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# Copolymerisation of 1,9-decadiene and propylene with binary and isolated metallocene systems

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## Abstract

1,9-Decadiene/propylene copolymers were obtained with isolated metallocenes and with a binary metallocene catalyst system activated by methylaluminoxane. The metallocenes under investigation were syndiospecific diphenylmethyl(cyclopentadienyl)(9-fluorenyl)zirconium dichloride (**1**) and isospecific *rac*-dimethylsilylbis(4-*tert*-butyl-2-methyl-cyclopentadienyl)zirconium dichloride (**2**). A copolymer structure, in which 1,9-decadiene linked isotactic and syndiotactic polymer chains, was obtained when copolymerisation was started with catalyst **2** at 80 °C followed by injection of catalyst **1** and instantaneous lowering of polymerisation temperature to 40 °C after 15 min of polymerisation. The copolymer was also shown to work as a compatibiliser in a blend of syndiotactic and isotactic polypropylene. We propose that catalyst **2** incorporates 1,9-decadiene into the isotactic main chain without any significant crosslinking within the first 15 min of polymerisation at 80 °C and the produced isotactic macromonomers are further incorporated at 40 °C into the syndiotactic main chain in polymerisation with catalyst **1**.

*Keywords:* Copolymer; Metallocene catalyst; Polypropylene

## 1. Introduction

Tailored polyolefin structures and properties, which cannot be produced with commercially widely used Ziegler–Natta-catalysts, can be synthesised with metallocene catalyst systems. Since the discovery of the metallocene catalyst family, research on metallocenes and their activation has been intensive, as reflected in several review articles [1–3].

Properties of metallocene-based polyolefins can greatly be affected by copolymerisation of different comonomers. Functional polyolefins have been produced by copolymerisation of comonomers containing different functional groups [4–7] and copolymerisation of longer α-olefins has been an efficient method for tailoring crystallinity and melting temperature [8,9].

Several groups have copolymerised non-conjugated dienes with ethylene and propylene [10–21]. The main focus of diene/propylene copolymerisation has been on introducing long-chain branched structures into the polymer in order to improve polypropylene processability [20,21]. Additionally, diene/propylene copolymers containing free double bonds have been used as intermediates to introduce functional groups, such as epoxy and maleic anhydride groups, into the polymer [12,17].

A diene monomer can be incorporated into a polymer main chain by cyclo- or linear addition. In cycloaddition, both the diene double bonds are incorporated into the same polymer main chain, forming cyclic structures, whereas in the linear addition, only one double bond is incorporated into a main chain, leaving the other double bond unreacted. The free double bond can further react during polymerisation, which causes long-chain branched structures and, eventually, polymer

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crosslinking. It has been reported that the amount of cyclic structures decreases with increasing length of diene chain [16,19] and that an increase in the polymerisation temperature decreases the tendency to form crosslinked structures [18].

Polyolefin structures and properties can be tailored by conducting polymerisation with two or more metallocene precursors simultaneously to produce a polyolefin mixture that consists of polymer fractions produced with different metallocenes individually. Several research groups have studied a mixture of metallocenes in propylene polymerisations, and polymerisation behaviour of homogeneous as well as heterogeneous catalyst systems has been investigated [22–27].

Recently, Arriola et al. [28] reported that a polyethylene block copolymer containing hard and soft segments was obtained with a mixture of two different catalysts when an efficient chain shuttling agent was present. In our previous work, we used a mixture of syndiospecific and isospecific catalysts in propylene polymerisations and demonstrated that trimethylaluminium worked as a chain shuttling agent, and a stereoblock-copolymer structure was formed due to the chain shuttling reactions between the active catalyst sites [27].

In the first part of the present work, 1,9-decadiene/propylene copolymerisations were conducted with isolated syndiospecific and isospecific metallocene precursors in order to understand 1,9-decadiene/propylene copolymerisation mechanisms of the studied metallocenes. In the second part, copolymerisations were carried out with a binary catalyst system. The goal was to synthesise a novel 1,9-decadiene/propylene copolymer structure, in which 1,9-decadiene links syndiotactic and isotactic polymer chains. The copolymer was tested as a compatibiliser in a blend of syndiotactic and isotactic polypropylenes.

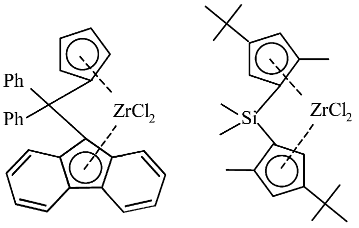
## 2. Experimental

### 2.1. Materials

Catalyst precursors diphenylmethyl(cyclopentadienyl)(9-fluorenyl)zirconium dichloride (**1**) and *rac*-dimethylsilylbis(4-*tert*-butyl-2-methyl-cyclopentadienyl)zirconium dichloride (**2**) from Boulder Scientific Co., 10 wt% methylaluminoxane (MAO) in toluene from Crompton Corp., nitrogen (99.999%) from AGA, and propylene (polymerisation grade) from Borealis were all used as received. Chemical structures of the catalyst precursors are depicted in Fig. 1. 1,9-Decadiene (96%) from Sigma–Aldrich was dried with molecular sieves. Toluene (p.a.) from Labscan Ltd. was refluxed over sodium/benzophenone and distilled under nitrogen atmosphere before use. Standard Schlenk and glovebox techniques were used for all manipulations.

### 2.2. Polymerisation procedure

All polymerisations were carried out in a 0.5 $dm^3$ stainless steel autoclave. The polymerisation medium (toluene, 200 mL) was fed into the evacuated and propylene purged reactor, after which MAO solution was fed. The reactor was pressurised with propylene to 4.0 bar total pressure, followed by addition of the desired amount of 1,9-decadiene. The polymerisation was started by injecting a toluene solution of the catalyst precursor. The solution was stirred at 2000 rpm to minimise gas/liquid transport limitations. The total pressure was held constant during the reaction and the instantaneous consumption of propylene was measured. The reaction was stopped by closing the propylene feed and the reaction mixture was poured into a solution of hydrochloric acid in methanol. The polymer product was washed, first with HCl/methanol solution and then with methanol, after which the polymer was filtered and dried in open air. The propylene concentration in toluene was estimated using an empirical model and parameters reported by Dariva et al. [29].



**1** **2**

Fig. 1. Structures of the catalyst precursors diphenylmethyl(cyclopentadienyl)(9-fluorenyl)zirconium dichloride (**1**) and *rac*-dimethylsilylbis(4-*tert*-butyl-2-methyl-cyclopentadienyl)zirconium dichloride (**2**).

For the isolated catalyst systems, the polymerisation time was 15 or 30 min and the polymerisation temperature was 40 or 80 °C. The catalyst concentration varied from 5.0 to 10.0 $\mu mol\,L^{-1}$ for catalyst **1** and from 10.0 to 15.0 $\mu mol\,L^{-1}$ for catalyst **2**. The Al/Zr ratio was kept constant at 2500 and the total aluminium concentration was between 12.5 and 37.5 $mmol\,L^{-1}$. The copolymerisations were carried out with 1,9-decadiene concentrations of 13.6 and 27.3 $mmol\,L^{-1}$.

With the binary catalyst system, the polymerisations were started by injecting the first catalyst precursor into the reactor, followed by the second catalyst precursor after 15 min of polymerisation time. The polymerisation time was 30 or 45 min and the polymerisation temperature was 40 or 80 °C. Runs 25–30 were started at 80 °C, and after 15 min the temperature was instantaneously lowered to 40 °C and the second catalyst was injected. The temperature was changed by switching between two separate heating media. The temperature change caused a decrease in the polymerisation pressure due to the changed solubility of propylene. The pressure decreased from 4.0 down to $\approx 2$ bar, and the 4.0 bar polymerisation pressure was achieved again approximately 13 min after the temperature change. The total catalyst concentration varied from 11.5 to 22.5 $\mu mol\,L^{-1}$ and the aluminium concentration was between 18.8 and 37.5 $mmol\,L^{-1}$. The copolymerisations were conducted with an 1,9-decadiene concentration of 27.3 $mmol\,L^{-1}$.

### 2.3. Blends

Polypropylene blends consisting of 50 wt% of syndiotactic polypropylene and 50 wt% of isotactic polypropylene were prepared by codissolving the blend components in hot mesitylene (bp 164.7 °C) under nitrogen atmosphere over a period of 30–60 min. 1 wt% of 2,6-di-*tert*-butyl-4-methylphenol (BHT) was added as an antioxidant. The blend was precipitated by pouring the solution into an excess of methanol. The product was washed with methanol, after which it was filtered and dried in open air.

### 2.4. Characterisation methods

Molecular weights ($M_n$, $M_w$, $M_z$ and $M_{z+1}$) and molecular weight distributions (MWD) were determined at 145 °C by gel permeation chromatography (GPC) with a Polymer Laboratories PL-210 GPC instrument equipped with four PLgel 20 μm MIXED-A LS columns, an RI detector, a viscometer and a light scattering detector. 1,2,4-Trichlorobenzene (TCB) stabilised with 0.125 wt% BHT was used as solvent at a flow rate of 1.0 cm$^3$ min$^{-1}$. The polymer was dissolved in TCB stabilised with 0.125 wt% BHT and the sample concentration was between 0.5 and 2.7 mg mL$^{-1}$. The instrument was calibrated against narrow polystyrene samples. Light scattering data were used to characterise the samples.

Melting temperature ($T_m$), crystallisation temperature ($T_c$) and enthalpy of crystallisation ($\Delta H_c$) were determined by differential scanning calorimetry (DSC) with a Perkin–Elmer 7 series thermal analyser. The samples (10 ± 1 mg of polymer) were heated from 25 to 180 °C (heating rate 50 °C min$^{-1}$), held at 180 °C for 3 min, cooled to 20 °C (cooling rate 10 °C min$^{-1}$), held at 20 °C for 3 min, heated to 180 °C (heating rate 10 °C min$^{-1}$) and finally cooled back to 25 °C (cooling rate 10 °C min$^{-1}$). The $T_c$ and $\Delta H_c$ values were measured during the first cooling period and the $T_m$ was measured during the second heating period.

The $^{13}$C NMR measurements were performed using a Bruker Avance 300 MHz spectrometer operating at 75 MHz. The sample temperature was 90 °C. The samples were dissolved in a mixture of deuterated benzene ($C_6D_6$) and TCB (weight ratio 10/90) in 5 mm sample tubes. The acquisition time was 1.9 s, the acquisition delay was 6.0 s and the number of transients was 5000 or greater. The pulse angle was 60°. Continuous proton decoupling was used to employ the Nuclear Overhauser Effect (NOE). Processing of the NMR spectra was performed with ACD Labs ACD/SpecManager software. A peak fitting procedure was used due to the overlapping peaks and the fitted peak areas were used in calculations.

Test specimens for tensile testing were injection moulded by using a mini-injection moulding machine (DSM). The barrel temperature was 190 °C and the mould temperature was 40 °C. Before injection moulding, polymer was melted in the barrel at 190 °C for 7 min. To avoid degradation, polymer for each test specimen was melted separately. The tensile tests were conducted with an Instron 4204 universal testing machine according to standard ISO 527-1993(E) using specimen type 1BA. The test speed was 1 mm min$^{-1}$ during the first 20% of the elongation (modulus, yield strain and yield strength), after which the test speed was increased to 10 mm min$^{-1}$ (tensile strain). Before tensile testing, the samples were conditioned at 23 °C and 50% relative humidity for 3–5 days.

## 3. Results and discussion

### 3.1. 1,9-Decadiene copolymerisations with isolated catalysts

1,9-Decadiene copolymerisations with catalysts **1** and **2** were conducted at 40 and 80 °C accompanied with different 1,9-decadiene concentrations and polymerisation times. Polymerisation conditions and catalyst activities are summarised in Table 1 and the characterisation results of the polymer samples are presented in Tables 2 and 3.

Table 1 shows that both the catalysts have higher activity at 80 °C than at 40 °C and that the presence of 1,9-decadiene has no marked effect on the catalyst activity.

Table 1
Polymerisation conditions and activities for catalysts **1** and **2**

| Run | Catalyst | $T$, °C | [Propylene], mol L$^{-1}$ | [Cat **1**], μmol L$^{-1}$ | [Cat **2**], μmol L$^{-1}$ | [Al], mmol L$^{-1}$ | [Diene], mmol L$^{-1}$ | Time, min | Activity, kg$_{PP}$ mol$_{Zr}^{-1}$ h$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|
| 1 | **1** | 40 | 1.91 | 7.5 | – | 18.8 | 0.0 | 30 | 4600 |
| 2 | **1** | 40 | 1.91 | 10.0 | – | 25.0 | 13.6 | 15 | 4800 |
| 3 | **1** | 40 | 1.91 | 10.0 | – | 25.0 | 27.3 | 15 | 4800 |
| 4 | **1** | 40 | 1.91 | 7.5 | – | 18.8 | 27.3 | 30 | 3300 |
| 5 | **1** | 80 | 1.76 | 7.5 | – | 18.8 | 0.0 | 15 | 17,000 |
| 6 | **1** | 80 | 1.76 | 7.5 | – | 18.8 | 13.6 | 15 | 20,000 |
| 7 | **1** | 80 | 1.76 | 7.5 | – | 18.8 | 27.3 | 15 | 17,000 |
| 8 | **1** | 80 | 1.76 | 5.0 | – | 12.5 | 27.3 | 30 | 11,000 |
| 9 | **2** | 40 | 1.91 | – | 15.0 | 37.5 | 0.0 | 30 | 2700 |
| 10 | **2** | 40 | 1.91 | – | 15.0 | 37.5 | 13.6 | 15 | 3300 |
| 11 | **2** | 40 | 1.91 | – | 15.0 | 37.5 | 27.3 | 15 | 4400 |
| 12 | **2** | 40 | 1.91 | – | 15.0 | 37.5 | 27.3 | 30 | 4100 |
| 13 | **2** | 80 | 1.76 | – | 15.0 | 37.5 | 0.0 | 15 | 7200 |
| 14 | **2** | 80 | 1.76 | – | 15.0 | 37.5 | 13.6 | 15 | 5800 |
| 15 | **2** | 80 | 1.76 | – | 15.0 | 37.5 | 27.3 | 15 | 6500 |
| 16 | **2** | 80 | 1.76 | – | 10.0 | 25.0 | 27.3 | 30 | 3800 |

Table 2
Results of characterisation of samples produced with catalyst **1**

| Run | $T$, °C | [Diene], mmol $L^{-1}$ | Time, min | $M_n$,[a] kg $mol^{-1}$ | $M_w$,[a] kg $mol^{-1}$ | $M_z$,[a] kg $mol^{-1}$ | $M_{z+1}$,[a] kg $mol^{-1}$ | MWD[a] | $T_m$,[b] °C | $T_c$,[b] °C | $\Delta H_c$,[b] J $g^{-1}$ | rrrr pentad,[c] % | Diene,[c] mol% |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 40 | 0.0 | 30 | 187 | 284 | 382 | 479 | 1.5 | 132.0/140.5 | 80.5 | −37 | 86.5 | – |
| 2 | 40 | 13.6 | 15 | 226 | 380 | 603 | 1026 | 1.7 | 125.5/133.7 | 71.6 | −35 | 83.8 | Traces |
| 3 | 40 | 27.3 | 15 | 204 | 522 | 1023 | 1708 | 2.6 | 119.5/126.9 | 60.0 | −34 | 83.6 | 0.66 |
| 4 | 40 | 27.3 | 30 | 234 | 666 | 1316 | 2049 | 2.9 | 116.0/120.9 | 57.1 | −29 | 83.2 | 0.68 |
| 5 | 80 | 0.0 | 15 | 51 | 80 | 108 | 135 | 1.6 | – | – | – | 61.0 | – |
| 6 | 80 | 13.6 | 15 | 50 | 181 | 474 | 1065 | 3.6 | – | – | – | 59.1 | Traces |
| 7 | 80 | 27.3 | 15 | 56 | 523 | 2327 | 4934 | 9.4 | – | – | – | 58.6 | 0.98 |
| 8 | 80 | 27.3 | 30 | 60 | 566 | 2266 | 4591 | 9.6 | – | – | – | 58.7 | 0.83 |

[a] By GPC.
[b] By DSC.
[c] By $^{13}C$ NMR.

Table 3
Results of characterisation of samples produced with catalyst **2**

| Run | $T$, °C | [Diene], mmol $L^{-1}$ | Time, min | $M_n$,[a] kg $mol^{-1}$ | $M_w$,[a] kg $mol^{-1}$ | $M_z$,[a] kg $mol^{-1}$ | $M_{z+1}$,[a] kg $mol^{-1}$ | MWD[a] | $T_m$,[b] °C | $T_c$,[b] °C | $\Delta H_c$,[b] J $g^{-1}$ | mmmm pentad,[c] % | Diene,[c] mol% |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 9 | 40 | 0.0 | 30 | 16 | 24 | 32 | 40 | 1.5 | 150.5 | 109.1 | −114 | 96.3 | – |
| 10 | 40 | 13.6 | 15 | 16 | 32 | 53 | 77 | 2.0 | 143.4 | 105.6 | −102 | 96.8 | Traces |
| 11 | 40 | 27.3 | 15 | 13 | 36 | 71 | 135 | 2.6 | 139.4 | 100.8 | −94 | 96.7 | 0.52 |
| 12 | 40 | 27.3 | 30 | 14 | 40 | 85 | 169 | 2.8 | 140.9 | 103.5 | −95 | 95.7 | 0.36 |
| 13 | 80 | 0.0 | 15 | – | <2 | – | – | – | – | – | – | 93.1 | – |
| 14 | 80 | 13.6 | 15 | – | <2 | – | – | – | – | – | – | 91.7 | 0.24 |
| 15 | 80 | 27.3 | 15 | – | <2 | – | – | – | – | – | – | 92.9 | 0.68 |
| 16 | 80 | 27.3 | 30 | – | <2 | – | – | – | – | – | – | 91.2 | 0.86 |

[a] By GPC.
[b] By DSC.
[c] By $^{13}C$ NMR.

### *3.1.1. Molecular weight*

The MWD curves of the samples produced with catalyst **1** are illustrated in Fig. 2(a) and (b). The $M_n$, $M_w$, $M_z$ and $M_{z+1}$ values are compared in Fig. 3(a) and (b). At 40 °C, copolymerisation of 1,9-decadiene increases the $M_w$ from 284 to 666 kg $mol^{-1}$ and the MWD value from 1.5 to 2.9 (Table 2). At 80 °C, the increase in the values is even more pronounced, and the $M_w$ increases from 80 to 566 kg $mol^{-1}$ and the MWD from 1.6 to 9.6. A very strong increase can be seen in the $M_z$ and $M_{z+1}$ values, which are sensitive to the high molecular weight fraction of a polymer, whereas the $M_n$ value is not affected. This is characteristic when long-chain branched structures are formed.

The MWD curves of the samples produced with catalyst **2** at 40 °C are illustrated in Fig. 2(c). The $M_n$, $M_w$, $M_z$ and $M_{z+1}$ values are compared in Fig. 3(c). The RI detector responses of the samples polymerised at 80 °C are shown in Fig. 2(d). The $M_w$ of the samples obtained with catalyst **2** at 80 °C is not discussed further, because propylene polymerisation with catalyst **2** at 80 °C yields very low $M_w$ polymer ($M_w < 2$ kg $mol^{-1}$) and the $M_w$ values cannot be determined reliably by GPC [30].

At 40 °C, copolymerisation of 1,9-decadiene increases the $M_w$ from 24 to 40 kg $mol^{-1}$ while the MWD increases from 1.5 to 2.8 (Table 3). The $M_n$ value remains unchanged, but an increase in the $M_z$ and $M_{z+1}$ values is observed. The RI detector responses of the samples produced with catalyst **2** at 80 °C (Fig. 1(d)) do not show marked crosslinking.

In sum, the GPC results show that catalyst **1** efficiently copolymerises 1,9-decadiene with propylene, which is followed by the formation of long-chain branched structures, especially at 80 °C. Catalyst **2** is capable of copolymerising 1,9-decadiene with propylene followed by the formation of branched structures at 40 °C. Unlike catalyst **1**, catalyst **2** does not seem to have a strong tendency to induce long-chain branching at 80 °C.

### *3.1.2. Thermal properties*

The samples produced with catalyst **1** at 40 °C show two melting peaks (Table 2). The lower temperature melting peak is related to melting of the primary crystals, whereas the higher temperature melting peak is caused by melting of crystallites recrystallised during the heating period [31]. The melting and crystallisation temperatures of the copolymers are markedly lower compared with the values determined for the homopolymer. The melting behaviour of the samples produced at 80 °C was not analysed since we have previously observed that propylene polymerisation with catalyst **1** at 80 °C yields amorphous material [30]. Incorporation of 1,9-decadiene decreases the melting and crystallisation temperatures of the samples produced with catalyst **2** at 40 °C accompanied with a decrease in the enthalpy of crystallisation value (Table 3). The low $M_w$ of the samples obtained with catalyst **2** at 80 °C dominates the melting behaviour, and the melting behaviour of these samples was not analysed.

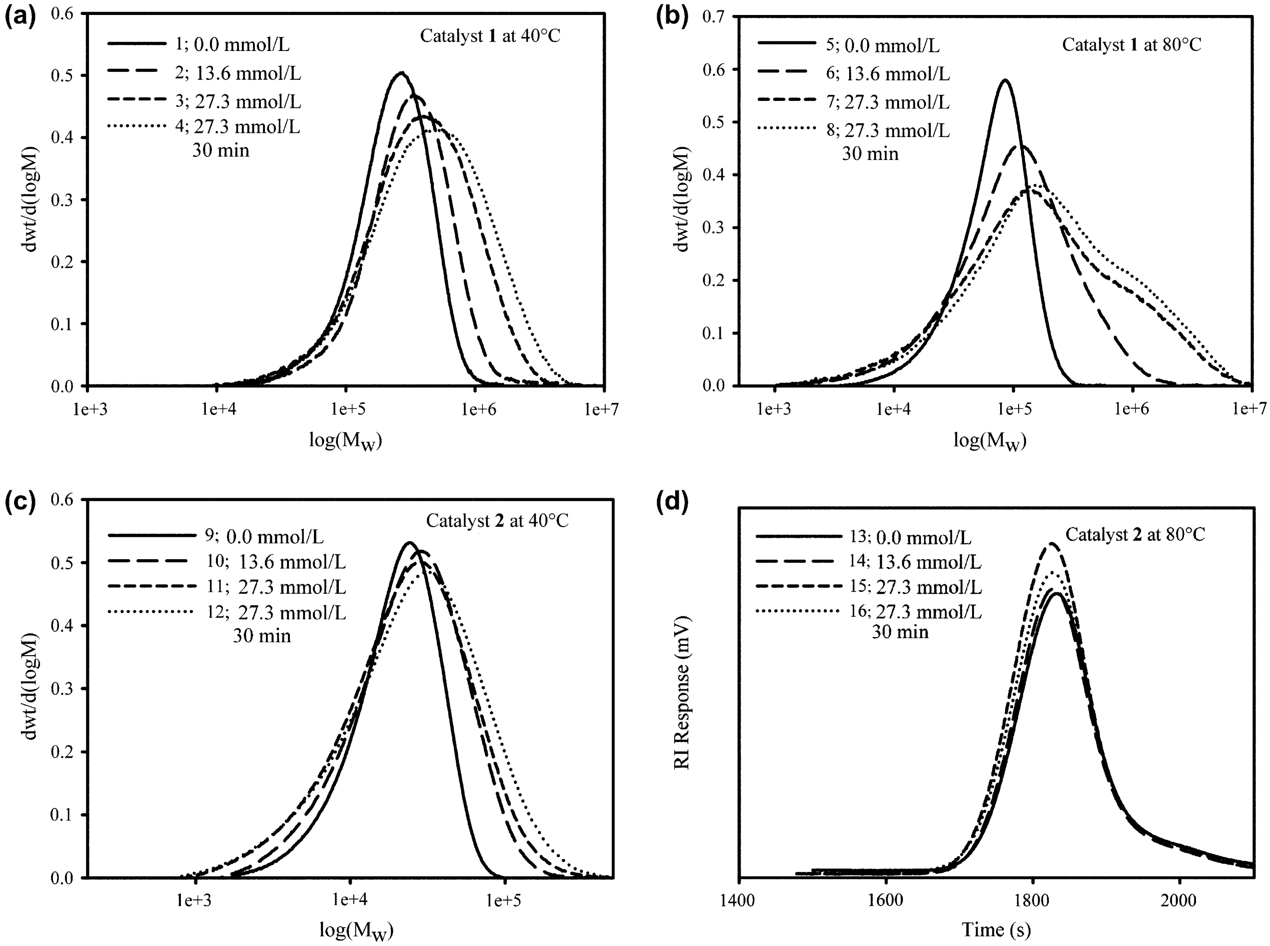


Fig. 2. MWD of samples produced with catalyst **1** at 40 °C (a), at 80 °C (b) and catalyst **2** at 40 °C (c). RI detector response for samples produced with catalyst **2** at 80 °C (d).

### 3.1.3. $^{13}$C NMR characterisation

To investigate the effect of 1,9-decadiene incorporation on termination reactions, the end groups of the samples obtained with catalyst **2** were analysed by $^{13}$C NMR. The end groups of the samples produced with catalyst **1** were not visible in the $^{13}$C NMR spectra. The result of the end group analysis is summarised in Table 4. As expected, based on our previous work [30], *n*-propyl and vinylidene end groups caused by β-H transfer to Zr and isobutyl end groups caused by chain transfer to aluminium were detected. It is evident that the same termination mechanisms were operative in both homo- and copolymerisations and that higher polymerisation temperature favoured termination by β-H transfer to Zr.

The copolymers obtained with catalyst **1** have lower rrrr pentad values than the homopolymers (Table 2), while the mmmm pentad values of the copolymers produced with catalyst **2** are not markedly affected (Table 3). Naga et al. [19] reported that the insertion of a propylene monomer was less enantioselective after the formation of cyclic structures in 1,5-hexadiene copolymerisations with catalyst **1**, but in the case of an isospecific metallocene, the enantioselectivity of the catalyst was not affected. This agrees well with our results. In our case, it is possible that the inserted 1,9-decadiene unit has a similar effect as the cyclic structure on the stereoregularity of catalyst **1**, causing the decrease in the rrrr pentad values, but it is not clear why syndiospecific and isospecific metallocenes behave differently.

Copolymer structures **I**–**IV** shown in Fig. 4 can be produced with the isolated catalysts **1** and **2**. Fig. 5 presents typical $^{13}$C NMR spectra of the copolymers and Table 5 summarises the characteristic chemical shifts. Previously reported $^{13}$C NMR data for 1,9-decadiene/propylene and 1-decene/propylene copolymers were used to identify the detected peaks [8,20,21]. $^{13}$C NMR analysis was used to quantitatively measure the comonomer content in the copolymers. An average of intensities of the carbons $d_2$–$d_4$ and $d_6$–$d_{10}$ relative to 1/3 intensity of all peaks was used to calculate the comonomer incorporation as mol%. The level of crosslinking in our case was too low to be observed by $^{13}$C NMR. As expected, cyclic structures were not detected, and it is clear that linear addition of 1,9-decadiene is dominant as reported by Paavola et al. [20].

At the diene concentration of 13.6 mmol $L^{-1}$, only trace amounts of the incorporated 1,9-decadiene were observed in the $^{13}$C NMR spectra of the copolymers produced with catalyst **1**. At the diene concentration of 27.3 mmol $L^{-1}$, the

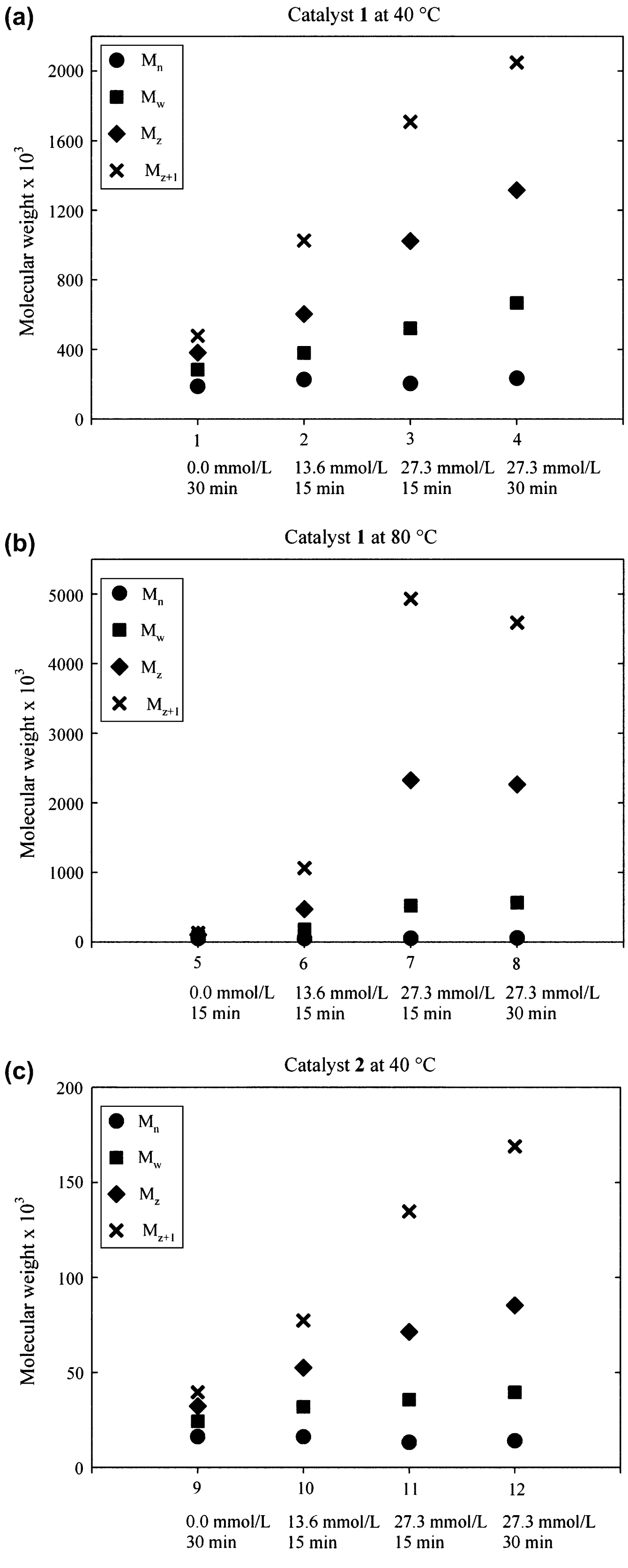


Fig. 3. $M_n$, $M_w$, $M_z$ and $M_{z+1}$ dependency on diene concentration and polymerisation time. Catalyst **1** at 40 °C (a), at 80 °C (b) and catalyst **2** at 40 °C (c).

amount of 1,9-decadiene in the copolymers varies from 0.66 to 0.68 mol% at 40 °C and from 0.83 to 0.98 mol% at 80 °C (Table 2). Catalyst **2** shows slightly weaker 1,9-decadiene response than catalyst **1** and the amount of 1,9-decadiene in the copolymers varies from a trace amount to 0.52 mol% at 40 °C and from 0.24 to 0.86 mol% at 80 °C (Table 3). Both catalysts show better 1,9-decadiene response at 80 °C than at 40 °C. Longer polymerisation times do not have a marked effect on the 1,9-decadiene amount in the copolymers.

### 3.2. 1,9-Decadiene copolymerisations with the binary catalyst system

Polymerisations were conducted with the binary catalyst system at different polymerisation temperatures and times in order to synthesise a polypropylene structure in which 1,9-decadiene links syndiotactic and isotactic polymer chains (structure **V** in Fig. 4). A diene concentration of 27.3 mmol $L^{-1}$ was chosen to be used in the copolymerisations. To produce a copolymer with a high amount of unreacted double bonds, polymerisation was started at 80 °C with catalyst **2**. Since catalyst **1** has a strong tendency to form long-chain branched polypropylene, catalyst **1** was injected after 15 min of polymerisation time in order to incorporate the isotactic macromonomers produced with catalyst **2** into the syndiotactic main chain. To minimise the amount of the very low $M_w$ polymer produced with catalyst **2** at 80 °C and to produce highly syndiotactic polypropylene with catalyst **1**, polymerisation temperature was lowered to 40 °C instantaneously at the injection of catalyst **1**. As control experiments, polymerisations with different catalyst injection orders and polymerisation temperatures were carried out.

The polymerisation reactions are summarised in Table 6 and the results of the characterisation of the samples are presented in Table 7. Runs 25–30 were started at 80 °C and the temperature was lowered to 40 °C after 15 min of polymerisation.

### 3.2.1. Catalyst activity

Table 6 shows that the activities of the catalysts in the copolymerisations are comparable with the activities in the homopolymerisations. This agrees well with the activity trends observed for the isolated catalysts and it can be concluded that the low 1,9-decadiene concentrations used in this work only have a moderate effect on the catalyst activities.

### 3.2.2. Molecular weight

Table 7 summarises the molecular weights and MWD of the samples obtained with the binary catalyst system. The GPC curves for the homo- and copolymers are illustrated in Fig. 6. Due to the very low $M_w$ of the polymer fraction produced with catalyst **2** at 80 °C, only the high $M_w$ fraction of samples 28 and 30 is shown in Fig. 6(d). Fig. 6(e) illustrates the RI detector responses of these samples including the low $M_w$ fraction produced with catalyst **2**.

The marked $M_w$ peak maxima of the homopolymers are in good accordance with the observed $M_w$ peak maxima of the homopolymers produced with the isolated catalyst systems

Table 4
End group intensities for polymers produced with catalyst **2** at 40 and 80 °C[a]

| Run | $T$, °C | [Diene], mmol $L^{-1}$ | Time, min | $n$-Propyl intensity, % | Vinylidene intensity, % | Isobutyl intensity, % | β-H transfer to Zr/Chain transfer to Al |
|---|---|---|---|---|---|---|---|
| 9 | 40 | 0.0 | 30 | n.d. | n.d. | n.d. | – |
| 10 | 40 | 13.6 | 15 | 0.1 | 0.2 | 0.2 | 0.7 |
| 11 | 40 | 27.3 | 15 | 0.1 | 0.2 | 0.1 | 1.4 |
| 12 | 40 | 27.3 | 30 | 0.1 | 0.1 | 0.1 | 0.7 |
| 13 | 80 | 0.0 | 15 | 0.8 | 0.7 | 0.3 | 2.4 |
| 14 | 80 | 13.6 | 15 | 0.8 | 0.8 | 0.4 | 2.1 |
| 15 | 80 | 27.3 | 15 | 0.8 | 0.7 | 0.3 | 2.3 |
| 16 | 80 | 27.3 | 30 | 0.8 | 0.8 | 0.3 | 3.0 |

[a] By $^{13}C$ NMR.

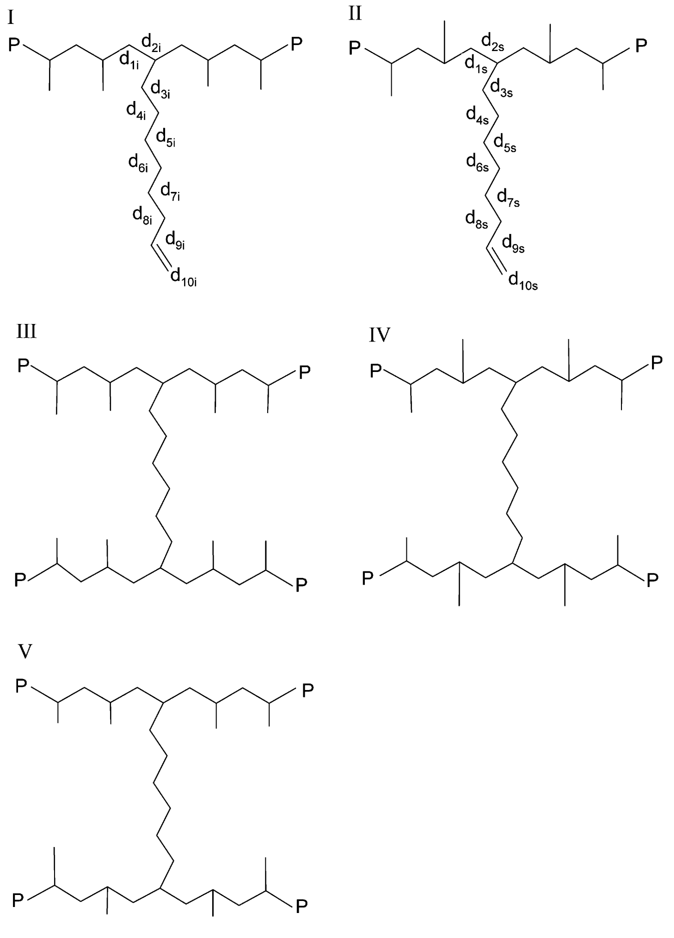


Fig. 4. Synthesised 1,9-decadiene/propylene copolymer structures.

(Fig. 6). The $M_w$ of the homopolymers varies between 37 and 328 kg $mol^{-1}$ and MWD varies from 3.2 to 12.3 (Table 7). Some added uncertainty is contained in these values when a polymer sample contains a very low $M_w$ fraction produced with catalyst **2** at 80 °C.

The copolymers have consistently higher $M_w$ and MWD values than their homopolymer counterparts. The $M_w$ of the copolymers varies between 72 and 917 kg $mol^{-1}$ and MWD values between 5.6 and 25.1 (Table 7). All copolymers obtained with the binary catalyst system show a significant increase in the MWD, $M_z$ and $M_{z+1}$ values, which is typical when long-chain branched structures are formed.

When the GPC curves of the homo- and copolymers are compared (Fig. 6), it can be seen that the high $M_w$ peak maxima of the copolymers are shifted to higher $M_w$ values compared with the homopolymer counterparts, whereas the low $M_w$ peak maxima are not strongly affected. This demonstrates that the increase in the molecular weight values and the broader MWD of the copolymers are mainly related to long-chain branched structures produced with catalyst **1**. Catalyst **2** shows a rather low tendency towards the formation of branched structures in the binary system since the low $M_w$ peak maxima were not affected. Sample 30 shows the most evident formation of long-chain branches. This is seen in the GPC curve and the RI detector response shown in Fig. 6(d) and (e), as well as in the $M_z$ and $M_{z+1}$ values.

Based on the GPC data alone it is not possible to discriminate between polymer structures **III**, **IV** and **V** presented in Fig. 4. However, especially in the case of sample 30, it is likely that 1,9-decadiene links syndiotactic and isotactic chains. Plausibly, catalyst **2** produces isotactic macromonomers at the beginning of the polymerisation at 80 °C, which are incorporated into the syndiotactic main chain in polymerisation with catalyst **1** at 40 °C, and structure **V** is formed.

### 3.2.3. Thermal properties

The melting temperatures, crystallisation temperatures and enthalpy of crystallisation values of the samples produced with the binary catalyst system are summarised in Table 7. In this case, the thermal properties of the copolymers are simultaneously affected by several factors: (i) ratio of syndio- and isotactic polypropylenes, (ii) 1,9-decadiene incorporation, (iii) formation of long-chain branched structures and (iv) formation of stereoblock copolymer caused by chain shuttling. These factors cause partly overlapping changes in the melting behaviour, thus hampering a meaningful detailed comparison of the thermal properties. As a general trend it is seen that the incorporation of 1,9-decadiene decreases the melting temperature, crystallisation temperature and enthalpy of crystallisation values, as expected. Additionally, homopolymers (samples 17 and 21) show a shoulder at 145.4 °C, which arises most likely from the stereoblock-copolymer structure formed by trimethylaluminium-assisted chain shuttling reactions in the binary catalyst system [27].

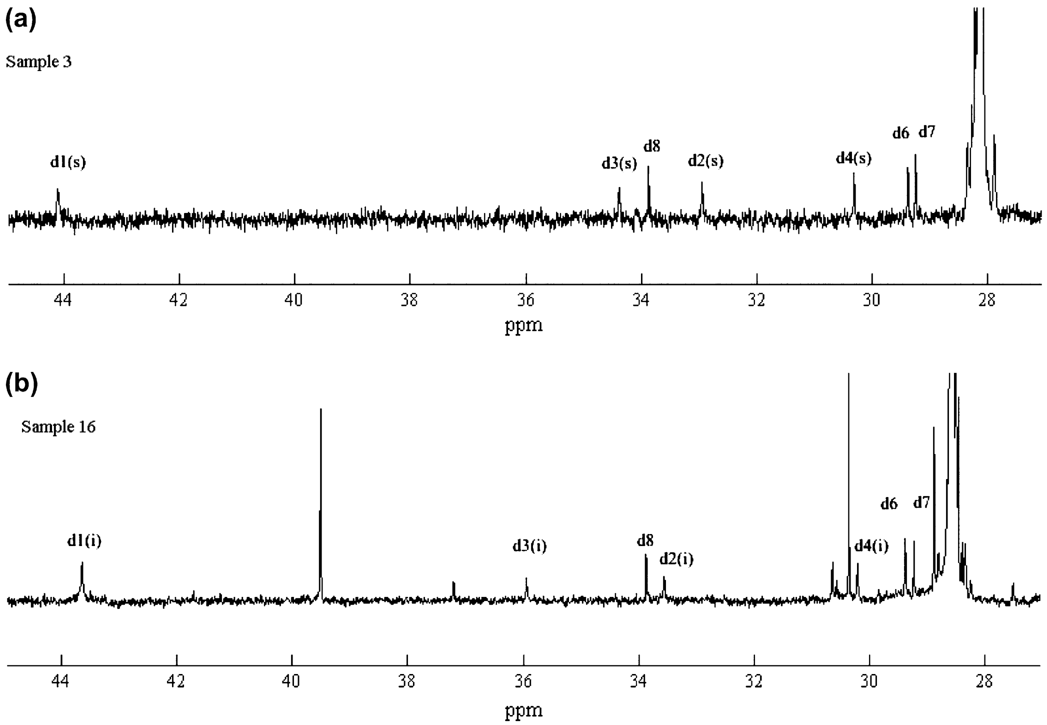


Fig. 5. $^{13}$C NMR spectra of samples 3 and 16.

Table 5
Identified characteristic chemical shifts for 1,9-decadiene/propylene copolymers

| Isotactic main chain | | Syndiotactic main chain | |
|---|---|---|---|
| Carbon | Chemical shift, ppm | Carbon | Chemical shift, ppm |
| $d_{1i}$ | 43.7 | $d_{1s}$ | 44.2 |
| $d_{2i}$ | 33.6 | $d_{2s}$ | 33.0 |
| $d_{3i}$ | 36.0 | $d_{3s}$ | 34.5 |
| $d_{4i}$ | 30.3 | $d_{4s}$ | 30.4 |
| $d_{5i}$ | n.d.[a] | $d_{5s}$ | n.d.[a] |
| $d_{6i}$ | 29.5 | $d_{6s}$ | 29.5 |
| $d_{7i}$ | 29.3 | $d_{7s}$ | 29.3 |
| $d_{8i}$ | 34.0 | $d_{8s}$ | 34.0 |
| $d_{9i}$ | 139.0 | $d_{9s}$ | 139.0 |
| $d_{10i}$ | 114.3 | $d_{10s}$ | 114.3 |

[a] Not detected.

### 3.2.4. $^{13}$C NMR characterisation

The results of the $^{13}$C NMR characterisation are presented in Table 7. The $^{13}$C NMR spectrum of sample 30 is shown in Fig. 7. Possible 1,9-copolymer structures obtained with the binary catalyst system are illustrated in Fig. 4 and the characteristic chemical shifts in Table 5. An average of intensities of the carbons $d_2$–$d_4$ and $d_6$–$d_{10}$ relative to 1/3 intensity of all peaks was used to calculate the comonomer incorporation as mol%. As was the case with the isolated catalysts, the level of crosslinking was too low to be detected by $^{13}$C NMR.

The tacticity of the main chain affects the chemical shifts of the carbons $d_1$–$d_4$, whereas the influence is not observed for carbons $d_6$–$d_{10}$ (Table 5). Based on the differences in the chemical shifts, it was possible to determine whether decadiene was incorporated into a syndiotactic or isotactic main chain. Reliable quantitative analysis was not possible due to a poor signal-to-noise ratio as the carbons $d_1$–$d_4$ signals were split into two peaks.

The rrrr and mmmm pentad values reported in Table 7 are indicative of the relative activities of catalysts **1** and **2** in the binary catalyst system. Typically, the amount of syndiotactic and isotactic polymer fractions in the copolymers agrees reasonably well with the expected activities. In sample 27, there is a very small amount of isotactic polymer, indicating that activity of catalyst **2** in this case was significantly lower than expected.

A comonomer content between 0.42 and 0.78 mol% was measured for the copolymers (Table 7). Excluding sample 27, which had only a small fraction of isotactic polymer, the peaks $d_{1s}$–$d_{4s}$ and $d_{1i}$–$d_{4i}$ in the $^{13}$C NMR spectra confirmed that 1,9-decadiene was incorporated with both catalysts.

It can be concluded that due to the high tendency of catalyst **1** to produce crosslinked structures, it is likely that when copolymerisations were started with catalyst **1** at 80 °C (runs 26 and 27) the incorporated 1,9-decadiene was significantly crosslinked before the temperature was lowered and catalyst **2** was injected. However, contrary to this finding, as discussed previously, the copolymers obtained with the isolated catalyst **2** at 80 °C did not show marked crosslinking. Therefore, when polymerisation was started at 80 °C with catalyst **2** (runs 29 and 30), a large number of isotactic macromonomers with unreacted double bonds were produced before the temperature was lowered and catalyst **1** was injected. Thus, it is most likely that the injected catalyst **1** incorporated the isotactic macromonomers into the syndiotactic main chain, so that structure **V** in Fig. 4 was formed.

Table 6
Polymerisation conditions and activities for the binary catalyst system

| Run | Catalyst | $T$, °C | [Propylene], mol $L^{-1}$ | [Cat **1**], μmol $L^{-1}$ | [Cat **2**], μmol $L^{-1}$ | [Al], mmol $L^{-1}$ | [Diene], mmol $L^{-1}$ | Time, min | Activity,[e] $kg_{PP}\ mol_{Zr}^{-1}\ h^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|
| 17[a] | $\mathbf{1}+\mathbf{2}$ | 40 | 1.91 | 5.0 | 15.0 | 37.5 | 0.0 | 30 | 3900 |
| 18[a] | $\mathbf{1}+\mathbf{2}$ | 40 | 1.91 | 4.0 | 10.0 | 25.0 | 27.3 | 30 | 2000 |
| 19[a] | $\mathbf{1}+\mathbf{2}$ | 80 | 1.76 | 4.0 | 10.0 | 25.0 | 0.0 | 30 | 4000 |
| 20[a] | $\mathbf{1}+\mathbf{2}$ | 80 | 1.76 | 4.0 | 7.5 | 18.8 | 27.3 | 30 | 3300 |
| 21[b] | $\mathbf{2}+\mathbf{1}$ | 40 | 1.91 | 7.5 | 15.0 | 37.5 | 0.0 | 30 | 4500 |
| 22[b] | $\mathbf{2}+\mathbf{1}$ | 40 | 1.91 | 7.5 | 15.0 | 37.5 | 27.3 | 30 | 3400 |
| 23[b] | $\mathbf{2}+\mathbf{1}$ | 80 | 1.76 | 10.0 | 7.5 | 25.0 | 0.0 | 30 | 5000 |
| 24[b] | $\mathbf{2}+\mathbf{1}$ | 80 | 1.76 | 10.0 | 7.5 | 25.0 | 27.3 | 30 | 5800 |
| 25[c] | $\mathbf{1}+\mathbf{2}$ | 80/40 | – | 4.0 | 10.0 | 25.0 | 0.0 | 30 | 3600 |
| 26[c] | $\mathbf{1}+\mathbf{2}$ | 80/40 | – | 4.0 | 10.0 | 25.0 | 27.3 | 30 | 5400 |
| 27[c] | $\mathbf{1}+(\mathbf{2})$[f] | 80/40 | – | 4.5 | 7.5 | 18.8 | 27.3 | 45 | 3100 |
| 28[d] | $\mathbf{2}+\mathbf{1}$ | 80/40 | – | 5.0 | 7.5 | 18.8 | 0.0 | 30 | 4400 |
| 29[d] | $\mathbf{2}+\mathbf{1}$ | 80/40 | – | 5.0 | 7.5 | 18.8 | 27.3 | 30 | 3800 |
| 30[d] | $\mathbf{2}+\mathbf{1}$ | 80/40 | – | 5.0 | 7.5 | 18.8 | 27.3 | 45 | 3200 |

[a] Polymerisation was started with catalyst **1**. Catalyst **2** was injected after 15 min.

[b] Polymerisation was started with catalyst **2**. Catalyst **1** was injected after 15 min.

[c] Polymerisation was started with catalyst **1** at 80 °C. After 15 min, temperature was lowered to 40 °C and catalyst **2** was injected.

[d] Polymerisation was started with catalyst **2** at 80 °C. After 15 min, temperature was lowered to 40 °C and catalyst **1** was injected.

[e] $n_{Zr} = n_{Zr,\mathbf{2}} + n_{Zr,\mathbf{1}}$.

[f] Activity of catalyst **2** was markedly lower than expected.

### 3.3. Polypropylene blends and tensile properties

Syndiotactic and isotactic polypropylenes are immiscible and phase separation occurs when they are blended [32–34]. Mechanical properties of phase separated blends can be improved by adding a third component, a compatibiliser, which interacts with both phases in the blend.

Neat syndiotactic and isotactic polypropylenes were blended with produced copolymers in order to investigate if the copolymers could be used as compatibilisers. Blends were prepared by codissolving the polymers in hot mesitylene as described in Section 2. The amount of each component in a blend was adjusted to give a final blend consisting of 50 wt% syndiotactic and 50 wt% of isotactic polypropylenes. The compositions of the prepared blends are summarised in Table 8. The polymerisation conditions used in runs 1 and 9 were applied to produce syndiotactic and isotactic polymers for the blends.

For tensile testing, dog-bone-shaped test specimens were injection moulded. The tensile properties of the blends are presented in Table 8. Fig. 8 shows the measured load–strain curves for blends A, C and F. The 1/1 blend of syndiotactic and isotactic polypropylenes without copolymer was used as a reference blend (A). The measured modulus for this blend was 530 MPa. The yield point was not observed because the test specimens were broken before it occurred (Fig. 8). The values for the tensile strain and tensile stress at break were 14% and 20.2 MPa, respectively. These values were further compared with the yield strain and stress values measured for the compatibilised blends.

Fig. 9 illustrates the percentage change in the modulus and yield strength values of the blends containing copolymer as a compatibiliser relative to the reference blend (A). Typically, the blended copolymer has a negative effect on both modulus and yield strength values, whereas the tensile strain values increase significantly (Fig. 8). A high variation was measured in the tensile strain values, thus they are not reported in Table 8. The observed general trend of decreasing modulus is likely related to octene side chains in the copolymers, which make the polymer chains more movable and soften the material. The long-chain branched structures are a plausible cause of the increase in the tensile strain values.

Except for blend G, the yield strain values are nearly constant and are not strongly affected by the addition of a copolymer (Table 8). The tested copolymer in blend G was from run 27. Because of the very low activity of catalyst **2** in run 27, the copolymer obtained contained a high amount of polypropylene with low syndiotacticity produced with catalyst **1** at 80 °C. It is plausible that the syndiotactic polymer fraction produced at 80 °C has a strong negative effect on modulus, but simultaneously increases the yield strain.

Table 8 and Fig. 9 show that blend F does not follow the general trend discussed above. In this case, both modulus and yield strength values increase relative to the reference blend (A). In blend F, the copolymer produced in run 30 was tested as a compatibiliser. The characterisation of sample 30 indicated that it contained copolymer, in which syndiotactic and isotactic chains were linked. It is likely that the isotactic segments of the copolymer co-crystallised with the isotactic phase of the blend and that the syndiotactic segments simultaneously co-crystallised with the syndiotactic phase, which caused strong interactions between the blend phases. The enhanced tensile properties of blend F affirm that the polymer structure **V** was obtained in run 30 and that this type of copolymer can be used as a compatibiliser in blends consisting of immiscible syndiotactic and isotactic polypropylenes.

Table 7
Results of characterisation of samples produced with the binary catalyst system

| Run | Catalyst | $T$, °C | [Diene], mmol $L^{-1}$ | Time, min | $M_n$,[e] kg $mol^{-1}$ | $M_w$,[e] kg $mol^{-1}$ | $M_z$,[e] kg $mol^{-1}$ | $M_{z+1}$,[e] kg $mol^{-1}$ | MWD[e] | $T_m$,[f] °C | $T_c$,[f] °C | $\Delta H_c$,[f] J $g^{-1}$ | rrrr pentad,[h] % | mmmm pentad,[h] % | Diene,[h] mol% |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 17[a] | **1** + **2** | 40 | 0.0 | 30 | 43 | 210 | 476 | 691 | 4.8 | 132.1/145.4[g]/155.5 | 100.3 | −76 | n.m.[i] | n.m. | – |
| 18[a] | **1** + **2** | 40 | 27.3 | 30 | 66 | 370 | 903 | 1470 | 5.6 | 118.7/142.2 | 80.8/95.8 | −56 | 59.6 | 25.2 | 0.71 |
| 19[a] | **1** + **2** | 80 | 0.0 | 30 | 12 | 37 | 89 | 123 | 3.2 | – | – | – | n.m. | n.m. | – |
| 20[a] | **1** + **2** | 80 | 27.3 | 30 | 12 | 72 | 211 | 327 | 6.1 | – | – | – | 28.0 | 46.9 | 0.74 |
| 21[b] | **2** + **1** | 40 | 0.0 | 30 | 29 | 161 | 453 | 687 | 5.6 | 131.2/145.4[g]/154.4 | 95.0/105.1 | −76 | n.m. | n.m. | – |
| 22[b] | **2** + **1** | 40 | 27.3 | 30 | 24 | 274 | 1388 | 2654 | 11.4 | 120.0/141.9 | 97.1 | −76 | 31.7 | 57.4 | 0.42 |
| 23[b] | **2** + **1** | 80 | 0.0 | 30 | 6 | 81 | 285 | 409 | 12.3 | – | – | – | n.m. | n.m. | – |
| 24[b] | **2** + **1** | 80 | 27.3 | 30 | 12 | 167 | 632 | 1076 | 13.6 | – | – | – | 23.6 | 51.5 | 0.67 |
| 25[c] | **1** + **2** | 80/40 | 0.0 | 30 | 22 | 108 | 352 | 695 | 4.8 | 128.0/145.8[g]/152.7 | 75.8/103.1 | −66 | n.m. | n.m. | – |
| 26[c] | **1** + **2** | 80/40 | 27.3 | 30 | 16 | 137 | 986 | 2896 | 8.5 | 138.0/142.4[g] | 98.0 | −68 | 20.6 | 62.4 | 0.78 |
| 27[c] | **1**+(**2**)[j] | 80/40 | 27.3 | 45 | 73 | 794 | 2572 | 4240 | 10.8 | 116.3/141.9 | 82.8 | −34 | 59.4 | 13.2 | 0.61 |
| 28[d] | **2** + **1** | 80/40 | 0.0 | 30 | 71 | 328 | 586 | 715 | 4.6 | 124.7/130.7/146.2 | 84.5/94.6 | −55 | n.m. | n.m. | – |
| 29[d] | **2** + **1** | 80/40 | 27.3 | 30 | 17 | 415 | 1539 | 2390 | 25.1 | 115.2/133.2/139.5 | 71.1/92.6 | −56 | 35.7 | 50.1 | 0.60 |
| 30[d] | **2** + **1** | 80/40 | 27.3 | 45 | 47 | 917 | 2591 | 3796 | 19.7 | 120.5/135.1[g]/142.4 | 72.7/85.5 | −52 | 47.8 | 36.7 | 0.63 |

[a] Polymerisation was started with catalyst **1**. Catalyst **2** was injected after 15 min.

[b] Polymerisation was started with catalyst **2**. Catalyst **1** was injected after 15 min.

[c] Polymerisation was started with catalyst **1** at 80 °C. After 15 min, temperature was lowered to 40 °C and catalyst **2** was injected.

[d] Polymerisation was started with catalyst **2** at 80 °C. After 15 min, temperature was lowered to 40 °C and catalyst **1** was injected.

[e] By GPC.

[f] By DSC.

[g] Shoulder.

[h] By $^{13}C$ NMR.

[i] Not measured.

[j] Activity of catalyst **2** was markedly lower than expected.

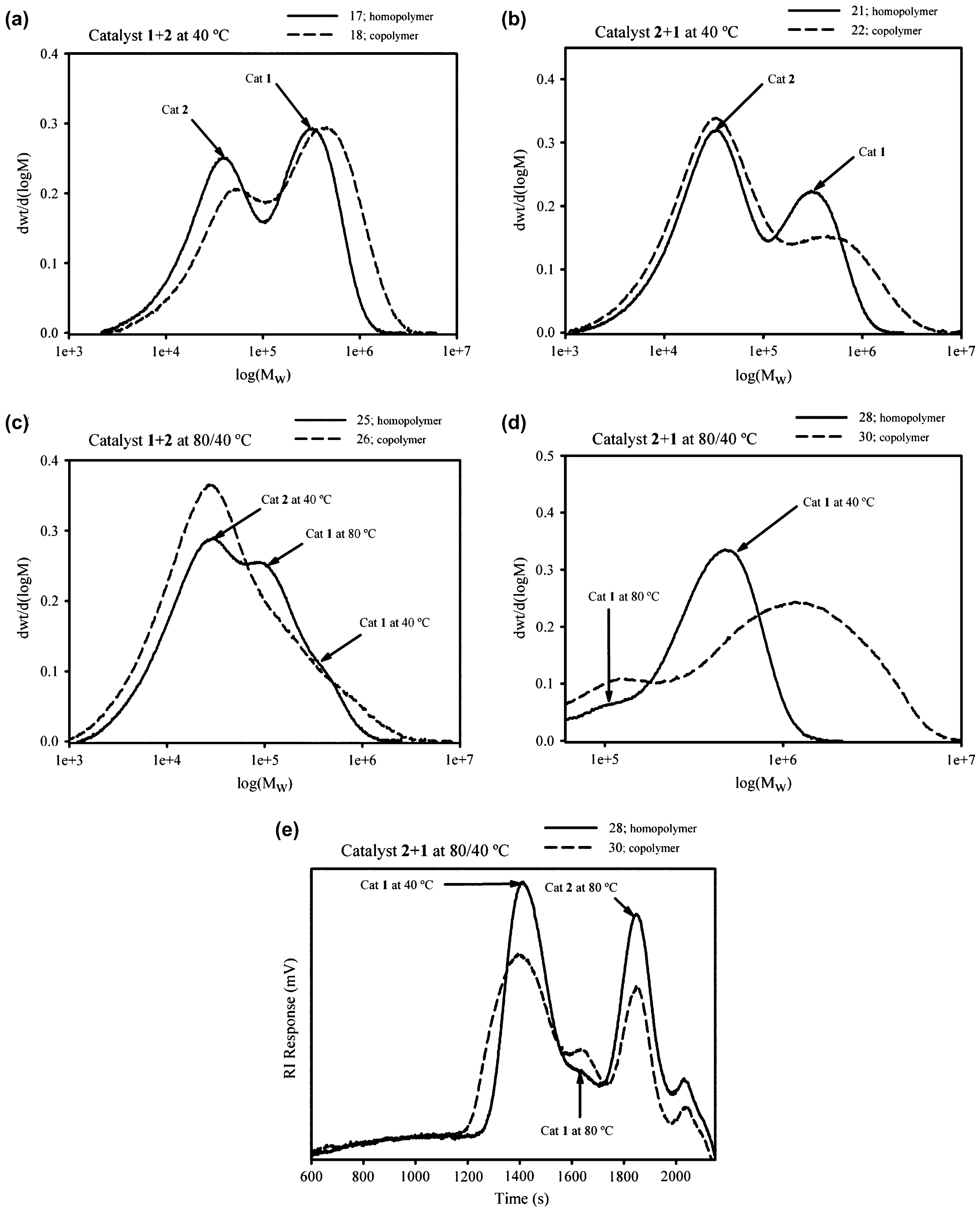


Fig. 6. MWD of homo- and copolymers produced with binary catalyst systems: **1** + **2** at 40 °C (a), **2** + **1** at 40 °C (b), **1** + **2** at 80/40 °C (c) and **2** + **1** at 80/40 °C (d). RI detector response of homo- and copolymers produced with **2** + **1** at 80/40 °C (e).

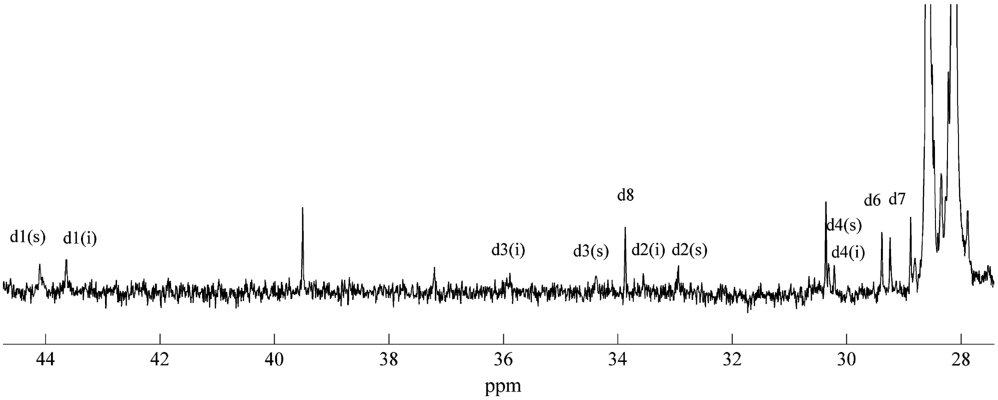


Fig. 7. $^{13}$C NMR spectrum of sample 30.

Table 8
Prepared blends and their tensile properties

| Blend | sPP, wt% | iPP, wt% | Copolymer, wt% | Blended copolymer | Unrecovered, % | Modulus, MPa | Yield strain, % | Yield strength, MPa |
|---|---|---|---|---|---|---|---|---|
| A | 50 | 50 | – | – | 5 | 530 ± 10 | 14 ± 1[a] | 20.2 ± 0.2[a] |
| B | 30 | 50 | 20 | 4 (cat **1**; 40 °C) | 1 | 500 ± 10 | 15 ± 0 | 20.5 ± 0.0 |
| C | 50 | 15 | 35 | 12 (cat **2**; 40 °C) | 2 | 460 ± 10 | 16 ± 1 | 18.4 ± 0.1 |
| D | 36 | 29 | 35 | 22 (cat **2** + **1**; 40 °C) | 2 | 490 ± 10 | 15 ± 1 | 19.6 ± 0.1 |
| E | 38 | 45 | 17 | 18 (cat **1** + **2**; 40 °C) | 1 | 520 ± 10 | 15 ± 1 | 20.0 ± 0.1 |
| F | 30 | 35 | 35 | 30 (cat **2** + **1**; 80/40 °C) | 4 | 540 ± 10 | 15 ± 0 | 21.7 ± 0.2 |
| G | 20 | 45 | 35 | 27 (cat **1** + **2**; 80/40 °C) | 2 | 440 ± 10 | 18 ± 0[b] | 19.9 ± 0.3[b] |

[a] Test specimens were broken before yield point and values for tensile strain and tensile strength at break are reported.

[b] Most of the specimens showed yield strain value higher than 20%, after which the test speed was increased to 10 mm min$^{-1}$. Values reported are calculated based on three parallel samples having yield strain less than 20%.

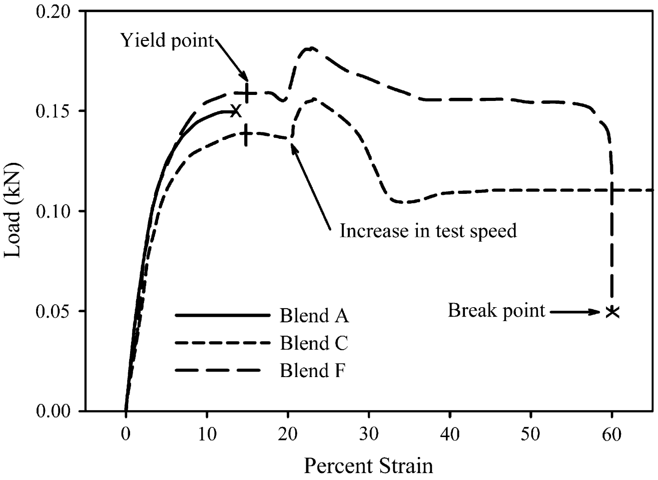


Fig. 8. Load–strain curves of blends A, C and F.

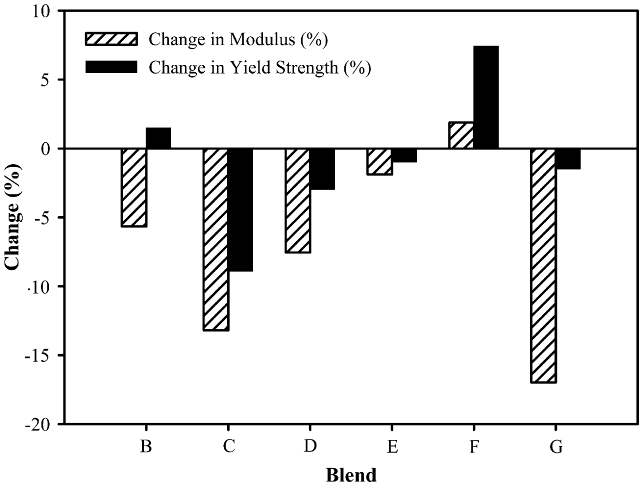


Fig. 9. Percentage change in the modulus and yield strength values of blends containing copolymer compared with blend A (1/1 blend of syndiotactic and isotactic polymer).

## 4. Conclusions

1,9-Decadiene/propylene copolymers with a comonomer content up to 0.98 mol% were obtained with the isolated catalysts **1** and **2**. Catalyst **1** had a slightly better comonomer response and a higher tendency to form long-chain branched structures, which were evident from the GPC data. Compared to the homopolymers, the copolymers showed a decrease in the melting and crystallisation temperatures and an increase in the molecular weight and MWD values. Incorporation of 1,9-decadiene did not affect the chain termination mechanism, which was confirmed by end group analysis of the copolymers produced with catalyst **2**. For the copolymers obtained with catalyst **1**, a decrease in the rrrr pentad values was measured, which indicated that stereoselectivity of **1** was influenced by 1,9-decadiene incorporation. This effect was not observed for catalyst **2**.

The binary catalyst system produced copolymers with the same level of 1,9-decadiene incorporation as the isolated catalysts. Formation of long-chain branched structures was evident and confirmed by GPC. Long-chain branching was most favoured in the copolymerisation started at 80 °C with catalyst **2** and followed by injection of catalyst **1** and 40 °C polymerisation temperature after 15 min of polymerisation. In this case, it is most likely that a polypropylene structure, in which 1,9-decadiene linked syndiotactic and isotactic chains, was formed. It was proposed that catalyst **2** incorporates 1,9-decadiene into the isotactic main chain without significant crosslinking within the first 15 min at 80 °C and the macromonomers produced with catalyst **2** are then incorporated at 40 °C into the syndiotactic main chain in polymerisation with catalyst **1**.

The copolymers produced were studied as compatibilisers in blends of syndiotactic and isotactic polypropylenes. The blend compatibilised with the copolymer, in which syndiotactic and isotactic polypropylene chains were linked, showed a simultaneous increase in the modulus and yield strength values compared with the values measured for a 1/1 tacticity blend. This result affirmed that such a copolymer was successfully synthesised with the binary catalyst system and that this type of copolymer works as a compatibiliser in a blend of syndiotactic and isotactic polypropylenes.

This study demonstrates that copolymerisation of 1,9-decadiene and propylene with a binary metallocene system is an attractive method for producing novel polypropylene structures that cannot be achieved by copolymerisation with isolated catalysts alone. Additionally, the novel copolymers can be used as compatibilisers to improve the mechanical properties of a blend consisting of polypropylenes with different tacticities.

## Acknowledgements

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