations were performed under an argon atmosphere using a glovebox (Braun MB-150 GI or LM-130) and Schlenk techniques. Light petroleum (bp 40−60 °C) and dichloromethane were passed over a column containing activated alumina. All solvents were freeze−thaw−degassed twice before use. 2,3-Bis(2,6-diisopropylphenylimino)butane nickel(II) dibromide[7] (**1**) and 2,6-bis(1-(2,4,6-trimethylphenylimino)ethyl)pyridine iron(II) dichloride[10] (**2**) were prepared according to previously reported procedures. 1-(8-Quinolyl)indenylchromium(III) dichloride[24] (**3**) was generously donated by Basell Polyolefins. The structures of

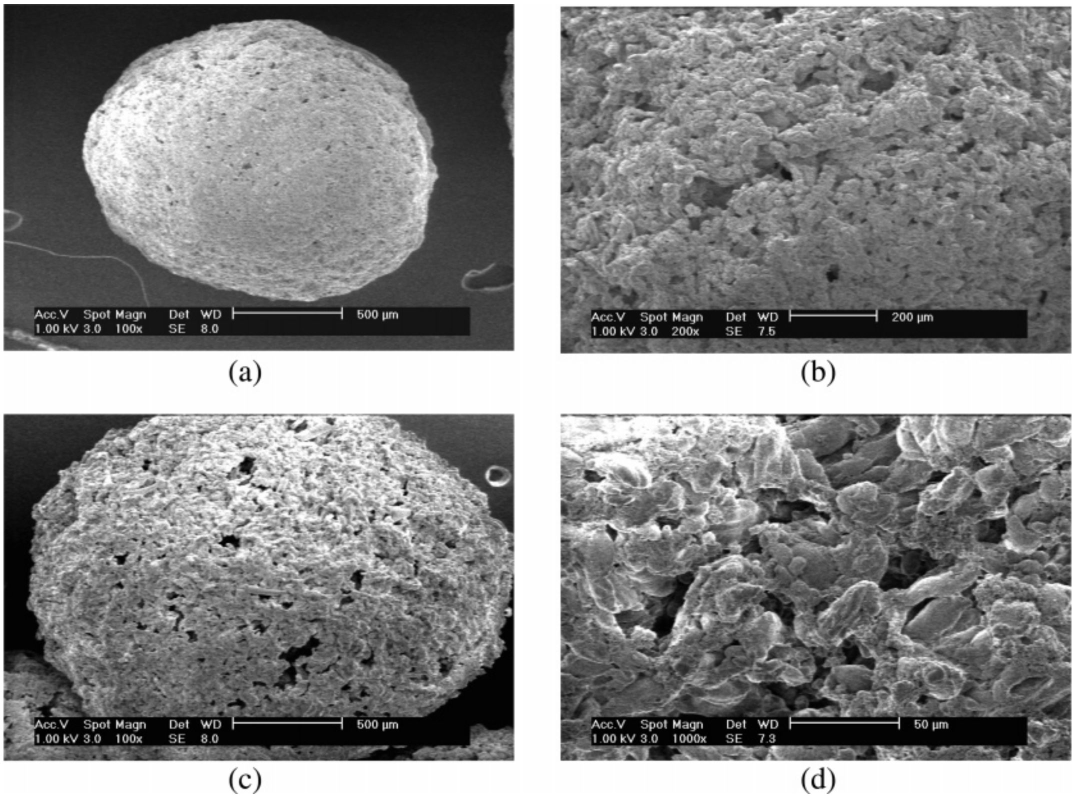

Figure 2. PE particle (surface) morphology produced by $AlEt_3$-activated immobilized catalysts at 50 °C: (a, b) catalyst **2**; (c, d) binary catalyst system **1** + **2**.

Table 4. Ethylene Polymerization Using Binary Chromium and Nickel Catalysts on a $MgCl_2$-Based Support[a]

	catalyst loading on support			
entry	Cr complex **3** (μmol/g)	Ni complex **1** (μmol/g)	temp (°C)	activity (kg/mol of Cr·h·bar)
1	20		50	3100
2	20		50	2950
3	20	5	50	3980
4	20	5	50	3810
5	20	10	50	4200
6		10	50	440[b]
7	20	20	50	3680
8		20	50	390[b]
9	20		60	3970
10	20	10	60	4670
11		10	60	240[b]
12	20		70	6560
13	20	10	70	6850
14		10	70	240[b]

[a] Polymerization conditions: 500 mL of light petroleum, immobilized catalyst 100 mg, $AlEt_3$ 1 mmol, ethylene pressure 5 bar, time 1 h. [b] Activity in kg/mol of Ni·h·bar.

catalysts **1**−**3** are shown in Scheme 1. $TiCl_4$ was purchased from Aldrich. $AlEt_3$ (1.3 M in heptane) and $Al\textit{i}Bu_3$ (25 wt % in toluene) were obtained from Acros and Akzo Nobel, respectively. Ethylene (3.5 grade supplied by Air Liquide) was purified by passing over columns of BASF RS3-11 supported Cu oxygen scavenger and 4 Å molecular sieves. The Ziegler−Natta catalysts used in this work were prepared by reaction of solid, spherical adducts of magnesium chloride and ethanol, $MgCl_2 \cdot nEtOH$, with excess $TiCl_4$ in several stages and in the presence of a donor, using procedures similar to those reported previously.[25]

Support Preparation and Catalyst Immobilization. The supports used in this work were prepared by addition of $AlEt_3$ to an adduct $MgCl_2 \cdot nEtOH$ ($n = 1.1$ or 2.1) in light petroleum ($AlEt_3$/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 supports were determined by the H. Kolbe Microanalytisches Laboratorium, Mülheim an der Ruhr, Germany. The ethoxide contents in the $MgCl_2/AlEt_n(OEt)_{3-n}$ supports were 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 for a support derived from $MgCl_2 \cdot 1.1EtOH$ were 3.70 and 5.26 wt %, respectively, indicating an overall support composition $MgCl_2 \cdot 0.16AlEt_{2.15}(OEt)_{0.85}$. A second support prepared under similar conditions contained 3.81 wt % Al and 6.90 wt % OEt, corresponding to a composition $MgCl_2 \cdot 0.17AlEt_{1.91}(OEt)_{1.09}$. For the support derived from $MgCl_2 \cdot 2.1EtOH$, the respective Al and OEt contents were 10.72 and 7.54 wt %, indicating composition $MgCl_2 \cdot 0.73AlEt_{2.58}(OEt)_{0.42}$.

Three different catalyst immobilization procedures (denoted as methods I, II, and III) were used:

Method I: The support (100 mg) was contacted with 2 mL of a dichloromethane solution containing the desired quantities of the iron or chromium and nickel catalysts and left overnight. The resulting slurry was, after dilution with light petroleum, used as such in polymerization. In the case of the (Fe + Ni) and (Cr + Ni) systems, the colors after immobilization were sandy red and light blue, respectively.

Method II: The support (100 mg) was contacted with 1 μmol of $TiCl_4$ in 3 mL of toluene at 50 °C for 4 h and subsequently with 0.5−1.0 μmol of the Ni complex in 2.5−3.0 mL of toluene at 50 °C for 4 h.

Method III: As method II, except that the order of addition was reversed, the support being treated first with the Ni complex and subsequently with $TiCl_4$.

In the case of the Ziegler−Natta catalysts of type $MgCl_2$/donor/$TiCl_4$, the catalyst (30−100 mg) was contacted with 0.5 μmol of the Ni complex in 3 mL of toluene at room temperature for 16 h.

Polymerization Procedure. Polymerization was carried out in a 1 L Premex autoclave by charging the immobilized catalyst, slurried in ~100 mL of light petroleum, to 400 mL of light petroleum containing the desired amount of cocatalyst, at the desired

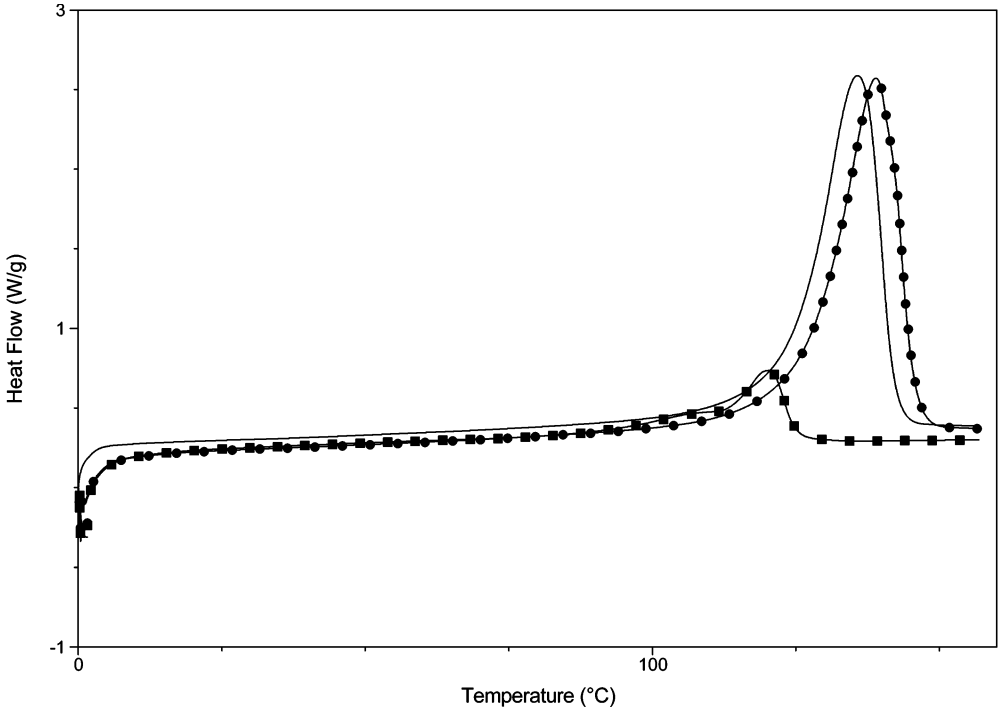

Figure 3. DSC thermogram of polyethylene prepared with binary Fe + Ni catalyst system (Table 2, entry 4), before and after solvent fractionation (—, unfractionated PE; ●, precipitated fraction I; ■, soluble fraction II).

temperature and at an ethylene pressure of 5 bar. After catalyst injection, polymerization was continued at constant pressure for 1 h with a stirring rate of 1000 rpm. After venting the reactor, 20 mL of acidified ethanol was 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.

Polymer Characterization. Molecular weight and molecular weight distributions of the resulting polymers were determined by means of gel permeation chromatography on a PL-GPC210 at 135 °C using 1,2,4-trichlorobenzene as solvent. Differential scanning calorimetry (DSC) was carried out with a Q100 differential scanning calorimeter (TA Instruments). The samples (1.5−2.5 mg) were heated to 160 °C at a rate of 10 °C/min and cooled down at the same rate to 20 °C. A second heating cycle at 10 °C/min was used for data analysis. The particle morphologies of the polymers were examined using a Philips S-250MK3 SEM-EDX.

Fractionation of selected polymers into linear and branched polyethylene was carried out by dissolving 1 g of polymer in 600 mL of *p*-xylene at 135−140 °C, after which the stirred solution was kept at this temperature for 1−2 h and then allowed to cool until turbidity was observed, which occurred between 75 and 80 °C. Stirring was continued at this temperature for 4 h, and the mixture was then filtered hot to separate the precipitated and soluble fractions, denoted fractions I and II. The latter fraction was recovered by evaporation of the solvent.

Results and Discussion

Binary Iron/Nickel Catalyst System. In previous work, we have investigated the effects of various cocatalysts in ethylene polymerization carried out using different bis(imino)pyridyl iron complexes immobilized on a MgCl$_2$/AlEt$_n$(OEt)$_{3-n}$ support.[20] The highest activities were obtained using AlEt$_3$, in combination with 2,6-bis(1-(2,4,6-trimethylphenylimino)ethyl)pyridine iron(II) dichloride (**2**), and we therefore selected this system for an investigation of the effects of 2,3-bis(2,6-diisopropylphenylimino)butane nickel(II) dibromide (**1**) as additional, coimmobilized catalyst component. In a previous communication, we reported that ethylene polymerization at 50 °C using complex **1** immobilized on a magnesium chloride support gave a polymer with 26 branches per 1000 carbon atoms.[18] In the present work, catalyst immobilization was carried out simply by mixing a support of composition MgCl$_2$·0.16AlEt$_{2.25}$(OEt)$_{0.75}$, prepared by reaction of MgCl$_2$·1.1EtOH with excess AlEt$_3$, with a dichloromethane solution of **1** and **2**. It was observed that, after contacting overnight at ambient temperature, the color of the solution was completely transferred to the solid support, indicating quantitative immobilization. The results of polymerizations carried out with the binary catalyst combination **1** + **2**, compared to results obtained with only the iron complex **2** or the nickel complex **1**, are given in Table 1. These polymerizations were carried out at different temperatures, at a constant monomer pressure of 5 bar. Two additional polymerizations were carried out using Al*i*Bu$_3$ in place of AlEt$_3$ as cocatalyst/scavenger. It is apparent from Table 1 that the binary catalyst system containing both Fe and Ni exhibited activities which are significantly higher than those of the system containing only Fe. Furthermore, the observed increases in activity, equivalent to around 3000−4000 kg/mol of Fe·bar·h, are much higher than the relatively low activities (400−640 kg/mol·bar·h) obtained with only the Ni catalyst. The activity of 560 kg/mol·bar·h obtained with the AlEt$_3$-activated nickel catalyst at 50 °C is lower than the value of 1190 kg/mol·bar·h obtained previously[18] using Al*i*Bu$_3$; it is likely that this is due to more rapid decay of the nickel catalyst in the presence of AlEt$_3$. In contrast, it is apparent from Table 1 that the immobilized iron catalyst gives much higher activity with AlEt$_3$ than is obtained with Al*i*Bu$_3$.

The synergetic effect of the presence of the nickel catalyst in the binary catalyst system is illustrated in Figure 1. Scanning electron micrographs of polyethylene particles obtained using catalyst **2** alone and with the binary system **1** + **2** are shown in Figure 2, which indicates a more porous particle morphology in the case of the polyethylene prepared with the binary system.

In further experiments, the effect of lowering the proportion of the nickel component in the binary catalyst system was investigated. The results in Table 2 showed that lowering the loading of the nickel catalyst **1**, keeping the loading of the iron catalyst **2** constant, unexpectedly led to an increase in catalyst

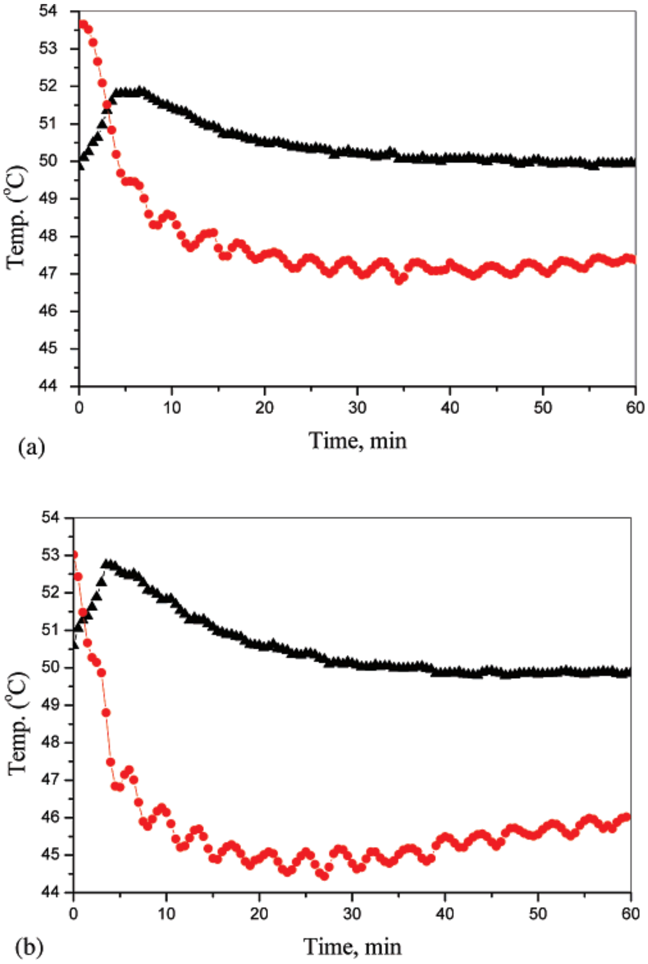

Figure 4. Temperature profiles of ethylene polymerizations carried out with immobilized iron catalyst **2**: (a) alone and (b) coimmobilized with Ni complex **1** (▲, internal temperature; ●, cooling mantle temperature).

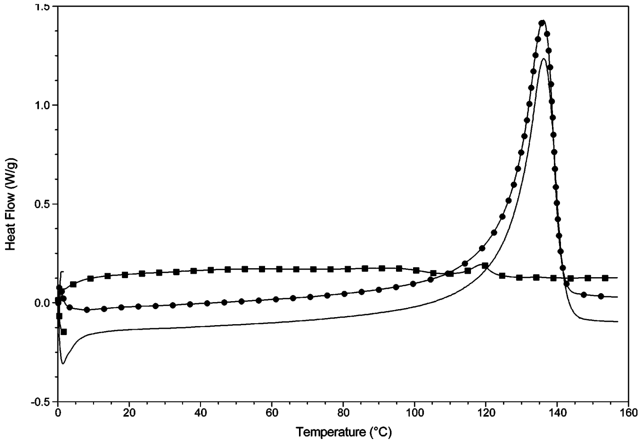

Figure 5. DSC thermogram of polyethylene prepared with binary Cr + Ni catalyst system (Table 4, entry 5), before and after solvent fractionation (—, unfractionated PE; ●, precipitated fraction I; ■, soluble fraction II).

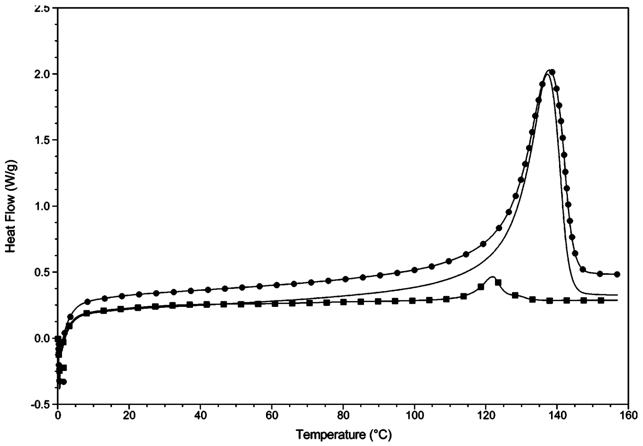

Figure 6. DSC thermogram of polyethylene prepared with binary Ti + Ni catalyst system (Table 5, entry 3), before and after solvent fractionation (—, unfractionated PE; ●, precipitated fraction I; ■, soluble fraction II).

activity expressed as kg/mol of Fe•bar•h. In other words, only a relatively low loading of the nickel catalyst is sufficient to obtain a significant effect. In order to demonstrate that the observed increases in catalyst activity following the incorporation of a Ni catalyst into Fe-catalyzed ethylene polymerization resulted predominately from increased productivity of the iron catalyst, selected samples were fractionated to separate and determine the relative amount of linear (iron-) and branched (nickel-) polyethylene. This was carried out by dissolving the polymer in *p*-xylene at 135−140 °C, after which the solution was allowed to cool until precipitation was observed, which occurred between 75 and 80 °C. The stirred mixture was kept at this temperature for 4 h and then filtered to obtain the crystallized and soluble fractions, representing linear and branched polymer, respectively. The suitability of the method was checked using a mixture of 50 mg of a Ni-catalyzed polyethylene (containing 26 branches per 1000 C atoms[18]) with 950 mg of a polyethylene (Table 5, entry 1) prepared using $TiCl_4$ immobilized on a $MgCl_2$-based support; the amount of soluble fraction recovered was 52 mg, indicating quantitative recovery of the branched polymer. Solvent fractionation of the polymers prepared at nickel catalyst loadings of 1 and 5 μmol/g support (Table 2, entries 2 and 4) yielded soluble fractions of 2.4 and 3.3 wt %, respectively. The DSC peak melting temperatures of the soluble fractions were 124 and 120 °C, as opposed to 137 and 136 °C for the unfractionated polymers. DSC thermograms for the polymer prepared at Fe and Ni loadings of 5 μmol/g support are shown in Figure 3. Additional evidence that the above synergetic effects resulted from physical effects related to the formation of both linear and branched polyethylene within a single particle was obtained by immobilizing the iron and nickel catalysts on separate portions of a support of composition $MgCl_2\cdot 0.17AlEt_{1.91}(OEt)_{1.09}$ and then carrying out ethylene polymerization with a mixture of the immobilized catalysts. The results in Table 3 (entries 4 and 5) show that this procedure, as expected, failed to generate any synergetic effect and gave activities which did not exceed the sum of the activities obtained with the individual iron- and nickel-catalyzed polymerizations (entries 1 and 2). In contrast, coimmobilization of the iron and nickel catalysts (entry 3) gave an activity more than 6000 kg/mol•h•bar higher than the combined activities of entries 1 and 2. Relatively stable activities were observed throughout these polymerizations, as illustrated by Figure 4, showing the temperature difference between the reactor contents and the cooling mantle during the course of 1 h. It is notable that the activities obtained in these polymerizations were significantly higher than the activities obtained (Table 1) with a different batch of support, although the beneficial effect of the catalyst coimmobilization is clearly evident in both series. Using the same batch of support, we have seen (vide infra) that the polymerization activities obtained in duplicate experiments are repeatable to within 5−10%.

Binary Chromium/Nickel Catalyst System. In a previous study,[17] we investigated the immobilization of the chromium-

Table 5. Ethylene Polymerization Using Binary Titanium and Nickel Catalysts on a $MgCl_2$-Based Support[a]

		catalyst loading on support			
entry	immobilization method[b]	$TiCl_4$ (μmol/g)	Ni complex **1** (μmol/g)	temp (°C)	activity (kg/mol of Ti•h•bar)
1		10		50	9 800
2		10		50	8 920
3	II	10	5	50	14 880
4	III	10	5	50	13 960
5	II	10	10	50	12 340
6			5	50	240[c]
7		10		60	13 400
8	II	10	5	60	12 260
9	III	10	5	60	14 420
10			5	60	160[c]
11		10		70	14 340
12	II	10	5	70	14 180
13	III	10	5	70	15 900
14			5	70	80[c]

[a] Polymerization conditions: 500 mL of light petroleum, immobilized catalyst 100 mg, $AlEt_3$ 1 mmol, ethylene pressure 5 bar, time 1 h. [b] See Experimental Section. [c] Activity in kg/mol of Ni•h•bar.

Table 6. Ziegler−Natta Catalyst Compositions

			internal donor	
catalyst	Ti (wt %)	Mg (wt %)	type	wt %
A	2.0	19.0	diisobutyl phthalate	6.8
B	2.9	16.9	diisobutyl phthalate	16.6
C	4.0	14.6	9,9-bis(methoxymethyl)fluorene	13.1
D	3.7	17.5	ethyl benzoate	14.8

(III) complex (η^1:η^5-$Me_2NCH_2CH_2C_5Me_4$)$CrCl_2$ on various supports of type $MgCl_2/AlR_n(OEt)_{3-n}$ and achieved ethylene polymerization activities comparable to those previously obtained[26] in MAO-activated homogeneous polymerization by Jolly and co-workers. Furthermore, the single-site characteristics of the catalyst were completely retained on immobilization, leading to narrow molecular weight distribution polyethylene. Only moderate deterioration in catalyst activity was observed during the course of polymerization, in contrast to the significant decay typically observed with homogeneous chromium catalysts. Recently, chromium complexes containing a rigid spacer group between the cyclopentadienyl ring and the nitrogen atom, giving improved stability in homogeneous polymerization, have been reported by Enders et al.[24] One example is the quinoline complex **3**. We have now investigated the immobilization and activation of **3** on $MgCl_2/AlEt_n(OEt)_{3-n}$ supports. Initial polymerizations carried out using Al*i*Bu_3 as cocatalyst gave activities of 740 and 1600 kg/mol•bar•h at 50 and 70 °C, respectively, but much higher catalyst activities, in the range 3100−6560 kg/mol•bar•h, were obtained when $AlEt_3$ was used as cocatalyst.

In order to determine whether the coimmobilization of a nickel catalyst could give a further increase in the productivity of the chromium catalyst, catalyst immobilization was carried out by contacting the support [$MgCl_2$•$0.16AlEt_{2.25}(OEt)_{0.75}$] with a dichloromethane solution of **3** or the binary catalyst combination **1** + **3**. It was observed that, after contacting overnight at ambient temperature, the blue color of **3** in the solution was completely transferred to the solid support, indicating complete immobilization. The ethylene polymerization results obtained are summarized in Table 4. It is apparent that the synergetic effect of incorporating the nickel catalyst into the chromium-based system is less spectacular than was the case for the Fe-based system and that the effects are dependent on polymerization temperature and Ni loading. Little effect is apparent at 70 °C, possibly due to a lower monomer diffusion limitation at higher temperature,[27] but at 50 °C the activities of binary catalyst systems were in most cases around 1000 kg/mol•bar•h higher than the unmodified Cr systems and again significantly greater than the activities obtained with only the Ni system. Several polymerizations were carried out in duplicate to confirm this effect. Fractionation of a polymer (Table 4, entry 5) into linear and branched fractions indicated that the soluble (branched) fraction amounted to 3.0 wt % of the total polymer. DSC melting endotherms of the unfractionated polymer and linear and branched fractions are shown in Figure 5.

Binary Titanium/Nickel Catalyst System. In order to determine whether the coimmobilization of a nickel catalyst could also lead to improvements of a Ziegler−Natta type catalyst system, further experiments were carried out with $TiCl_4$ as the main precatalyst component. In initial experiments it was found that the use of dichloromethane as immobilization solvent for $TiCl_4$ resulted in relatively low activities, so for these studies catalyst immobilization was carried out in toluene, either by impregnating the support with $TiCl_4$ and then the nickel component **1**, or vice versa. These experiments were carried out with a different, less porous support than was used with the Fe/Ni and Cr/Ni systems. The support was prepared via the reaction of $AlEt_3$ with $MgCl_2$•2.1EtOH and had the composition $MgCl_2$•$0.73AlEt_{2.58}(OEt)_{0.42}$. Ethylene polymerization was carried out at 50, 60, or 70 °C, using 1 mmol of $AlEt_3$ as cocatalyst/scavenger. It was observed that the ethylene mass flow increased during the course of each 1 h polymerization, indicating acceleration kinetics with both the single (Ti) and binary (Ti/Ni) catalyst systems. The activities obtained are summarized in Table 5. It is clear from the polymerizations carried out at 50 °C that a very significant synergetic effect was obtained, the catalyst activity increasing from around 9000 kg/mol of Ti•bar•h in the absence of Ni to around 14 000 kg/mol of Ti•bar•h in the presence of Ni, while with this support the activity with Ni alone was only 240 kg/mol of Ni•h•bar. For the polymerizations carried out at 50 °C, positive synergy was obtained irrespective of the immobilization method used, whereas at 60 and 70 °C the results indicated positive synergy when the support was contacted first with the Ni complex **1** and then with $TiCl_4$, but not when the contact order was reversed.

As was observed with the Fe- and Cr-based binary catalyst systems, an increase in Ni loading (entry 5 in Table 5) led to a decrease rather than a further increase in overall activity, indicating that a low Ni loading is optimal for the greatest synergistic effect. This is of course advantageous with respect to minimizing both the amount of Ni complex used and the proportion of branched polyethylene in the final product.

Fractionation of a polymer prepared with Ti and Ni loadings of 10 and 5 μmol/g, respectively (Table 5, entry 3), as described above, yielded 1.6 wt % of a soluble fraction having a DSC peak melting temperature of 122 °C, as opposed to 137 °C for the unfractionated polymer, indicating a very low proportion of branched polyethylene in the final product. DSC melting endotherms of the overall polymer and soluble and crystallized fractions are shown in Figure 6.

The positive results obtained from the coimmobilization of $TiCl_4$ and the nickel complex **1** on a $MgCl_2$-based support prompted us to investigate the effects of incorporating the nickel catalyst into various Ziegler−Natta catalysts differing in both porosity and chemical composition. For this, we selected catalysts prepared by the reaction of $MgCl_2$•*n*EtOH with excess $TiCl_4$ in several stages and in the presence of a donor.[25] The compositions of these catalysts are given in Table 6. Catalyst

Table 7. Ethylene Polymerization Using Ziegler−Natta Catalysts in Presence and Absence of Nickel Complex 1[a]

entry	catalyst type	catalyst mg	Ni complex **1** (μmol)	temp (°C)	time (h)	productivity (g/g of cat·h)
1	A	50	0	50	1	220
2	A	50	0.5	50	1	1054
3	A	50	0	70	1	1926
4	A	50	0.5	70	1	2524
5	B	50	0	50	1	58
6	B	50	0.5	50	1	72
7	B	50	0	70	1	664
8	B	50	0.5	70	1	764
9	C	50	0	50	1	32
10	C	50	0.5	50	1	36
11	C	30	0	70	1	943
12	C	30	0.5	70	1	2483
13	D	100	0	50	2	46
14	D	100	0.5	50	2	101
15	D	100	0	70	2	771
16	D	100	0.5	70	2	960

[a] Polymerization conditions: 500 mL of light petroleum, $AlEt_3$ 1 mmol, ethylene pressure 5 bar.

A was prepared with a porous, partially dealcoholated support of composition $MgCl_2$·1.1EtOH, whereas catalysts B, C, and D were prepared from supports with EtOH/$MgCl_2$ molar ratios in the range 2−3. Impregnation of these catalysts with **1** was carried out at room temperature, simply by contacting the catalyst overnight with a solution of the nickel complex in toluene. The results of ethylene polymerizations carried out with these catalysts, in the presence and absence of the nickel complex, are given in Table 7. In every case, precontact of the catalyst with **1** is seen to increase the catalyst productivity. However, the productivities are strongly dependent on both catalyst type and polymerization temperature. The highest productivities, with and without the nickel complex, were obtained with catalyst A, prepared with the porous $MgCl_2$·1.1EtOH support. With this catalyst, the synergetic effect of the presence of the nickel complex was particularly large at 50 °C but also significant at 70 °C. Much lower productivities were obtained with catalyst B, in stark contrast to propylene polymerization, where catalysts of type B typically give productivities around 4 times higher than those obtainable with catalysts of type A.[28] This difference illustrates the much greater effect of monomer mass transfer limitation on particle growth in ethylene, as opposed to propylene, polymerization. In mass transfer limited particle growth, only the outer shell is at first available for polymerization, until the hydraulic stresses generated by the growing polymer are able to expose a new shell.[29] In such cases, a rapid initial peak in activity is followed by a drop in rate, after which the rate gradually increases as fragmentation takes place during the course of polymerization. Such phenomena are not generally observed in propylene polymerization with $MgCl_2$-supported catalysts, but Fink and co-workers have reported similar effects of diffusion limitation in propylene polymerization with a SiO_2-supported metallocene.[30] Changes in ethylene mass flow for the polymerizations carried out at 70 °C are shown in Figure 7, and a drop in rate in the early stages of polymerization is indeed apparent with catalyst B but not with catalyst A. In the case of catalyst C, a small initial drop in rate was observed with the unmodified catalyst, but not when the catalyst was impregnated with complex **1**. With this catalyst, the presence of Ni gave rise to a much steeper increase in rate throughout the polymerization carried out at 70 °C, leading to a large increase in productivity. It is interesting to note that increasing mass flow throughout the polymerization, evident from Figure 7 and indicative of acceleration kinetics, was a common feature in all the ethylene polymerizations carried out with the Ziegler−Natta catalysts. Acceleration-type rate curves are indicative of intraparticle diffusion limitations and become more pronounced as the diffusion resistance becomes more severe.[31] Detailed investigation of the possible effects of catalyst and support characteristics such as friability and pore size distribution is beyond the scope of the present study, but it is likely that the enhanced activation profiles observed with the various Ziegler−Natta systems result from more rapid particle fragmentation and growth for the catalysts impregnated with the nickel complex. It is interesting to note that, in contrast to the Ziegler−Natta systems, the catalysts prepared via immobilization of the iron complex **2** on $MgCl_2/AlEt_n(OEt)_{3-n}$ supports exhibited (Figure 4) relatively stable activity throughout polymerization, with no evidence of an acceleration profile. This is likely to be due to easier fragmentation of the support in the early stages of polymerization, but it should also be taken into account that the loadings of transition metal on the support in these systems were much lower than those in the Ziegler−Natta catalysts.

Polymer Properties. In order to determine whether the incorporation of the nickel catalyst **1** had any detectable effect on the molecular weight, molecular weight distribution, and melting behavior of the polyethylene prepared with the iron-, chromium-, and titanium-based catalyst systems, selected polymers prepared at 50 °C as indicated in Tables 1, 2, 4, and 5 were analyzed by GPC and DSC. The results are summarized in Table 8. As expected, no large differences are apparent after coimmobilization of the nickel catalyst along with the main catalyst component. On the other hand, very significant differences are observed when comparing the Fe-, Cr-, and Ti-based systems. The iron catalyst **2** gives polyethylene with moderate molecular weight and broad polydispersity index (PDI), in line with previous observations.[19,20] Higher molecular weight and a somewhat narrower polydispersity are obtained with $TiCl_4$, while very high molecular weight and narrow polydispersity ($M_w/M_n = 2$) are obtained with the immobilized chromium complex **3**. This represents a further example of the retention of the single-site characteristics of a chromium catalyst following immobilization on a $MgCl_2$-based support, similarly high molecular weight and narrow polydispersity having been obtained with the complex (η^1:η^5-$Me_2NCH_2CH_2C_5Me_4$)$CrCl_2$.[17]

The DSC data in Table 8 reveal significant differences in the melting enthalpy (ΔH) for the polymers synthesized with the Fe-, Cr-, and Ti-based systems, irrespective of the presence or absence of the nickel catalyst. Taking a ΔH value of 293 J/g for 100% crystalline polyethylene,[32] the values in Table 8 correspond to crystallinities of 41% for the polymers prepared

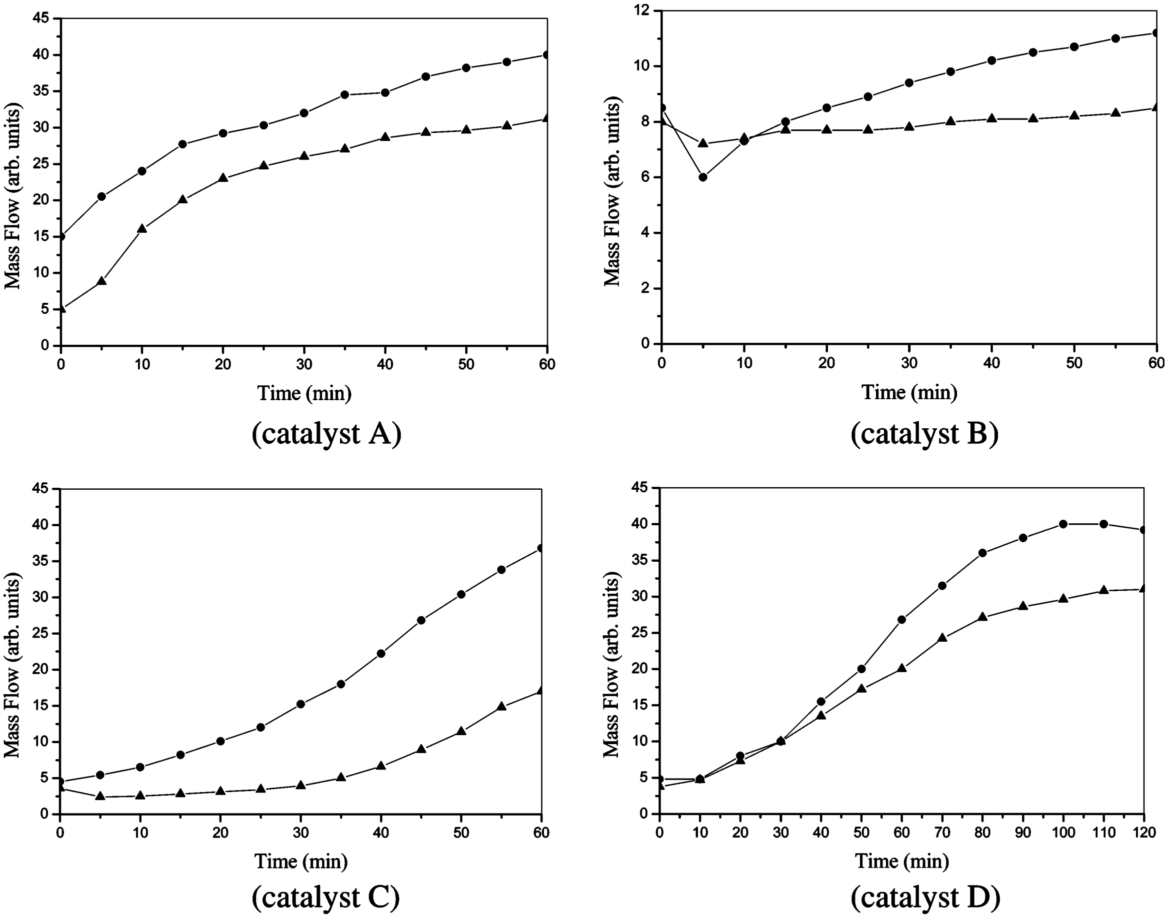

Figure 7. Rate−time profiles for polymerizations carried out at 70 °C with Ziegler−Natta catalysts A−D in the presence (●) and absence (▲) of the Ni complex **1**.

Table 8. Polymer Molecular Weight Distribution and Melting Behavior

main catalyst component							
complex	loading (μmol/g)	Ni complex **1** loading (μmol/g)	M_n (g/mol)	M_w (g/mol)	PDI (M_w/M_n)	mp (°C)	ΔH (J/g)
Fe (**2**)	5		29 500	300 000	10.2	137.7	205.4
Fe (**2**)	5	1	27 400	278 000	10.1	137.3	203.5
Fe (**2**)	5	5	28 100	316 000	11.2	135.7	184.5
Cr (**3**)	20		751 000	1480 000	2.0	135.4	118.7
Cr (**3**)	20	5	527 000	1077 000	2.0	134.6	121.4
$TiCl_4$	10		158 000	893 000	5.7	135.7	137.2
$TiCl_4$	10	5[a]	224 000	894 000	4.0	137.3	142.2
$TiCl_4$	10	5[b]	228 000	888 000	3.9	137.5	140.2

[a] Immobilization method II. [b] Immobilization method III.

with the chromium complex **3**, 47−49% for those prepared with $TiCl_4$, and 63−70% in the case of the iron catalyst **2**. Clearly, the crystallinity of these polyethylenes is influenced primarily by molecular weight and molecular weight distribution rather than by the presence of a small proportion of branched polymer.

Conclusions

Significant improvements in the activities of $MgCl_2$-immobilized iron-, chromium-, and titanium-based catalysts for ethylene polymerization can be achieved by the incorporation of a limited amount of a diimine nickel catalyst producing branched polyethylene. The increases in activity are much higher than the activities obtained in reference polymerizations with only the nickel component and are ascribed to partial alleviation of the monomer diffusion limitation inherent in ethylene homopolymerization with heterogeneous catalysts. Particularly advantageous is the fact that the synergetic effect is obtained with relatively low proportions of nickel in the immobilized binary catalyst systems, such that the polyethylenes obtained retain the characteristics of the polymers obtained with the individual Fe-, Cr-, or Ti-based catalyst systems. It may be anticipated that the beneficial effect on productivity of introducing a component giving branched polyethylene into a heterogeneous catalyst system for high-density polyethylene should not only apply to the systems investigated in the present work.

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