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Synthesis and Characterization of iPP-sPP Stereoblock Produced by a Binary Metallocene System

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ABSTRACT: Stereoblock polypropylenes comprising of iPP and sPP segments are synthesized by polymerization of the following binary system of metallocenes: the Cs-symmetric [2,7-t-Bu₂(FLu)₂Ph₂C(Cp)ZrCl₂] and the C₂-symmetric rac-Me₂Si(2-Me-4-Ph-Ind)₂ZrCl₂. Blends of samples made either by each catalyst individually (solution blend) with materials obtained with the mixed catalyst system (reactor blend) are compared. The simultaneous presence of MAO and DEZ, enhancing fast and reversible transfer of the growing chains between the two active centers, leads to the formation of a stereoblock microstructure. In this case, low molecular weight polymers are obtained. The junction between the blocks is qualitatively observed in 13C NMR. When made in toluene, the stereoblock material consists of a majority of syndiotactic sequences, whereas the ratio is more equilibrated when the polymerization was conducted in the more polar chlorobenzene. This is confirmed by the results obtained with 13C NMR, CRYSTAF, HT HPLC, DSC, SSA, WAXD, and optical microscopy.

INTRODUCTION: Despite the already impressive history of polypropylene (PP), this world famous polymer continues to spark the curiosity of many scientists. Some of the most intriguing members of the "PP family" are stereoblock PPs. They are generally sought after because they could act as heterophase compatibilizers. For instance, iPP-oPP stereoblock copolymers, besides the quest for elastomeric properties, could prevent phase separation at the interface of the crystalline and amorphous domains. Similarly, sPP-iPP could serve as compatibilizer in iPP/sPP blends, components notoriously immiscible with each other in the melt. However, these nephews of classical PP are still neither easy to synthesize nor to characterize.

As a matter of fact, within the last 20 years attempts to synthesize stereoblocks as well as homostereoblocks have been burgeoning, both on homogeneous and heterogeneous systems. Classical Ziegler-Natta (Z-N) catalysts lead to a blend that contains a certain fraction of stereoblock that one can isolate by solvent fractionation. When looking at metallocene type of catalysts, elegant examples of unbridged "oscillating" catalysts have been published, as well as "dual-side" or haptoflexible catalysts. Binary systems, where different active species are mixed, have also been examined. So far, no indisputable case of sole formation of stereoblocks was demonstrated and blends were obtained in diverse proportions, which generally requires tedious separation procedures before analysis can be done and full characterization was yet not achieved.

Very recently, other strategies to build stereoblocks have been explored, such as living polymerization (Coordination Chain Transfer Polymerization, CCTP) with degenerative transfer or using the sensitivity of some catalysts to the...
polarity of the solvent\textsuperscript{2c,8} and/or the monomer pressure.\textsuperscript{9} They lead to the exclusive formation of the target material but are uneconomical since only one chain per metal center is produced.

With respect to characterization, these PPs present a considerable analytical challenge.\textsuperscript{10} For PPs, the method of choice for microstructure characterization is solution $^{13}$C NMR spectroscopy as this allows direct observation of the stereosequences based upon their different chemical shifts. For ideal PP stereoblock systems, a proof of \textit{iPP}–\textit{sPP} block junctions is possible via stereosequence distribution analysis at the pentad level, with the $\text{mmmr}$, $\text{mmrr}$, and $\text{mrrr}$ pentads only occurring at the block junctions. However, when isolated stereomerors are also considered to be present in both the \textit{iPP} and \textit{sPP} blocks, alternate sources for those supposed stereoblock junction diagnostic pentads occur, for example, isolated stereodefects in the \textit{iPP} blocks would also result in $\text{mmmr}$ and $\text{mmrr}$ pentads. Thus, to distinguish between isolated stereodefects within the stereoblocks and the block junctions themselves, stereosequence analysis at the heptad level is needed. To further complicate matters, regiodefects may also occur in either or both of the \textit{iPP} and \textit{sPP} blocks.

As well as their direct investigation by $^{13}$C NMR spectroscopy, stereoblocks may also be indirectly investigated via solvent fractionation techniques. Nevertheless, it is important to note that stereoblocks can be made from either a noncrystallizable or a crystallizable block or from two crystallizable blocks. The former case is more complicated to analyze by $^{13}$C NMR since all possible stereosequences are expected in comparable amounts, whereas in the latter case the polymers can be isolated more easily by precipitation (no soluble fraction) but cannot always be separated by fractionation. Therefore, there remains a need for efficient methods to come to convincing conclusions or simply for more efficient chemistry.

Although it is obvious that a higher probability of chain-transfer should result in a higher number of stereoblocks, the question remains how to increase chain-transfer in a controlled manner. Effective and reversible chain transfer can be used to produce more chains per catalytic center, resulting in a more economical strategy to produce the desired architecture. In addition, it can also open the way to new architectures (not accessible otherwise), for example, multi(stereo)block copolymers. Despite the nature of the catalysts themselves, this process requires a subtle balance between the chain transfer agent (CTA) and other “environmental” factors:\textsuperscript{10(a)} for example, solvent and activator type.

Looking at the examples in literature of early transition metals, aluminum (Al) and zinc (Zn) are typically studied independently as CTA. Recently, Sita and coworkers\textsuperscript{11} reported a synergistic effect between the two metals. Other examples where both aluminum and zinc were used together have been published but with the different scope of studying catalyzed chain growth.\textsuperscript{12,13} Zinc has been used in classical Z-N catalysis in order to reduce molecular weight,\textsuperscript{14} to further functionalize\textsuperscript{15} the obtained materials or to change the comonomer incorporation level.\textsuperscript{16} Besides, it has been proven to be an efficient CTA for metallocenes and has been compared to diverse Al alkyls by Brintzinger and coworkers\textsuperscript{17} The authors claim that the exchange between Zn and Zr was fast but a decrease in the productivity showed that zinc alkyls form rather strong heteronuclear adducts with zirconocene alkyl (polymeryl) cations. The observed transfer can be either reversible or not.\textsuperscript{18} A general kinetic model to investigate the effects of reversibility in chain transfer to metal in olefin polymerization was derived by Arriola and coworkers.\textsuperscript{19} independently, several reports on the use of aluminum alone have seen the light. Winter and coworkers\textsuperscript{6(a)} studied a binary system of metallocenes in different ratios for the synthesis of \textit{iPP}-\textit{sPP} stereoblocks using Triisobutyl aluminum/trityl tetrais(pentafluorophenyl)borate (TIBA/TBF\textsubscript{20}) as activating cocktail. The effect of supportation\textsuperscript{6(b),20} was also studied. Lieber and Brintzinger\textsuperscript{6(c)} tackled the tricky case of \textit{iPP}-\textit{sPP} (that can only be partially separated by TREF) as \textit{aPP}-\textit{iPP}. A comparison was made between Methylaluminoxane (MAO) and TIBA/TBF\textsubscript{20} activators, the latter leading to the absence of transfer. Interestingly, the less MAO was used, the more stereoblock was formed. Thoman et al.\textsuperscript{6(d)} also looked into \textit{iPP}-\textit{sPP} in the presence of MAO and concluded to have successfully achieved the desired material by using $^{13}$C NMR, FT-IR, and WAXD. The effect of MAO vs. MAO + BHT on chain shuttling by Al was investigated.\textsuperscript{6(e),21} Longer Al alkyls have also been explored.\textsuperscript{22} Some effort has also been dedicated to the characterization of PP stereoblocks, but paying greater attention to \textit{iPP}-\textit{sPP} types of copolymers (for their elastomeric properties). Studies of their mechanical properties have most often been performed on fractionated materials,\textsuperscript{23} since it is very difficult to characterize this type of samples otherwise. A few reports of other characterization techniques have appeared one on HT HPLC\textsuperscript{24} where macromolecules can be separated according to tacticity, and one on thermal fractionation (Successive Self-nucleation and Annealing, SSA) in combination with Atomic Force Microscopy.\textsuperscript{25}

In this work, the synergistic effect of combining Al and Zn,\textsuperscript{11} that might result in a more efficient formation of stereoblocks, is investigated. Besides, to the best of our knowledge, the use of a binary system of metallocenes operating in a homogeneous way in the presence of both Al and Zn has never been reported. In fact, despite the considerable advances in unraveling what happens at the molecular level, it is still not fully understood which circumstances favor or suppress the formation of stereoblocks. Most importantly, we believe that there is room for improvement in the characterization of (hypothetical) \textit{iPP}-\textit{sPP} stereoblocks. As a matter of fact, it is not uncommon to obtain somehow conflicting outcomes from different characterization techniques (for instance between SSA and CRYSATAF/TREF where different

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separation mechanisms rule). Therefore, a careful comparison of classical techniques (DSC, NMR, and WAXD) and more recently developed ones (or simply less commonly used, such as SSA) would certainly bring added value.

The strategy adopted here aims to encourage the formation of stereoblocks by mixing a C₅ and a C₇-symmetric metalloocene and to facilitate chain transfer by the addition of zinc in the presence of aluminum. For the binary system, the runs in toluene will be compared to the ones in a more polar solvent (here, chlorobenzene, CB). To test the validity of our hypotheses and assess the formation of stereoblocks, in-depth characterization will be performed using HT SEC, DSC, SSA, ¹³C NMR, CRYSTAF, HT HPLC, WAXD, and POM.

EXPERIMENTAL

General Considerations

All syntheses and manipulations of air- and moisture-sensitive compounds were carried out in oven-dried Schlenk-type glassware on a dual manifold Schlenk line, a vacuum line (typically 1–100 mbar), or in a nitrogen-filled glovebox (typically <1.0 ppm of oxygen and moisture).

Materials

Toluene (Merck) was purified by passing over beds with BTS material (BASF). CB (Aldrich) was purified by passing over Al₂O₃. Toluene (Merck) was purified by passing over beds with BTS material. All syntheses and manipulations of air- and moisture-sensitive compounds were carried out in oven-dried Schlenk-type glassware on a dual manifold Schlenk line, a vacuum line (typically 1–100 mbar), or in a nitrogen-filled glovebox (typically <1.0 ppm of oxygen and moisture).

Polymerization

All polymerizations were carried out in stainless steel PEEK autoclaves, mounted on a semiautomated polymerization platform. The autoclaves had an internal volume of 125 mL and the reactors were equipped with a mechanical stirrer (impeller), operated at 250 rpm. Reactors were dried by heating to 130°C under vacuum.

Solution Blending

The desired amounts of both samples (1:1 by weight) were dissolved in 150 mL toluene at 110°C in a round bottom flask equipped with a reflux condenser, under a nitrogen atmosphere. After dissolution, the mixture was precipitated in a large amount of cold methanol, filtered, and dried to constant weight at 70°C under vacuum.

Characterization

High temperature SEC analyses performed to determining the molecular weight were carried out on a Waters Alliance GPCV 2000 chromatograph equipped with three columns (three PL Olexis, 250 × 8.5 mm, Polymer Laboratories). Samples of 1 mg/mL concentrations were eluted with trichlorobenzene (TCB) at a flow rate of 1 mL/min at 160°C. Linear polyethylene standards (PSS GmbH, Mainz, Germany) with an average molecular weight in the range of 5–1,500 kg/mol were used for calibration of the SEC columns. Thermal analysis was conducted using a TA Instruments DSC Q1000. Approximately 4–5 mg of polymer were encapsulated in hermetically sealed aluminum pans and measured at a standard heating and cooling rate of 10°C/min in a nitrogen atmosphere. Prior to recording the cooling and heating runs, the samples were held at 185°C for 5 min to erase thermal history, then cooled at 10°C/min to −20°C. The sample was held at this temperature for 2 min and reheated from up to 180 at 10°C/min. The reported melting temperatures are those obtained from the second heating (but may display several melting/crystallization peaks). Thermal fractionation was undertaken according to the SSA procedure using a Mettler Toledo 820 device. The initial crystalline state was created by melting 3 mg of sample at 160°C, holding for 5 min to allow relaxation and then cooling to 20°C at a rate of 10°C/min. Successive seeding and annealing steps were then subsequently applied covering a temperature range of 130–80°C in 5°C steps. The melting behavior of the thermally fractionated sample was then recorded using a heating rate of 10°C/min. The chemical composition distribution was investigated using the CRYSTAF procedure with a Polymer Char Model 200 device. Approximately 20 mg of sample was dissolved in 40 mL of 1,2-dichlorobenzene. The crystallization profiles were recorded between 25 and 150°C at 0.1°C/min. High temperature HPLC was used to investigate the chemical composition distribution of the polymers. Samples were dissolved in 1-decanol for between 2 and 3 h and injected onto a Hypercarb column (100 × 4.6 mm, particle diameter 5μm, Thermo Scientific) flushed with 1-decanol at 160°C at a flow velocity 0.8 mL/min (98μL sample loop). For all HPLC measurements a Polymer Laboratories Chromatograph PL GPC 210 system equipped with a quaternary pump (Agilent Technologies) and a Polymer Laboratories PL-ELS 1000 evaporative light scattering detector was used.
Three minutes after starting to pump, a linear gradient of 1-decanol and TCB was generated starting with 1-decanol and ending with pure TCB after 10 min. After pumping with pure TCB for 2 min, a further linear gradient from pure TCB to pure 1-decanol was undertaken over 2 min. Finally, the adsorption equilibrium of the column was re-established by pumping with pure 1-decanol for 20 min. Wide-angle X-ray diffraction (WAXD) was used to study the morphology. All measurements were performed directly on the powders using a Rigaku diffractometer with Bragg-Brentano configuration and an X-Ray wavelength of 1.54 Å. Polarized optical microscopy was performed to further study the morphology. Before applying the right thermal history, samples were prepared by compression molding a small amount of each material between two glass slides at 180 °C for 30 s and subsequent quenching in air. Optical micrographs were taken in polarized transmission mode with an Zeiss LM Axioplan optical microscope equipped with a Zeiss Axiocam camera and Linkam THMS 600 hot stage. Optical micrographs were obtained on samples with different thermal histories. 13C NMR spectroscopy was used to investigate the polymer microstructure with respect to stereo- and regioregularity. All NMR spectroscopy was performed within the analytical department of Boréalis Polylef in GmbH, Linz. Quantitative 13C{1H} NMR spectra were recorded in the solution-state using a Bruker Advance III 400 NMR spectrometer operating at 400.15 and 100.62 MHz for 1H and 13C, respectively. All spectra were recorded using a 13C optimized 10 mm selective excitation probehead at 125 °C using nitrogen gas for all pneumatics. Approximately 200 mg of material was dissolved in 1,2-tetrachloroethane-d2 (TCE-d2). This setup was chosen primarily for the high resolution needed for PP microstructure quantification. Standard single-pulse excitation was employed using the NOE and bi-level WALTZ16 decoupling scheme applied to remove the influence of heteronuclear scalar coupling. A total of 8192 (8k) transients were acquired per spectra. Quantitative 13C{1H} NMR spectra were processed, integrated and relevant quantitative properties determined from the integrals using proprietary computer programs developed at Boréalis, Linz. All chemical shifts were indirectly referenced to the central signal of the 13C-2H multiplet of the solvent such that the methyl signal of the isotactic pentad mmmm in all systems would occur at 21.85 ppm. This procedure allows direct comparison of all systems even when the mmmm pentad was not present. Spectral assignment was achieved through comparison to previously reported spectra measured under similar conditions.

RESULTS AND DISCUSSION

Two metallocenes were selected for the polymerization of propylene: one syndiospecific C5-symmetric (1) and one isospecific C2-symmetric (2) (Scheme 1).

Polymerizations Using a Single Complex

Before using them together, the individual response of each catalyst to chain transfer using ZnEt2 (DEZ) was investigated in toluene at 30 and 50 °C with MAO as a scavenger at a level of 1000 eq. (Table 1). Polymerization at temperatures higher than 50 °C was deemed not meaningful as catalyst 1 (Cs) is rather temperature-sensitive, for example, at 80 °C.

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**TABLE 1** Propylene Polymers Polymerized using Either Catalyst 1 or 2

<table>
<thead>
<tr>
<th>Entry</th>
<th>Cat.</th>
<th>T (°C)</th>
<th>ZnEt2 (eq.)</th>
<th>Yield (g)</th>
<th>Mn (g/mol)</th>
<th>PDI</th>
<th>Tm (°C)a</th>
<th>ΔH (J/g)</th>
<th>Tc (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>1</td>
<td>30</td>
<td>/</td>
<td>2.73</td>
<td>133,000</td>
<td>2.2</td>
<td>141.2, 147.8</td>
<td>49.6</td>
<td>92.6</td>
</tr>
<tr>
<td>S2</td>
<td>1</td>
<td>30</td>
<td>40</td>
<td>3.55</td>
<td>57,500</td>
<td>2.0</td>
<td>141.6, 149.6</td>
<td>55.0</td>
<td>94.2</td>
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<tr>
<td>S3</td>
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<td>30</td>
<td>400</td>
<td>4.15</td>
<td>4300</td>
<td>1.7</td>
<td>140.7, 149.5</td>
<td>74.6</td>
<td>106.8</td>
</tr>
<tr>
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<td>1</td>
<td>50</td>
<td>/</td>
<td>2.90</td>
<td>57,000</td>
<td>2.0</td>
<td>117.8</td>
<td>26.1</td>
<td>48.2b</td>
</tr>
<tr>
<td>S5</td>
<td>1</td>
<td>50</td>
<td>100</td>
<td>0.92</td>
<td>5400</td>
<td>2.3</td>
<td>113.3, 128.4</td>
<td>44.0</td>
<td>81.0</td>
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<tr>
<td>I1</td>
<td>2</td>
<td>30</td>
<td>/</td>
<td>3.81</td>
<td>69,400</td>
<td>3.1</td>
<td>157.6</td>
<td>100.4</td>
<td>113.3</td>
</tr>
<tr>
<td>I2</td>
<td>2</td>
<td>30</td>
<td>50</td>
<td>0.58</td>
<td>6100</td>
<td>1.7</td>
<td>152.1</td>
<td>109.0</td>
<td>116.6</td>
</tr>
<tr>
<td>I3</td>
<td>2</td>
<td>30</td>
<td>500</td>
<td>0.60</td>
<td>1300</td>
<td>1.9</td>
<td>140.5</td>
<td>116.5</td>
<td>106.5</td>
</tr>
<tr>
<td>I4</td>
<td>2</td>
<td>50</td>
<td>/</td>
<td>2.06</td>
<td>94,000</td>
<td>2.2</td>
<td>159.6</td>
<td>47.5</td>
<td>111.5</td>
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<tr>
<td>I5</td>
<td>2</td>
<td>50</td>
<td>100</td>
<td>2.22</td>
<td>3000</td>
<td>1.8</td>
<td>148.3</td>
<td>113.8</td>
<td>113.0</td>
</tr>
</tbody>
</table>

Reported Tm and Tc were extracted from the second heating and cooling runs at 10 °C/min. Conditions: 75 mL toluene, 3 bar propylene, 1 mmol MAO (1000 eq.), 1 μmol catalyst, 1 h.

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a The DSC thermograms can present two endotherms upon heating.

b Cold-crystallization observed upon heating.
the PDI broadened significantly to 3.3 due to the presence of a low molecular weight component.

For both catalysts the decrease in molecular weight in response to the addition of DEZ indicated that DEZ was acting as a CTA or chain-transfer mediator as described by Sita and coworkers. The decrease in molecular weight with increased concentration of DEZ was more pronounced for the C\textsubscript{2}-symmetric catalyst than the S\textsubscript{x} catalyst. Actually, if one calculates the number of chains per zinc, the resulting number is very close to 2 for the S\textsubscript{x}, whereas it remains below 1 for the I\textsubscript{x}. This estimation implies that the chain transfer is more efficient for catalyst 1 (C\textsubscript{s}) than 2 (C\textsubscript{2}). For most experiments, the PDI remained close to 2 with a slight decrease in PDI observed where DEZ was present.

Thermal analysis by DSC showed that all systems had the expected melting temperatures (T\textsubscript{m}) of stereoregular PP synthesized using metallocene catalysts, that is, at best close to 160 °C for iPP and to 150 °C for sPP (Table 1, runs at 30 °C). These T\textsubscript{m} values were reduced upon addition of DEZ. It should be noted that the typical double melting endotherm was observed for sPP samples and was described in the literature. It was attributed to the recrystallization of just melted less stable crystallites followed by the subsequent melting of the just formed more perfect crystallites.

Besides, sPP made at 50 °C in the absence of DEZ underwent cold crystallization: the chains did not crystallize upon cooling but upon (relatively slow) heating and subsequently melted during the same cycle. Melting enthalpies (ΔH) were dependent on the polymerization temperature. They increased with a lower polymerization temperature resulting in higher stereoregularity, similarly as T\textsubscript{m}. For the sPP series, the T\textsubscript{m} and the crystallization temperature (T\textsubscript{c}) were also significantly higher when polymerized at 30 °C instead of 50 °C. However, T\textsubscript{m} and T\textsubscript{c} were affected to a lesser degree when varying the polymerization temperature in the iPP series. Upon addition of DEZ, higher T\textsubscript{c} and ΔH values (thus crystallinity) were measured for both iPP and sPP. This observation may be related to the lower molecular weight of the polymers, resulting in an easier crystallization at higher temperatures due to the lower melt viscosity.

Results of the microstructure analysis by \textsuperscript{13}C NMR spectroscopy of the samples are shown in Table 2. The results of two representative runs for each catalyst are given. All the S\textsubscript{x} samples were polymerized in a similar fashion. For 1, reasonably syndiotactic PPs were produced as demonstrated by an intense rrrr pentad. Evidence of both isolated stereodefects and regiodefects was also observed. These stereodefects could in fact be reversible chain transfer events: since the C\textsubscript{s}-symmetric sites are enantiotopic (and not homotopic, like in the C\textsubscript{2}-symmetric case), about 50% of the reversible exchanges could lead to the same errors as site epimerization. Obviously, for the C\textsubscript{2}-symmetric catalyst, highly isotactic PP was produced, as represented by a high mmmm content. Here as well, evidence of both isolated stereo- and regiodefects was found but in lower amounts. In particular, the presence of a racemic mixture of C\textsubscript{2}-symmetric species

<table>
<thead>
<tr>
<th>Entry</th>
<th>mmmm</th>
<th>mmrr</th>
<th>rmmr</th>
<th>mmrr</th>
<th>xmr</th>
<th>mrr</th>
<th>rr</th>
<th>mrrr</th>
<th>mrrr</th>
<th>mrrm</th>
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<tbody>
<tr>
<td>S1</td>
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<td>0.0</td>
<td>0.8</td>
<td>1.6</td>
<td>1.1</td>
<td>0.4</td>
<td>91.0</td>
<td>5.2</td>
<td>0.1</td>
<td></td>
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<tr>
<td>S2</td>
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<td>0.0</td>
<td>0.8</td>
<td>1.8</td>
<td>1.3</td>
<td>0.4</td>
<td>90.0</td>
<td>5.5</td>
<td>0.2</td>
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<tr>
<td>I1</td>
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<td>0.5</td>
<td>0.0</td>
<td>0.3</td>
<td>0.4</td>
<td>0.2</td>
<td>0.0</td>
<td>0.1</td>
<td>0.1</td>
<td></td>
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<tr>
<td>I2</td>
<td>97.1</td>
<td>1.8</td>
<td>0.1</td>
<td>0.4</td>
<td>0.2</td>
<td>0.0</td>
<td>0.3</td>
<td>0.0</td>
<td>0.1</td>
<td></td>
</tr>
</tbody>
</table>

TABLE 2 Stereosequence Analyses at the Pentad Level of Propylene Polymers Polymerized Using Either Catalyst 1 or 2

**FIGURE 1** Demonstration of tacticity-based separation using (a) CRYSTAF and (b) HT HPLC on model polymers. Reproduced from Dr. T. Macko. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
should be detected by the presence of the \( \text{xmrx} \) pentad signature. Nevertheless, this signal is not distinctly intense in the spectra of the homopolymers made under these conditions. The presence of \( \text{iPP-iPP} \) stereoblock will be further addressed in the next section. Both for low molecular weight \( \text{iPP} \) and \( \text{sPP} \) systems, standard isobutyl end groups were observed. Due to their low absolute concentration, regioeffects and end-groups were not quantified and their influence on pentads was assumed to be insignificant.

Recent advances in both CRYSTAF and TREF have demonstrated the ability to differentiate between \( \text{sPP} \) and \( \text{iPP} \), with \( \text{iPP} \) eluting at room temperature as it is unable to crystallize. Despite their resolving power, none of these techniques allows discrimination between different degrees of tacticity i.e. \( \text{mmm}m \) content. Recent advances by Macko and Pasch\(^\text{31}\) have shown that high-temperature HPLC (HT HPLC) using a Hypercarb column can separate PPs according to tacticity (Fig. 1). These advanced methods were applied to the polymers described in this work. When produced in the absence of DEZ, \( \text{sPP} \) eluted in CRYSTAF as a sharp peak (Fig. 2). \( \text{sPP} \) obtained in the presence of DEZ yielded an additional fraction that eluted at room temperature, identically to Figure 1. This extra feature indicates the presence of a chemically distinct compound, either exhibiting a different microstructure (\( \text{sPP} \)) or molecular weight. In general, if \( M_n > 6 \text{ kg/mol} \), CRYSTAF does not depend on the molecular weight anymore but most samples shown in Figure 2 have a molecular weight lower than this limit. Besides, due to its relatively low crystallization temperature under these conditions (30–47°C) it is also possible that part of the \( \text{sPP} \) simply remained soluble to some extent below 30°C. In contrast, the \( \text{iPP} \) always eluted as a single component, and only shifted towards a higher crystallization temperature upon addition of DEZ. It has to be considered that these results cannot be directly related to the DSC data presented in Table 1, since in one case, the crystallization takes place in bulk at a faster cooling rate whereas in the other it occurs from dilute solution at a much lower cooling rate.

In HT HPLC, both \( \text{oPP} \) and \( \text{sPP} \) are expected to be fully adsorbed onto the column when 1-decanol is used as eluent. However, \( \text{iPP} \) is not retained and eluted from the column in 1-decanol (Fig. 1). All absorbed polymers are then desorbed after addition of TCB to the mobile phase, that is, after the start of the gradient from 1-decanol to TCB.

A similar absorption behavior was obtained for the homopolymer synthesized with a single catalyst (\( I_\text{p} \) and \( S_\text{p} \), Table 1) and the reference material showed in Figure 1. \( I_1 \), high molecular weight \( \text{iPP} \), eluted in two peaks whereas \( I_5 \), having a low molecular weight, eluted in only one peak.

In Figure 3, the only difference between our homopolymers and the reference samples presented in Figure 1 is that for the \( \text{sPP} \) produced in the presence of DEZ (S3), a shoulder at lower elution volume is observed. This feature may be explained by some possible microstructure heterogeneity or molecular weight related effects, since unfortunately at smaller \( M_n \) values the molecular weight does have an influence on the elution volume.

To summarize so far, both catalysts showed a clear response to the addition of DEZ, as demonstrated by a sharp decrease in molecular weight. In this case, low molecular weight stereoregular and regioregular \( \text{iPP} \) and \( \text{sPP} \) were obtained. The characteristics of the materials (DSC, \(^{13}\text{C} \text{ NMR}, \text{CRYSTAF}, \text{and HT HPLC})\), synthesized in the absence or presence of DEZ with one catalyst at a time, can be used as reference in the rest of the study (Table 3).

**Polymerizations Using Two Complexes**

This section now addresses the polymers produced by mixtures of the two complexes. In particular, we will focus on...
the question of enhanced polymer exchange between the different active centers of the two complexes, mediated by the presence of zinc, thus targeting the formation of iPP-sPP stereoblocks in a similar way as utilized in the elegant shuttle chemistry of the Dow Chemical Company.32 Polymerization was undertaken in toluene and additionally in CB. In fact, the use of a more polar solvent is expected to promote better separation of the ion pair (between the active cationic site and the non-coordinating anion) and yield a more efficient chain transfer.2(c)

In line with the previous section, even in the presence of DEZ the PDI remained around 2 in toluene whereas lower values emerged from the polymerizations in CB. For IS1 in toluene a broader PDI could have been expected if both catalysts alone would yield clearly different molecular weights but it is not the case here. A lower PDI for the runs in CB is in good agreement with a more efficient chain transfer. As expected with increased DEZ concentration, the molecular weight decreased. For the two polymerizations carried out in toluene, assuming 100% activation, 34 and 490 chains/metal center were calculated in the absence and presence of DEZ, respectively. In toluene, the yields were comparable to the ones obtained when the catalysts are used alone. However, a significant drop in yield was visible in CB, most likely due to poisoning of the catalysts.

For comparison purposes in this microstructural elucidation, simple blends of the individual materials (iPP and sPP made with a single complex, 1:1 by weight) were prepared by solution blending. They will be referred to as solution blends as opposed to reactor blends when the two catalysts were mixed during polymerization. It is worth noting that, as much as possible, the comparison will be established between groups of materials of comparable molecular weights: (1) high molecular weight species, IS1 vs. blend S1 + I1 and (2) low molecular species IS2 vs. blend S3 + I5. In addition, the influence of the solvent can be estimated by comparing IS2 vs. IS4, synthesized in toluene and CB, respectively. It was decided to select IS4 instead of IS3 due to the very low amount of IS3 that was obtained, although it is fair to note that IS4 has a comparatively lower molecular weight than IS2.

The crystal structures of the selected samples were investigated by WAXD (Fig. 4). The X-ray diffraction patterns show the presence of crystals corresponding to both iPP and sPP crystals. All the samples bear sequences that are long enough to crystallize. The diffraction peak at 20 = 12°, observable for all samples except the one synthesized in CB (IS4), indicates the presence of crystallizable syndiotactic sequences.34 Moreover, the reflection at 20 = 15.8° indicates the formation of Form I (sharp 020 reflection) of sPP, which is the most stable one. Only the sample made by an intensified site epimerization or a more reversible chain transfer of the C₅-symmetric catalyst in a more polar solvent.

When looking at the iPP reflections, all the diffraction profiles seem to correspond to the α phase as confirmed by the diagnostic reflection at 20 = 18.6° of the (130)₁. This is consistent with the formation of relatively long isotactic sequences, promoting the formation of the α form.30

The DSC thermograms are represented in Figure 5. Beyond the obvious simultaneous presence of sPP segments that melt at lower temperature than the iPP ones, it is not

<table>
<thead>
<tr>
<th>Entry</th>
<th>T (°C)</th>
<th>Solvent</th>
<th>ZnEt₂ (eq.)</th>
<th>Yield (g)</th>
<th>Mₙ (g mol)</th>
<th>PDI</th>
<th>Tₘ (°C)</th>
<th>Tₑ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IS1</td>
<td>30</td>
<td>tol</td>
<td>/</td>
<td>3.57</td>
<td>102,200</td>
<td>2.0</td>
<td>136.7, 145.0, 154.9</td>
<td>98.2, 111.8</td>
</tr>
<tr>
<td>IS2</td>
<td>30</td>
<td>tol</td>
<td>100</td>
<td>2.11</td>
<td>4300</td>
<td>1.9</td>
<td>136.7, 145.3</td>
<td>87.1, 102.8</td>
</tr>
<tr>
<td>IS3</td>
<td>30</td>
<td>CB</td>
<td>50</td>
<td>0.20</td>
<td>3800</td>
<td>1.6</td>
<td>/</td>
<td>40.2&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>IS4</td>
<td>50</td>
<td>CB</td>
<td>100</td>
<td>0.70</td>
<td>1000</td>
<td>1.5</td>
<td>132.7/140.4</td>
<td>101.0</td>
</tr>
</tbody>
</table>

Reported Tₘ and Tₑ values were extracted from the second heating and cooling runs at 10°C/min. Conditions: 75 mL solvent [Toluene (tol) or Chlorobenzene (CB)], 3 bar propylene, 1 mmol MAO (1000 eq.), 1 μmol catalyst, 1 h.

* The DSC thermograms can present several endotherms and/or exotherms upon heating or cooling, respectively.

<sup>b</sup> Cold-crystallization observed upon heating.

![FIGURE 4 WAXD patterns of selected samples](https://example.com/figure4.png)

**FIGURE 4** WAXD patterns of selected samples. The diagnostic reflection of (130)₁ of iPP at 20 = 18.6° is indicated by the solid arrow,<sup>33</sup> the reflection of (020)₁ of sPP at 20 = 15.8° is showed by the dashed arrow.<sup>26(a)</sup> [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
straightforward to point out the origin of the multiple endo-
therms. The different crystal sizes could contribute to this
observation, due to the presence of a broad distribution of
crystallizable isotactic and syndiotactic segments. In Figure
5(a), slightly higher \( T_m \)s are observed when the catalysts are
mixed (blend S1 + I1 opposed to IS1) in the absence of
DEZ. In contrast, for the lower molecular weight polymers
(blend S3 + I5 compared to IS2 and IS4) the \( T_m \)s are simply
shifted to lower temperatures when the catalysts are mixed,
with the number of peaks unchanged. Those shifts can be
attributed to the presence of shorter regular sequences. Such
a decrease in melting temperature could either indicate the
presence of stereoblocks with shorter crystallizable sequen-
ces, or it could imply that the \( \tau PP/sPP \) junctions hamper the
crystallization of the respective blocks. The \( T_m \) was further
lowered through the use of CB (IS4) as solvent and the
shape of the peak seems indicative of a narrower distribu-
tion of lamellar thicknesses, giving only a small high melting
endotherm instead of several distinct endotherms.

The samples were subsequently thermally fractionated by
SSA (Fig. 6). The corresponding heating curves clearly dem-
onstrate that the microstructure is affected by the presence
of DEZ during polymerization. Irreversible transfer does not
occur, as this would result in identical SSA traces for the
reactor blends and the mixed catalyst system. Interestingly,
the high melting endotherm in the blend S3 + I5 is absent
in IS2 and IS4, which can be accounted for shorter stereoreg-
ular sequences in the latter. This feature is even more pro-
nounced for IS4, confirming the hypothesis that in a more
polar solvent better ion separation promotes chain transfer,
leading to shorter blocks or possibly more defective ones.

CRYSTAF and HT HPLC were employed as complementary
techniques. With respect to CRYSTAF, when both catalysts
were used in the absence of DEZ, or when both were inde-
pendently produced and solution blended, two distinct peaks
were observed (Fig. 7). In contrast, when polymerized in the
presence of DEZ the polymer produced resulted in a single
major elution at 45 °C, with a minor shoulder at 60 °C. This
proves that when polymerized in the presence of DEZ the
two complex systems produced one population of macromom-
ecules, that is, those suspected to be \( \tau PP/sPP \) of the stereo-
block type. Nonetheless, the relatively low crystallization
temperature suggests a predominantly syndiotactic micro-
structure. This might be due to the more open structure of

FIGURE 5 DSC thermograms of the second heating and cool-
ing runs at 10 °C/min of (a) higher molecular weight and (b)
lower molecular weight \( \tau PP/sPP \) solution blend (S3 + I5) and
presumed \( \tau PP/sPP \) stereoblock via DEZ-mediated polymeriza-
tion in toluene (IS2) and CB (IS4). [Color figure can be viewed in
the online issue, which is available at wileyonlinelibrary.com.]

FIGURE 6 SSA thermographs of selected samples: the solution
blends and the mixed catalysts systems (ISx). [Color figure
can be viewed in the online issue, which is available at
wileyonlinelibrary.com.]

FIGURE 7 CRYSTAF profiles of low molecular weight solution
blend (S3 + I5) and reactor blend with DEZ (IS2) and without
DEZ (IS1) in toluene and (IS4) with DEZ in CB. DEZ is in indi-
cated as Zn. [Color figure can be viewed in the online issue,
which is available at wileyonlinelibrary.com.]
the \( C_2 \)-symmetric catalyst, which might result in a stronger interaction with the CTA than the \( C_2 \)-symmetric catalyst, leading to longer syndiotactic sequences. HT HPLC results show similar characteristics (Fig. 8). When the polymers are synthesized in the absence of DEZ, the three expected peaks were detected (two for \( iPP \) and one for \( sPP \)). The blends show a similar pattern, although the peaks at high elution volume somehow overlap for the low molecular weight blend. Remarkably, the peak around 6 mL, that is, at intermediate elution volume, was completely absent for materials made in toluene in the presence of DEZ (IS2). Like in CRYSTAF, the absorption of this stereoblock seems slightly dominated by the \( sPP \) segments (main elution peak around 7.5 mL). Importantly, the reactor blend produced in CB (IS4) that did not crystallize during CRYSTAF analysis eluted in HPLC, like an \( iPP \). This is in line with its predominantly isotactic structure also observed by WAXD and \( ^{13} \)C NMR (vide infra, Table 4). An undisputable proof that a true \( iPP \)-\( sPP \) stereoblock PP is formed is provided by \( ^{13} \)C NMR spectroscopy. However, the pentad level does not allow distinction between the stereoblock junctions and the isolated stereoeerrors in either the \( iPP \) or \( sPP \) blocks (Scheme 2). In addition to the \( iPP \)-\( sPP \) stereoblock junction (\( C_2 \) to Zn to \( C_\alpha \) or \( C_\alpha \) to Zn to \( C_2 \)) the \( iPP \)-\( iPP \) stereoblock junction also has to be considered (\( C_2 \) to Zn to \( C_2 \)).

In contrast, going further into the \textit{mmm} centered heptads would allow distinction between isolated stereodefects in \textit{iPP} (\textit{mmm} + \textit{mmm} \textit{mmm}) isolated stereodefects in \textit{sPP} (\textit{mmm} + \textit{rmr} \textit{mmm}) and \textit{iPP}-\textit{sPP} stereoblock junctions (\textit{mmm} + \textit{mrmr} \textit{mmm}). In fact, the \textit{iPP}-\textit{sPP} block junction has the unique diagnostic \textit{mmm} \textit{mmm} \textit{mmm} heptad, which is not present in other microstructural elements. Similarly, the \textit{iPP}-\textit{iPP} block junction has the unique diagnostic \textit{mmm} \textit{mmm} \textit{mmm} heptad.

To increase resolution of routine measurements, non-standard signal processing was applied (at the expense of line-shape). Therefore, the proof is limited to identification via qualitative detection of diagnostic heptads (Fig. 9).

This being said, evidence of all expected structures (Scheme 2) is visible from the pentad distribution of the blocky systems presented in Table 4. Significant amounts of defects in some of the samples do not hamper the ability of these materials to crystallize (e.g., IS4), indicating the formation of stereoblock microstructures. For this sample, the qualitative \textit{iPP}-\textit{sPP} stereojunction is the clearest (Fig. 9, zoomed-in region to the right).

Importantly, it can be confirmed that predominantly syndiotactic systems were formed, with only IS4 revealing a majority isotactic backbone. This feature is well in line with the outcome of the CRYSTAF analysis, especially for IS2, for which the ratio of \textit{rmmm} to \textit{mmm} \textit{mmm} is about 4/1. Different rates of chain transfer between the \( C_\alpha \) and \( C_2 \)-symmetric catalysts could explain this finding, as already mentioned above. Indeed, the decrease in molecular weight is more pronounced with the \( C_2 \)-symmetric catalyst, which is possibly more prone to reversible transfer and thus gives rise to shorter blocks as a result of the weaker interaction with the CTA. Another explanation could be an increased termination for the \( C_\alpha \)-symmetric catalyst, leading to a fraction of chains with no isotactic segment. However, this seems to be ruled out by CRYSTAF analysis that shows the presence of only one population of macromolecules for each IS\textsubscript{x} sample. To corroborate the differences already observed between the solution blends and reactor blends, the morphology of the materials was investigated. Preliminary observation was performed by applying a thermal history similar to DSC in Optical Microscopy (Figs. 10 and 11).

When considering the high molecular weight samples, namely, blend \( i1 \) + \( s1 \) and IS1, similar ill-defined morphologies were formed when cooled from the melt at 10 °C/min (Fig. 10). After isothermal crystallization at 140 °C, apparent

**TABLE 4** Stereosequence Analysis at the Pentad Level of Propylene Polymers, Polymerized Using Either Catalyst 1 or 2

<table>
<thead>
<tr>
<th>Entry</th>
<th>\textit{mmmm}</th>
<th>\textit{mmm}</th>
<th>\textit{mm}</th>
<th>\textit{m}</th>
<th>\textit{x}</th>
<th>\textit{m}</th>
<th>\textit{r}</th>
<th>\textit{m}</th>
<th>\textit{m}</th>
</tr>
</thead>
<tbody>
<tr>
<td>IS1</td>
<td>26.7</td>
<td>0.4</td>
<td>0.7</td>
<td>1.6</td>
<td>1.8</td>
<td>0.3</td>
<td>63.5</td>
<td>4.8</td>
<td>0.3</td>
</tr>
<tr>
<td>IS2</td>
<td>17.2</td>
<td>0.7</td>
<td>0.8</td>
<td>1.6</td>
<td>1.7</td>
<td>0.4</td>
<td>70.2</td>
<td>7.2</td>
<td>0.3</td>
</tr>
<tr>
<td>IS3</td>
<td>1.8</td>
<td>0.7</td>
<td>1.3</td>
<td>3.1</td>
<td>16.1</td>
<td>2.4</td>
<td>52.9</td>
<td>20.8</td>
<td>0.9</td>
</tr>
<tr>
<td>IS4</td>
<td>41.0</td>
<td>3.6</td>
<td>2.3</td>
<td>3.7</td>
<td>14.4</td>
<td>4.8</td>
<td>13.8</td>
<td>14.5</td>
<td>1.9</td>
</tr>
</tbody>
</table>
Macrophase separation was obtained in both cases, as expected for (solution and reactor) blends of relatively high molecular weight iPP and sPP. However, the low molecular weight species all displayed spherulitic morphologies upon crystallization from the melt at 10 °C/min, although of very different shape and size. This

**Scheme 2** Relevant microstructure elements and associated n-ad sequences, where ES represents isolated defects related to enantiomorphous site control mechanism and BS relating to the chain back-skip mechanism (or site epimerization). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

**Figure 9** Full scale (left) P_{11} region, (middle) methyl region, and (right) mmrr region of the $^{13}$C NMR spectra of solution and reactor blends and reference iPP and sPP.
observation can be correlated to the presence of distribution of defects. The biggest spherulites were formed in the solution blend $S_3 + I_5$, whereas for IS2 (binary reactor system in the presence of DEZ), only relatively ill-defined microspherulites were present. IS4, of lower molecular weight, had a needle-like morphology, sometimes obtained in very low molecular weight iPP. Even after annealing (for 2 h at 140 °C), no macro/microphase separation occurred in any of those samples (Fig. 12).

The spherulitic growth rates of blend $S_3 + I_5$ and IS2 were evaluated. At 140 °C, the growth rate of the blend was measured to be $\sim 0.011 \ \mu m/s$, a value two times higher than the one of IS2, which was estimated to be $\sim 0.0069 \ \mu m/s$. This result indicates that the chains of the reactor blend are hampered in their crystallization. This finding is coherent with a blocky microstructure where the covalently bonded blocks hamper each other’s crystallization.

CONCLUSIONS

CCTP (or more accurately, chain shuttling polymerization) was investigated for the formation of PP stereoblock copolymers using a binary system of metallocenes exhibiting different stereoselectivities. Standard reaction conditions were selected in order to study the influence of the presence versus absence of diethyl zinc (DEZ), as well as the effect of a more polar solvent on the chain transfer. Low molecular weight iPP-sPP stereoblocks were obtained upon addition of DEZ and clear proof of such microstructure was obtained by a combination of techniques. In fact, clear differences between reactor blends (mixed catalysts) and reference solution blends (of single catalysts) emerge. The main achievement of the present study is that the addition of DEZ leads to the quasi-sole formation of stereoblocks (one population) as demonstrated, for example, by the CRYSTAF profiles. Importantly, the $mmmrrr$ heptad corresponding to the $iPP$-$sPP$ junction is qualitatively visible in the $^{13}C$ NMR spectra in these cases. However, due to the differences in rate of chain transfer and/or termination between the selected catalysts, more syndiotactic sequences than isotactic ones were

FIGURE 10 Optical micrograph of the blend $S_1 + I_1$, obtained after the following thermal history: heated up to 180 °C (at 50 °C/min, held for 6 min) then quenched to 140 °C (at 30 °C/min), held for 20 min to allow slow crystallization and then cooled down to RT at 10 °C/min. An identical picture was obtained for IS1. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

FIGURE 11 Optical micrographs obtained after cooling at 10 °C/min from the relaxed melt (6 min at 180 °C). The scale bars are all 50 μm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
ally, the hypothesis of the presence of stereoblock structures obtained, or at least longer syndiotactic segments. Additional- investigations.

The high concentration of defects calculated by pentad analysis in 13C NMR. The impact of such a complex microstructure on the physical properties definitely deserves further investigations.

ACKNOWLEDGMENTS

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REFERENCES AND NOTES