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Propylene polymerisations with novel heterogeneous combination metallocene catalyst systems

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Abstract

Propylene was polymerised with novel combination metallocene catalyst systems prepared by an emulsion-based heterogenisation method in liquid monomer conditions. The catalyst combinations investigated were *rac*-dimethylsilanylbis(2-methyl-4-phenyl-1-indenyl)zirconium dichloride/*rac*-[ethylenebis(2-(*tert*-butyldimethylsiloxy)indenyl)]zirconium dichloride/methylaluminoxane (MAO) (**1** + **2**) and *rac*-dimethylsilanylbis(2-methyl-4-phenyl-1-indenyl)zirconium dichloride/*rac*-dimethylsilanylbis(2-isopropyl-4-[3,5-dimethylphenyl]indenyl)zirconium dichloride/MAO (**1** + **3**). The effects of polymerisation temperature and hydrogen on catalyst performance and polymer properties, as well as copolymerisation with hexene and ethylene were investigated. Depending on the polymerisation conditions, M_w of polypropylene varied from 144 to 286 kg/mol for **1** + **2** and from 200 to 390 kg/mol for **1** + **3**. Combination **1** + **2** produced broader molecular weight distribution (MWD) than **1** + **3**, and a bimodal MWD with clearly separated low- and high- M_w polymer fractions was observed with **1** + **2**. The two catalyst systems showed similar hydrogen and hexene responses. Each metallocene precursor showed individual response towards the polymerisation conditions, especially polymerisation temperature, suggesting that interaction between the catalyst active sites was negligible in the studied systems.

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1. Introduction

Metallocene catalysts enable production of tailored polypropylene structures. Deeper understanding of polymerisation and activation behaviour of the metallocenes has been pursued through intensive research, and several reviews have been published [1–4]. Most of this research has focused on homogeneous catalyst systems, but since most industrial processes require heterogeneous systems, implementation of the results is somewhat limited.

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Relative to their Ziegler–Natta-catalysed counterparts, metallocene-based isotactic polypropylenes have a major drawback in their narrow processing window, which originates in the narrow molecular weight distribution (MWD) and consequently they show poor shear thinning properties [5]. A typical MWD for a metallocene-catalysed polypropylene is about 2, whereas the MWD value for Ziegler–Natta-catalysed polypropylenes typically varies between 5 and 7.

A means to overcome the limitations associated with narrow MWD is to mix together two polypropylenes of different molecular weight (M_w). A more attractive and economical route is to use two or more metallocene precursors simultaneously yielding a polypropylene mixture consisting of the polymer fractions produced by the different metallocenes individually. While several groups have published studies in which they used two metallocenes simultaneously, the main focus

has been on the chain transfer reactions between the active sites, and on the possibility to synthesise block copolymers with different block tacticities [6–8].

Metallocene precursors can be heterogenised by immobilising them on a carrier. Many support materials, including silica and other inorganic porous oxides, starches, clays, metals and ceramics, metal halides and polymers, have been investigated [9]. The most common carrier by far is silica. Poor catalyst homogeneity and low maximum metal content of the silica-supported metallocene catalysts have been limiting factors, and to overcome the limitations, a novel emulsion-based catalyst heterogenisation method has recently been developed. The main idea of the emulsion-based heterogenisation method is to carry out the catalyst chemistry in a liquid phase in an emulsion, after which the emulsion droplets are solidified [11]. The basic concept is illustrated in Fig. 1. This method produces catalyst particles with an inherently perfect spherical shape and unique intra- and interparticle homogeneity [10,11].

The aim of the present study was to investigate the possibility of overcoming the processing limitations associated with narrow MWD metallocenes by using combination metallocene systems. Metallocene precursors and methylaluminoxane (MAO) were heterogenised by the emulsion-based heterogenisation method to prepare novel combination catalyst systems. To ensure that the polymerisation conditions were comparable with those of industrial processes, we carried out the polymerisations in liquid propylene conditions. The effects of polymerisation temperature and hydrogen on polymerisation behaviour and polymer properties were of interest, as well as the possibility to copolymerise hexene and ethylene.

2. Experimental part

2.1. Materials

The combination heterogeneous catalysts systems *rac*-dimethylsilylanylbis(2-methyl-4-phenyl-1-indenyl)zirconium dichloride/*rac*-[ethylenebis(2-(*tert*-butyldimethylsiloxy)indenyl)]zirconium dichloride/MAO (**1** + **2**) and *rac*-dimethylsilylanylbis(2-methyl-4-phenyl-1-indenyl)zirconium dichloride/*rac*-dimethylsilylanylbis(2-isopropyl-4-[3,5-dimethylphenyl]indenyl)zirconium dichloride/MAO (**1** + **3**) were synthesised according to the literature [11]. The metallocene precursors **1–3** are illustrated in Fig. 2, and Table 1 describes the heterogenised catalysts. Triethylaluminum (TEA) supplied by Crompton

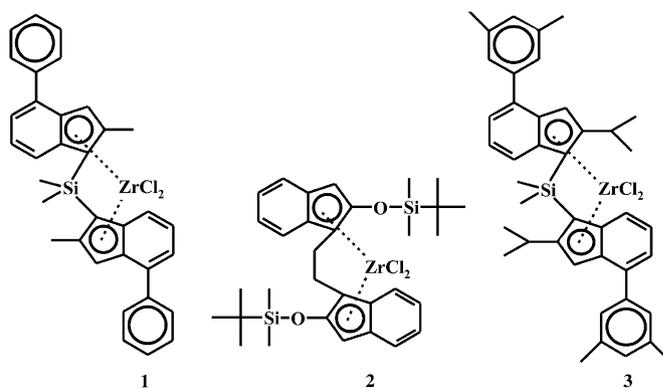


Fig. 2. Studied metallocene precursors: *rac*-dimethylsilylanylbis(2-methyl-4-phenyl-1-indenyl)zirconium dichloride (**1**), *rac*-[ethylenebis(2-(*tert*-butyldimethylsiloxy)indenyl)]zirconium dichloride (**2**), *rac*-dimethylsilylanylbis(2-isopropyl-4-[3,5-dimethylphenyl]indenyl)zirconium dichloride (**3**).

Table 1
Studied heterogeneous catalyst systems

	Percentage composition (mol%/mol%)	Al/Zr (mol/mol)
Catalyst system 1 + 2	63.6/36.4	200
Catalyst system 1 + 3	13.7/86.3	200

Corporation was diluted with *n*-pentane (Sigma–Aldrich, pro analysis). Analytical grade 1-hexene (Sigma–Aldrich) was dried with molecular sieves. Polymerisation grade propylene (Borealis Polymers Oy), hydrogen (AGA, grade 5.0) and ethylene (AGA, grade 3.5) were used without further purification. All operations with these materials were carried out in nitrogen atmosphere using standard vacuum or glovebox techniques.

2.2. Polymerisation procedure

Polymerisations were carried out in liquid monomer conditions in a 0.1 dm³ Büchi stainless steel autoclave at 50 or 70 °C. *n*-Pentane-diluted TEA solution (1.0 ml, 1.75 wt%) was injected into the evacuated and N₂-purged reactor as scavenger, after which hydrogen or 1-hexene was introduced if needed. Liquified propylene (35 g, 57 ml) was fed to the reactor simultaneously with the catalyst system, and followed by ethylene in ethylene–propylene copolymerisations. The reactor was heated up to the polymerisation temperature in about

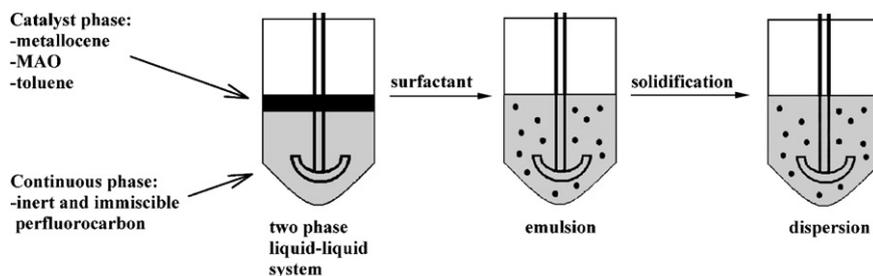


Fig. 1. Basic concept of emulsion-based heterogenisation method [11].

15 min. Constant polymerisation conditions were ensured by stirring the solution at 600 rpm. The polymerisation time was one hour, after which the propylene was flushed out, and the polymer was dried, weighed and analysed without further treatment.

2.3. Characterisation methods

M_w and MWD were measured at 140 °C by a Waters Alliance 2000 gel permeation chromatograph (GPC) equipped with Waters HMW7, 2 × HMW6 and HMW2 styragel columns, RI detector and viscometer. 1,2,4-Trichlorobenzene was used as solvent and the flow rate was 1.0 cm³/min. The columns were universally calibrated with narrow molecular weight polystyrene standards.

Thermal properties (melt temperature and heat of fusion) were determined with a Perkin–Elmer DSC-7 differential scanning calorimeter (DSC). The samples (10 ± 1 mg of polymer) were heated from 30 or 40 °C to 180 °C (heating rate 10 °C/min), held at 180 °C for 2 min, cooled to 30 or 40 °C (cooling rate 10 °C/min), held at 30 or 40 °C for 2 min, heated to 180 °C (heating rate 10 °C/min), and finally cooled to room temperature (cooling rate 10 °C/min). The melting point (T_m) and heat of fusion (ΔH_f) were measured during the second heating period. Samples were also characterised by a step crystallisation method using a Perkin–Elmer DSC-7 instrument [12]. After fast heating to 180 °C, the samples (10 ± 1 mg of polymer) were annealed, typically at 160, 155, 150, 145, 140, 135, 130 and 125 °C. The time for each annealing step was 120 min. After annealing, the temperature was dropped to room temperature, and the melting curve of the crystallised sample was run at 10 °C/min.

¹³C NMR analyses were performed using a Varian Inc. (Palo Alto, CA) Gemini 2000XL NMR spectrometer (10 mm broadband probe, 75 MHz). Polymer samples were dissolved

in a mixture of deuterated benzene (10 wt%) and 1,2,4-trichlorobenzene (90 wt%) and measured at 125 °C with 45° pulse angle, 2 s acquisition time, 6 s delay and 2048 scans. The carbon signals [13,14], end groups [15,16] and reactivity ratios [17] were assigned according to the literature. Processing of the NMR spectra, including peak fitting over the peaks of the methyl region, was performed with ACD Labs ACD/SpecManager software (version 9.06).

3. Results and discussion

Compared with homogeneous metallocenes, heterogenised catalysts produce morphologically more uniform polymer product. This was also observed in our polymerisations. More uniform polymer product prevents reactor fouling, which is advantageous in industrial processes. Particle forming process in propylene polymerisation with an emulsion-based heterogeneous catalyst system compared with a silica-supported counterpart, has been recently investigated by Bartke et al. [11].

The polymerisation results with catalyst systems **1 + 2** and **1 + 3** are summarised in Table 2. The results for the two systems are presented and discussed separately below.

3.1. *rac*-Dimethylsilanylbis(2-methyl-4-phenyl-1-indenyl)zirconium dichloride/*rac*-[ethylenebis(2-(*tert*-butyldimethylsiloxy)indenyl)]zirconium dichloride/MAO

3.1.1. Molecular weight

The M_w of the samples polymerised with catalyst system **1 + 2** varied from 144 to 286 kg/mol and the MWD from 6.4 to 11.8 (Table 2). A typical GPC curve for the system is shown in Fig. 2. Previously catalyst **1** has been shown to produce higher M_w than catalyst **2** [18,19], and, as expected, the GPC curve shows a bimodal MWD consisting of high- and

Table 2
Results of polymerisation of propylene with catalysts **1 + 2** and **1 + 3**

Run	Catalyst	T (°C)	m_{cat} (mg)	[hexene] ^a (mmol/l)	H ₂ (mmol)	C ₂ (mmol)	Yield (g)	Activity (kg _{PP} /g _{cat} h)	M_w^b (kg/mol)	MWD ^b	T_m^c (°C)	ΔH_f^c (J/g)	$T_{m,SC}^{c,d}$ (°C)
418	1 + 2	70	4.0	—	—	—	8.5	2.13	286	11.8	147	90	145, 151
420	1 + 2	50	4.9	—	—	—	8.5	1.74	180	9.7	150	107	147, 151
428	1 + 2	70	5.6	70	—	—	8.6	1.53	189	7.9	139	88	140, 144, 146
424	1 + 2	70	6.1	140	—	—	12.2	2.00	144	6.4	135	82	135, 142
446	1 + 2	70	3.1	—	2.5	—	5.1	1.65	275	11.4	147	96	146, 152
443	1 + 2	70	3.0	—	5.0	—	10.6	3.53	223	10.2	146	98	146, 153
438	1 + 3	70	7.1	—	—	—	4.1	0.58	254	4.5	152	97	148, 154, 158, 162
439	1 + 3	50	8.6	—	—	—	2.1	0.24	390	3.2	159	99	164, 168
441	1 + 3	70	10.4	70	—	—	6.4	0.62	215	3.8	147	82	143, 150
440	1 + 3	70	9.0	140	—	—	5.1	0.57	217	3.3	139	81	135, 142, 149
453	1 + 3	70	2.7	—	2.5	—	4.1	1.51	200	5.3	156	98	150, 157, 159, 162
442	1 + 3	70	3.9	—	5.0	—	7.6	1.95	236	4.3	155	99	149, 155, 159, 162
448	1 + 3	70	2.7	—	—	36	2.3	0.84	203	3.5	137	73	137, 144
449	1 + 3	70	2.9	—	—	71	2.5	0.85	208	2.9	126	53	106, 129

^a Initial hexene concentration.

^b By GPC.

^c By DSC.

^d Melting peaks after step crystallisation treatment.

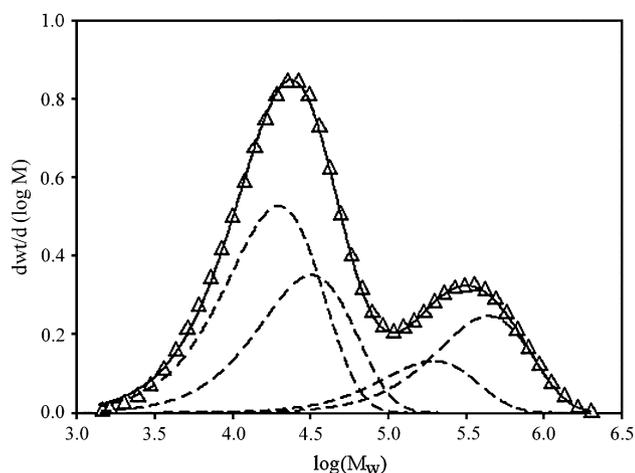


Fig. 3. GPC curve and Schultz–Flory fractions of sample 418 produced with catalyst combination **1** + **2** at 70 °C. (Δ): observed GPC data points, (---): Schultz–Flory fractions, (—): sum of Schultz–Flory fractions.

low- M_w fractions produced by catalysts **1** and **2**, respectively. Copolymerisation of hexene and lower polymerisation temperature decrease M_w , whereas the effect of hydrogen is less marked (Table 2).

The Schultz–Flory distribution [20] predicts MWD of 2.0 for a single-site catalyst, and the broader MWD must be explained by variations in the polymerisation conditions or the presence of two or more active catalyst sites. If one Schultz–Flory function is too narrow to model the MWD of the observed GPC curve, a combination of several functions can be used [21]. For the samples produced with catalyst combination **1** + **2**, a good fit is obtained with four Schultz–Flory functions representing the presence of four polymer fractions (F1–F4). The Schultz–Flory fractions and the sum of the fractions for sample 418 are illustrated in Fig. 3.

The presence of four Schultz–Flory fractions in our case is due to variations in the polymerisation conditions rather than interactions between the active sites. The catalyst and liquified

propylene were fed to the reactor at room temperature, after which the temperature was raised to the polymerisation temperature. Thus, some polymerisation took place during the heating period, causing broader MWD than predicted by the Schultz–Flory theory.

The M_w of each Schultz–Flory fraction was determined, and the results are summarised in Table 3 and Fig. 4. The M_w of the fractions polymerised with catalyst **2** (fractions F1 and F2) is nearly independent of the polymerisation conditions, whereas the fractions polymerised with catalyst **1** (fractions F3 and F4) show a dependency. The strongest dependency is observed for the highest M_w fraction (F4), which varies between 440 and 860 kg/mol. The copolymerisation of hexene decreases the M_w of fraction F4, and also hydrogen has a negative effect.

Hydrogen has been widely used as a chain transfer agent to control M_w of polymers [22], and the decrease in M_w in the presence of hydrogen was expected. The strong negative effect of hexene on the M_w was surprising, however, because the opposite effect has been reported [23,24]. A decrease in the M_w has been observed earlier for ethylene/hexene copolymers [19,25]. Bruaseth and Rytter [25] concluded that chain termination in ethylene–hexene copolymerisations takes place after hexene insertion, thus decreasing M_w . It seems probable that the same mechanism was operative in our study, and that the decrease in M_w is caused by favoured β -H transfer to Zr after hexene 1,2 or 2,1 insertion, as presented in Scheme 1.

The observed differences in M_w are in good accordance with differences in M_w in the highest M_w fraction (F4). The only exception to this is the effect of the polymerisation temperature on the M_w . We observed a strong decrease in M_w , from 286 to 180 kg/mol, when the polymerisation temperature was lowered from 70 to 50 °C, even though the M_w values of the individual fractions were not markedly affected by the temperature. The lower M_w is due to the greater amount of the low- M_w fraction produced with catalyst **2**. As reported in Table 2, the sample polymerised at 50 °C (run 420) has

Table 3
Low- and high M_w -fractions produced with catalysts **1** + **2** and **1** + **3**

Run	Low- M_w fraction							High- M_w fraction				
	F1		F2		F1 + F2	F3		F4		F3 + F4		
	M_w (kg/mol)	wt%	M_w (kg/mol)	wt%		M_w (kg/mol)	wt%	M_w (kg/mol)	wt%			
418	1 + 2	70 °C	24	41	46	26	67	320	11	866	22	33
420	1 + 2	50 °C	24	33	39	49	82	299	4	840	14	18
428	1 + 2	[hexene] = 70 mmol/l	25	51	51	19	70	288	13	624	18	30
424	1 + 2	[hexene] = 140 mmol/l	23	41	45	28	69	221	11	440	20	31
446	1 + 2	H ₂ = 2.5 mmol	23	39	47	25	64	309	12	762	24	36
443	1 + 2	H ₂ = 5.0 mmol	23	39	44	29	68	294	10	695	21	32
438	1 + 3	70 °C	31	9	78	43	52	211	31	754	17	48
439	1 + 3	50 °C	—	—	117	30	30	260	46	662	23	70
441	1 + 3	[hexene] = 70 mmol/l	33	11	41	40	51	206	33	610	16	49
440	1 + 3	[hexene] = 140 mmol/l	39	9	87	40	49	211	36	602	15	51
453	1 + 3	H ₂ = 2.5 mmol	22	15	68	43	58	206	30	802	11	57
442	1 + 3	H ₂ = 5.0 mmol	33	11	78	39	50	210	34	711	16	50
448	1 + 3	C ₂ = 36 mmol	33	12	83	38	50	216	38	561	12	50
449	1 + 3	C ₂ = 71 mmol	34	4	88	35	39	219	45	503	15	61

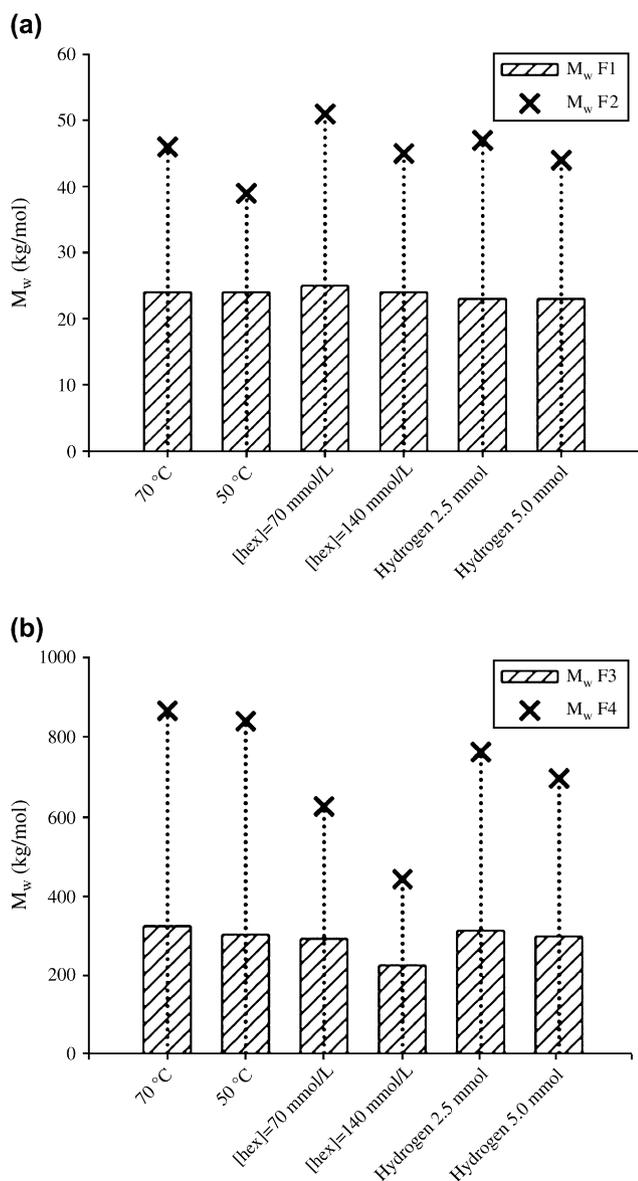
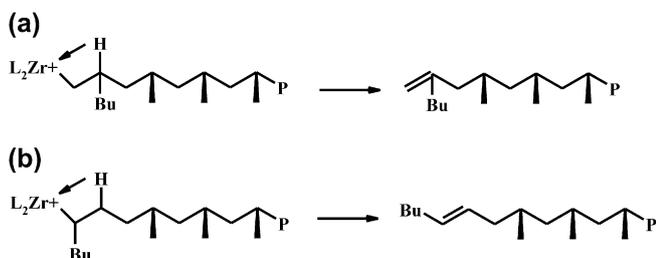


Fig. 4. M_w dependency of different fractions on polymerisation conditions with catalyst combination **1** + **2**. Low- M_w fractions (F1 and F2) (a), high- M_w fractions (F3 and F4) (b).

a considerably higher content of the low- M_w fraction than do the other samples. Our result, indicating that the activity of **1** decreases and the activity of **2** increases when the polymerisation temperature is decreased from 70 to 50 °C, is in good



Scheme 1. Chain termination reactions after hexene 1,2 insertion (a) and after hexene 2,1 insertion (b).

accordance with the results reported previously for these catalysts. Leino et al. [19] have reported the maximum activity for catalyst **2** to be at 40 °C, whereas the activity of **1** increases rapidly with temperature [26].

3.1.2. Catalyst activity

The catalyst activity varied between 1.53 and 3.53 kg_{pp}/g_{cat} h (Table 2). Some of the variation may have been caused by impurities in the polymerisation system. The activity response of catalysts **1** and **2** to different polymerisation conditions seems to be similar, and polymer samples consisting of 70% of low- M_w fraction and 30% of high- M_w fraction were consistently obtained.

Hydrogen had a positive influence on the catalyst activity; the activity increased when 5.0 mmol of hydrogen was introduced to the reactor (run 443). The relative amounts of the high- M_w and low- M_w fractions remained unchanged, however, which shows that the hydrogen responses of catalysts **1** and **2** are similar. A strong increase in the activity in the presence of hydrogen has been reported for catalyst **1**/MAO [26], but to our knowledge the hydrogen response of catalyst **2** has not been investigated earlier.

Several theories to explain the enhanced activity in the presence of hydrogen have been proposed, including reactivation of dormant sites [27]; preventing the formation of unsaturated chain end groups, which may decrease the catalyst activity [28]; and increase in the overall activity by shortcutting the slow propagation step that occurs after isolated secondary insertion [29]. 2,1 Misinsertions have been observed even earlier in polypropylene samples produced with catalysts **1** and **2** [18,30], why it is likely that the activity enhancement is caused by shortcutting of the slow propagation step after a secondary monomer insertion. The other mechanisms cannot be ruled out, however, because, as will be discussed below, hydrogen did not have any significant effect on polymer microstructure.

3.1.3. Thermal properties

The samples showed typical melting behaviour for metallocene-based isotactic polypropylene, and a single melting peak is observed. The sample polymerised at 50 °C (run 420) has a slightly higher melting point and heat of fusion value, which suggests increase in stereo- or regioregularity (Table 2) [4]. Hydrogen does not have an effect on the thermal properties, but, as expected, the copolymerisation of hexene decreases the melting point and heat of fusion value due to the exclusion of hexene units from polypropylene crystals (Table 2). Our results agree well with those of Poon et al. [24], who demonstrated that the melting point of a copolymer containing less than 10 mol% of hexene decreased systematically with increasing hexene content.

The melting traces after the step crystallisation treatment are presented in Fig. 5. The step crystallisation method has mostly been used to study comonomer distribution in ethylene copolymers [12,31]. For propylene homopolymer, Hanyu and Wheat [32] report that several melting peaks originate from heterogeneity in the stereo defect distribution among polymer

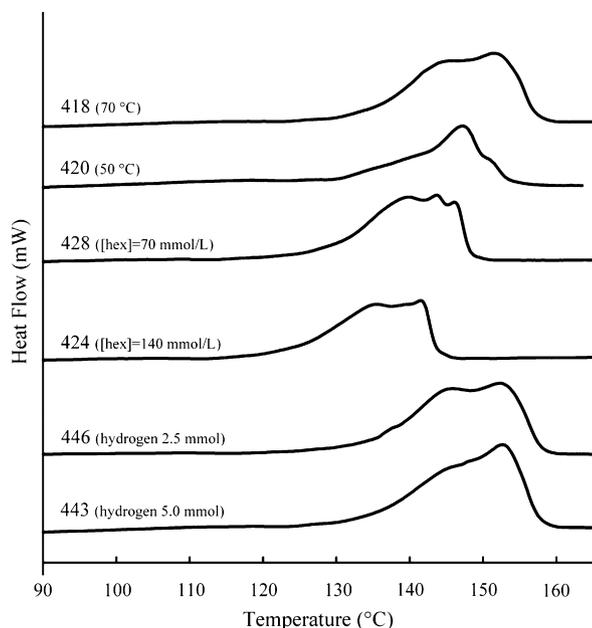


Fig. 5. Melting curves of samples produced with catalyst combination **1** + **2** after step crystallisation.

chains. After the step crystallisation treatment, we observed two melting peaks, and it is most likely that these peaks arise from polymer fractions with slightly different tacticities, one polymerised with catalyst precursor **1** and the other with catalyst precursor **2**.

As can be seen from Fig. 5, the polymerisation temperature and copolymerisation of hexene have an effect on melting behaviour after the step crystallisation treatment, whereas the effect of hydrogen is insignificant. The sample polymerised at 50 °C (run 420) shows a strong melting peak at 147 °C, due to the larger amount of the low- M_w polymer in the sample. The copolymerisation of hexene shifts both melting peaks to lower temperatures, which shows that both

catalysts are capable of copolymerising hexene. A third melting peak at 144 °C is observed for the sample polymerised with lower hexene concentration (run 428). For the time being, we cannot explain the appearance of this third peak, and further studies are required.

3.1.4. ^{13}C NMR characterisation

Table 4 displays the analysis of the polymers based on carbon NMR spectra. Lowering the temperature from 70 to 50 °C has no effect on either the stereoregularity or the regio-regularity of the polymer produced with combination **1** + **2**. The regioerrors consist mostly of 2,1 misinsertions, and the total amount of the observed regioerrors (3,1 + 2,1 misinsertions) is about 0.6 mol%. This lack of effect of polymerisation temperature is in contrast to the observed higher melting point and heat of fusion value for the sample polymerised at 50 °C (run 420). In a previous study, we observed that at 70 °C and 1.5 bar propylene pressure in heptane, catalyst **1** produces propylene homopolymer with 0.3 mol% regioerrors consisting mainly of 2,1 misinsertions [18].

Fig. 6 shows four different types of end groups present in the polymers: *n*-propyl, vinyl, vinylidene and isobutyl. The possible routes of formation of these end groups are presented in Scheme 1 for propylene–hexene copolymers and in our previous work [18] for ethylene–propylene copolymer and propylene homopolymer. *n*-Propyl and vinylidene are detected in the homopolymerisations showing β -H transfer reactions to Zr or propylene monomer. Since only small amounts of vinyl and traces of isobutyl are seen, neither β -methyl transfer nor chain transfer to aluminum plays a leading role in the homopolymerisations. Hexene copolymerisation with **1** + **2** increases the amount of vinylidene end groups. This supports the finding of lower M_w with hexene indicating the tendency to β -H transfer reactions immediately after the incorporation of hexene monomer.

Table 4
Results of the ^{13}C NMR characterisation

	418	420	424	438	439	440	442	448
	1 + 2	1 + 2	1 + 2	1 + 3	1 + 3	1 + 3	1 + 3	1 + 3
	70 °C	50 °C	[hexene] = 140 mmol/l	70 °C	50 °C	[hexene] = 140 mmol/l	H ₂ = 5.0 mmol	C ₂ = 36 mmol
mrrm (%)	1.0	1.0	1.0	0.8	0.4	0.7	0.7	— ^a
rrrm (%)	0.2	0.2	0.1	0.0	0.3	0.0	0.1	— ^a
rrrr (%)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	— ^a
rmrm (%)	0.0	0.1	0.0	0.0	0.0	0.0	0.0	— ^a
mmrm + rmrr (%)	0.7	0.5	0.5	0.5	0.3	0.3	0.3	— ^a
mmrr (%)	2.6	2.5	2.6	1.9	1.2	1.6	0.0	— ^a
rmmr (%)	0.4	0.2	0.2	0.4	0.2	0.2	0.4	— ^a
mmmr (%)	2.9	3.4	3.5	3.0	0.1	2.5	2.6	— ^a
mmmm (%)	92.3	92.1	92.1	93.4	97.6	94.7	95.9	— ^a
2,1 Insertion (%)	0.5	0.5	0.5	0.2	0.3	0.2	0.2	0.1
2,1 E (%)								0.1
3,1 Insertion (%)	0.1	0.1	0.2	0.2	0.5	0.6	0.5	0.1
Total regioerror (%)	0.6	0.6	0.7	0.4	0.9	0.9	0.7	0.4
Hexene in polymer (mol%)			0.8			1.1		
Ethylene in polymer (mol%)								3.0

^a Unresolvable ethylene sequences in methyl region.

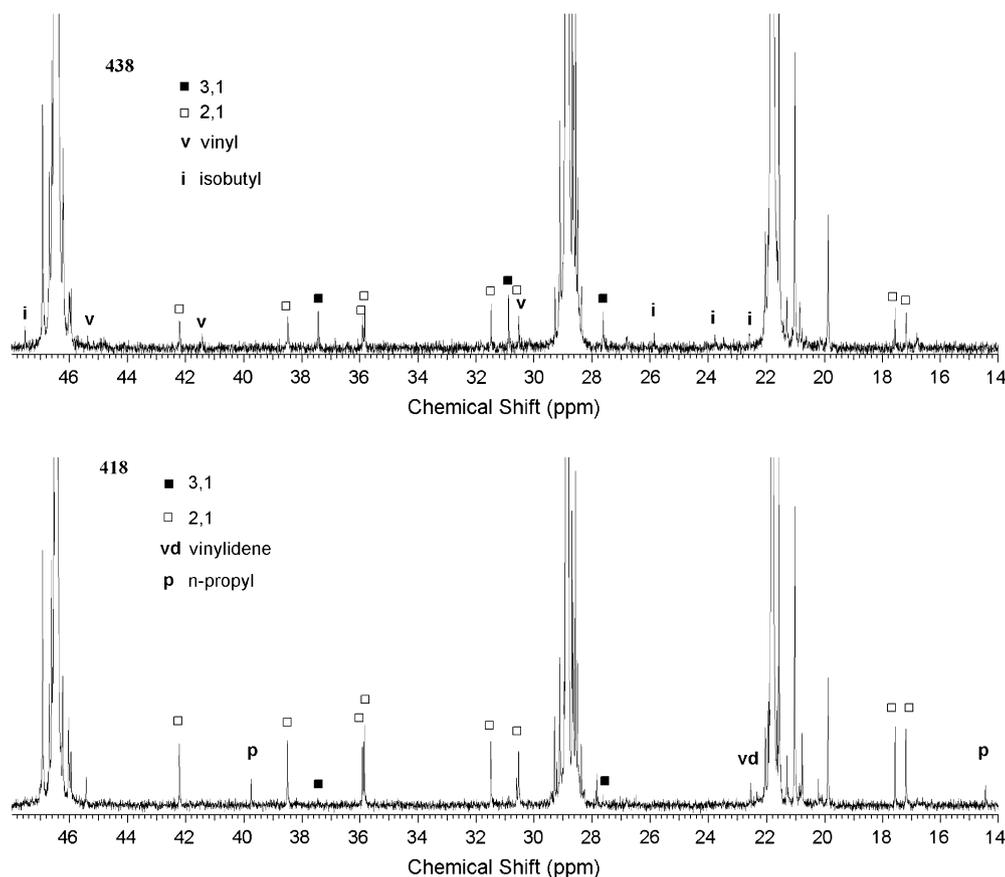


Fig. 6. ^{13}C NMR spectra of samples 438 and 418.

3.2. *rac*-Dimethylsilanylbis(2-methyl-4-phenyl-1-indenyl)zirconium dichloride/*rac*-dimethylsilanylbis-(2-isopropyl-4-[3,5-dimethylphenyl]indenyl)zirconium dichloride/MAO

3.2.1. Molecular weight

A typical GPC curve for the samples produced with the catalyst combination **1 + 3** is illustrated in Fig. 7. As reported in Table 2, catalyst combination **1 + 3** produces a polymer with higher M_w and narrower MWD than catalyst combination **1 + 2**. The lower polymerisation temperature increases M_w , whereas hydrogen and copolymerisation with hexene or ethylene have a negative effect.

The Schultz–Flory fractions and the sum of the fractions for sample 438 are presented in Fig. 7. As for the **1 + 2** catalyst system, the explanation for four Schultz–Flory fractions is the variations in the polymerisation conditions rather than interactions between the catalyst sites.

The M_w values and weight fractions of the Schultz–Flory fractions are summarised in Table 3 and Fig. 8.

The M_w dependency on the polymerisation conditions of the fractions F3 and F4 is comparable with the dependency of the F3 and F4 fractions produced with catalyst combination **1 + 2**. The result demonstrates that these fractions are produced by catalyst **1**, and that the fractions F1 and F2 are polymerised with catalyst **3**. The M_w response of the fraction F4 to polymerisation conditions is closely similar for the two

catalyst systems, but the combined M_w of the fractions F3 and F4 is slightly lower for catalyst combination **1 + 3** than catalyst combination **1 + 2**.

Ethylene–propylene copolymers were produced with catalyst combination **1 + 3** and, as can be seen (Table 3), ethylene has a considerable negative effect on the M_w of fraction F4. The effect on the M_w of fractions F1 and F2, in contrast, is negligible. We have previously reported [18] that increased

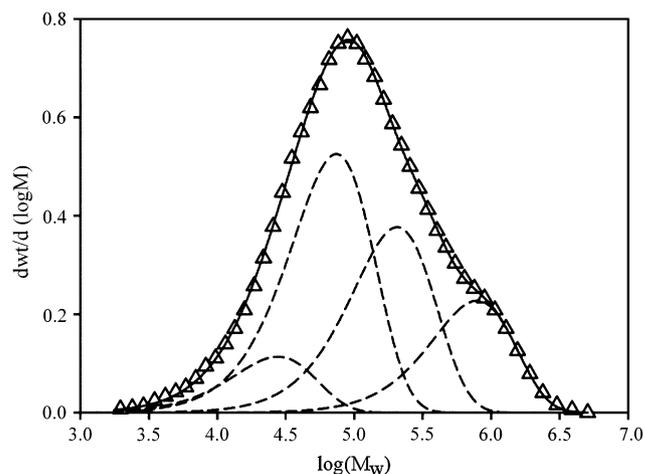


Fig. 7. GPC curve and Schultz–Flory fractions of sample 438 produced with catalyst combination **1 + 3** at 70 °C. (Δ): observed GPC data points, (---): Schultz–Flory fractions, (—): sum of Schultz–Flory fractions.

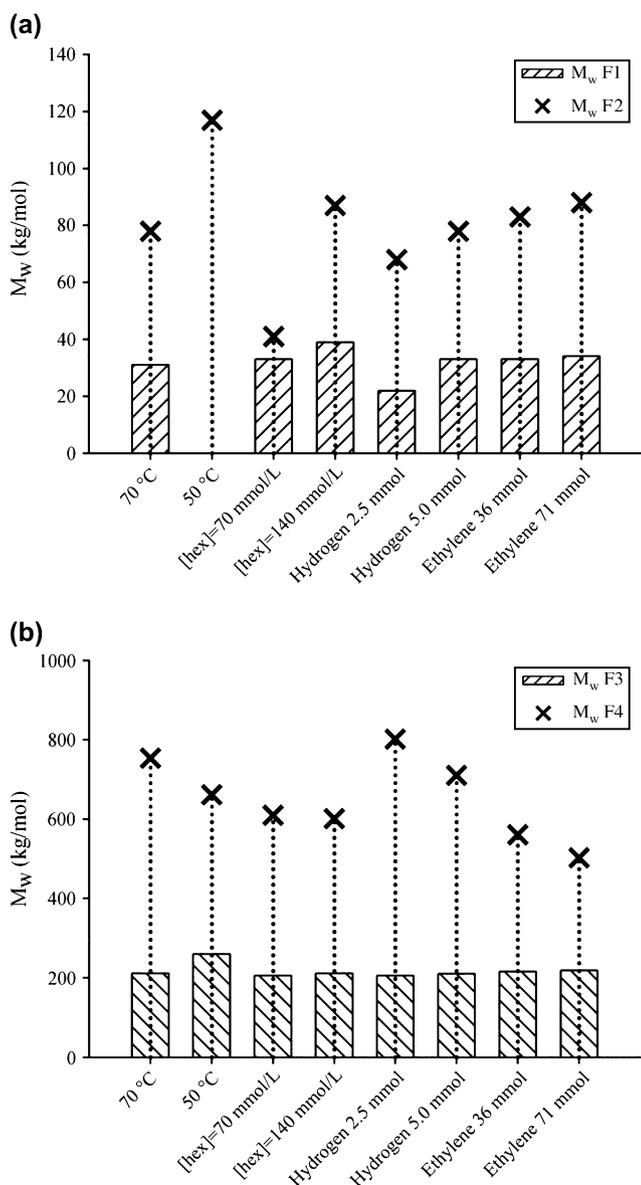


Fig. 8. M_w dependency of different fractions on polymerisation conditions with catalyst combination **1** + **3**. Low- M_w fractions (F1 and F2) (a), high- M_w fractions (F3 and F4) (b).

steric hindrance created by the bulky substituents of catalyst **3** blocks chain transfer to the ethylene monomer, whereas for the less sterically hindered catalyst precursor **1**, the chain transfer to the ethylene monomer is an important termination mechanism. Steric hindrance explains the observed differences in M_w in the ethylene–propylene copolymerisations. In the presence of ethylene, chain transfer to the ethylene monomer becomes an important termination mechanism for catalyst **1**, and M_w of fraction F4 decreases. Since this termination mechanism is blocked for catalyst **3**, the presence of ethylene monomer does not have a negative effect on the M_w .

3.2.2. Catalyst activity

The activity of the catalyst combination **1** + **3** is lower than that of catalyst combination **1** + **2** and varies from 0.24 to

1.95 kg_{PP}/g_{cat} h. Lower polymerisation temperature decreases the catalyst activity, whereas hydrogen and ethylene increase it.

Typically the polymer samples consist of 50% of low- M_w fraction and 50% of high- M_w fraction, which show similar activity response of catalysts **1** and **3** to the polymerisation conditions. When the ratio of the catalyst precursors in catalyst combination **1** + **3** is compared with the polymer fractions produced by catalysts **1** and **3** separately, it is clear that in the combined catalyst system the activity of **1** is considerably higher than the activity of **3**. Decrease in the polymerisation temperature to 50 °C has a negative effect on the activity of catalyst **3**, and decreases the amount of the low- M_w fraction in the sample. Some decrease in the relative activity of catalyst precursor **3** is also seen in the ethylene–propylene copolymerisation with the highest portion of ethylene. Catalyst **3** has similar hydrogen response to catalyst **1**, and both catalysts show substantially higher activity in the presence of hydrogen.

3.2.3. Thermal properties

A decrease in polymerisation temperature and addition of hydrogen increases melting point and heat of fusion value of the samples produced with **1** + **3** due to changes in polymer microstructure. As expected, copolymerisation of hexene or ethylene decreases the melting point and heat of fusion values because comonomer units in the polypropylene chain disturb the formation of polypropylene crystals.

The traces of melting of the samples produced with **1** + **3** after step crystallisation treatment are displayed in Fig. 9. Several melting peaks are observed, demonstrating that the samples produced with system **1** + **3** are less homogeneous than the samples produced with **1** + **2**. The highest melting points (164 and 168 °C) are observed for the sample polymerised at 50 °C (run 439), showing that the lower polymerisation temperature favours the formation of highly stereo- and regioregular fractions. The same trend is observed for the samples produced in the presence of hydrogen. The copolymerisation of hexene or ethylene, in turn, shifts the melting peaks to lower temperatures, which shows that both catalysts **1** and **3** copolymerise hexene and ethylene under the polymerisation conditions utilised.

3.2.4. ^{13}C NMR characterisation

Catalyst combination **1** + **3** produces slightly more stereoregular polypropylene than **1** + **2**, as is evident from the isotactic pentads (mmmm) (see Table 4). The same trend applies to the copolymerisations. Under the different polymerisation conditions in our previous study [18], catalyst **3** produced less isotactic polypropylene than catalyst **1**. The high isotacticity of the samples produced here shows that the stereospecificity of catalyst **3** is strongly dependent on polymerisation conditions such as monomer concentration. Lowering the polymerisation temperature from 70 to 50 °C increases the isotacticity of **1** + **3** consistent with the observed increases in the melting point and heat of fusion value. This increase in stereoregularity differs from the effect in samples polymerised with **1** + **2**, which do not show any difference in the tactic

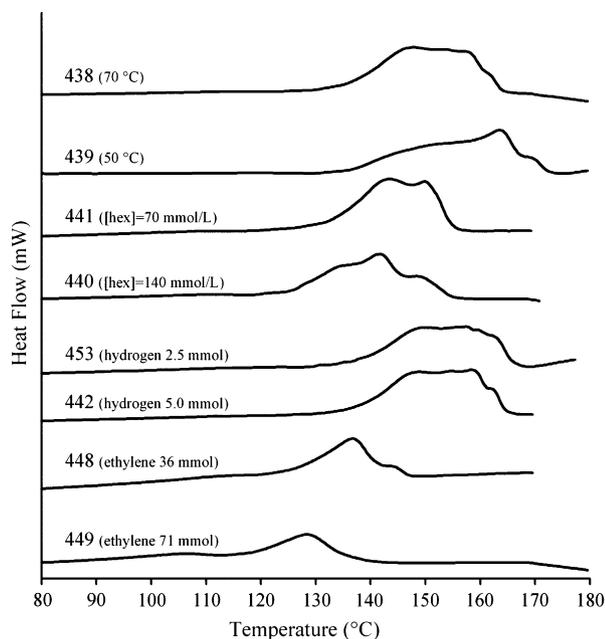


Fig. 9. Melting curves of samples produced with catalyst combination **1 + 3** after step crystallisation.

sequences at the two polymerisation temperatures. In contrast to **1 + 2**, where the regioerrors consist mostly of 2,1 misinsertions, 3,1 misinsertion is more typical for **1 + 3**, and the amount of 3,1 misinsertions is increased at the lower polymerisation temperature. With **1 + 3**, hydrogen marginally increases the stereoregularity, but simultaneously increases the amount of 3,1 misinsertions.

Catalyst combination **1 + 3** shows better comonomer response than catalyst combination **1 + 2**; the amount of hexene in the copolymer is greater at the same initial comonomer concentration. However, hexene increases the amount of regioerrors in copolymer produced with **1 + 3** mainly by facilitating 3,1 misinsertion. With ethylene, 2,1 misinsertions are located next to propylene and ethylene units in equal quantities. No stereoselectivity is calculated for the ethylene copolymer due to unresolvable ethylene sequences in methyl region. Ethylene reduces the amount of 3,1 misinsertions by incorporating into the polymer chain after 2,1 misinsertion faster than propylene and thus leaving less time for isomerization reactions.

At the higher polymerisation temperature (lower M_w), traces of vinyl and isobutyl end groups appear in homopolymers produced with **1 + 3** suggesting β -methyl transfer to Zr. In contrast to the hexene copolymerisations with **1 + 2**, no vinylidene end groups are observed in the hexene copolymers produced with **1 + 3**. This is due to the low portion of catalyst **1** in **1 + 3**; it is likely that hexene insertion into a growing polymer chain facilitates immediate β -hydrogen transfer in the case of catalyst **1**, but in the case of catalyst **3**, the inserted hexene monomer does not have a marked effect on the termination mechanisms. Hydrogen increases the amounts of isobutyl and *n*-propyl end groups due to the inherent chain transfer reactions to molecular hydrogen. In ethylene copolymerisation with **1 + 3**, *n*-propyl and vinylidene end groups disappear, and

isobutyl together with traces of vinyl remain. The observed end group pattern can be explained either by chain termination by β -hydrogen transfer after ethylene insertion followed by reinitiation with propylene monomer, or by β -methyl transfer reactions. Also chain transfer to aluminum cannot be ruled out as regards isobutyl. β -Methyl transfer was found in propylene-rich ethylene–propylene copolymerisations with catalyst **1** in our previous work [18].

4. Conclusions

Heterogeneous catalyst combinations **1 + 2** and **1 + 3** prepared by the new emulsion-based heterogenisation method behaved as efficient combination metallocene catalysts in propylene polymerisations in liquid monomer conditions.

Depending on the polymerisation conditions, M_w varied from 144 to 286 kg/mol for **1 + 2** and from 200 to 390 kg/mol for **1 + 3**. The combination **1 + 2** yielded bimodal MWD with clearly distinct low- and high- M_w polymer fractions. The MWD range was between 6.4 and 11.8, which was significantly broader than the MWD produced with **1 + 3**. Higher mmmm-pentad values and higher melting points indicated that **1 + 3** produces slightly more stereoregular polypropylene than does **1 + 2**. The main regioerror for **1 + 2** was the 2,1 misinsertion, whereas for **1 + 3** it was the 3,1 misinsertion. For **1 + 2** the amount of misinsertions was independent of temperature, whereas for **3 + 1** both the amount of 2,1 misinsertions, and particularly the amount of 3,1 misinsertions increased at lower polymerisation temperature. In the catalyst combination **1 + 2**, the activities of the individual catalysts were at the same level, but in the catalyst combination **1 + 3**, catalyst **1** showed markedly higher activity than catalyst **3**. Molecular hydrogen had a positive effect on the activity of all metallocene precursors, and an increase in activity was observed. It was demonstrated that both catalyst systems are capable of copolymerising hexene, and that the overall hexene response is slightly better for **1 + 3**. In the combined catalyst systems, each metallocene precursor showed an individual response towards polymerisation temperature, which was seen as differences in the activity level of metallocenes.

The copolymerisation of hexene had a strong negative effect on the M_w , especially on the polymer fractions produced with catalyst **1**. With catalyst combination **1 + 2**, the amount of vinylidene end groups was increased in the hexene copolymers, demonstrating that chain termination took place immediately after incorporation of hexene monomer into the growing polymer chain. In the absence of hexene, the leading termination mechanism for system **1 + 2** was β -hydrogen transfer to Zr or propylene monomer, and for system **1 + 3** β -methyl transfer to Zr.

In this study, it is likely that the combined metallocenes worked individually. We did not find any evidence of interactions between the active catalyst centres. Moreover, the responses to polymerisation conditions of the individual metallocenes in the combined systems followed the pattern observed earlier for the same catalyst used separately. It needs to be added, however, that the two metallocene systems

produced polypropylene with the same tacticity as the polypropylene produced with the individual catalysts, and detecting interaction in such a situation would be very difficult based on polymer properties such as microstructure.

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