# Microstructural analysis of polypropylenes polymerized with Ziegler–Natta catalysts without external donors

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The molecular structure of three isotactic polypropylenes polymerized using either slurry or bulk process and heterogeneous Ziegler–Natta catalysts without external donors was studied in this work. The influence of external donor addition was also examined. The samples were fractionated according to stereoregularity using a solvent gradient extraction method, and calorimetric properties, $^{13}C$ nuclear magnetic resonance (n.m.r.) pentad tacticities and molecular weights of the fractions were determined. Statistical analysis was also applied to the $^{13}C$ n.m.r. results. The samples polymerized with the novel catalyst system had the conventional stereostructure arising from a catalyst-site-controlled propagation mechanism. When compared with commercial polypropylenes, the amount of clustered defects was increased in the products made with the novel catalyst system. The addition of an external donor diminished the amount of highly atactic material, but the isotacticity of long-chain material was also increased. Qualitatively similar defects were detected in all samples, only the amount of defects varied depending on the catalyst structure and polymerization process used. Surprisingly, the bulk polymerization process seemed to favour the formation of non-isotactic material.

**(Keywords: isotactic polypropylene; Ziegler–Natta catalysts; microstructural analysis)**

## INTRODUCTION

With $MgCl_2/TiCl_4$ catalysts high activities are reached, but their stereospecificities are poor without the addition of electron donors[1,2]. By a proper choice of donors, one a component of the solid catalyst (internal donor) and the other a component of the co-catalyst mixture with Al trialkyl (external donor), isotacticities over 95% can be reached. Both internal and external donors are thought to be necessary for achieving high stereospecificities, and the performance of a catalyst system depends on the specific internal donor/external donor pair rather than on single donors[3]. The main effects of the donors are the selective poisoning of the centres with low stereospecificity and the activation of isospecific sites[4,5]. It has been suggested that the role of an external donor is, besides deactivating aspecific active centres, to replace the internal donor extracted from $MgCl_2$ surface by an Al alkyl[6].

However, a novel catalyst system, by which high isospecificities are reached using only Al trialkyl as a co-catalyst, has been introduced recently[7,8]. The internal donor of this catalyst system is 2,2-dialkyl-1,3-dimethoxypropane, which is not extractable by Al alkyl because of its strong coordination and 'umbrella'-like shielding effect[7].

We have previously performed a detailed study[9],[10] on the molecular structure of commercial polypropylenes. The structure analyses were carried out on fractions obtained by fractionation according to stereoregularity. In those studies, slight differences in molecular structure were found to exist between samples made by different heterogeneous catalyst systems and different polymerization processes[9]. Those differences had a significant effect on the average sequence length of isotactic chains[9], and crystallization and melting behaviour was also influenced by the chain defects[10].

In this work the same fractionation technique was applied to the characterization of polypropylenes polymerized with the novel catalyst system, by which a high isospecific activity is reached without external donors. The samples studied were polymerized using two different 2,2-dialkyl-1,3-dimethoxypropanes as internal donors[7]. The influence of external donor addition on the chain stereostructure was also examined. For evaluation of the possible influence of polymerization process on stereoregularity, two samples made by the same catalyst but different processes were analysed. Statistical analysis was applied on the pentad tacticities obtained for each sample and their fractions by $^{13}C$ n.m.r. spectroscopy. Characterization results are compared with those previously obtained for commercial samples[9,10].

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## EXPERIMENTAL

### *Materials*

The catalyst used in the preparation of polypropylenes (PPs) F and G was prepared by heating a mixture of $MgCl_2{\cdot}3C_2H_5OH$ (24.5 g), $TiCl_4$/heptane (600 ml, volume ratio 1:1) and 2,2-diisobutyl-1,3-dimethoxypropane (5 ml) to 105°C. After 1 h the mixture was filtered and the solid product contacted with $TiCl_4$ (300 ml) for 1 h at 120°C. The final product was further washed with heptane at +80°C and dried in a nitrogen stream at room temperature. 2,2-Dihexyl-1,3-dimethoxypropane was used as an internal donor in the preparation of PPs H and I. In the preparation of sample I, cyclohexylmethyldimethoxysilane was used as an external donor with an Al/donor ratio of 2. Preparation of the catalysts and the polymerization procedures are described in detail in ref. 7 (see also *Table 1*).

### *Fractionations*

Fractionations were carried out according to stereostructure using the procedure described in ref. 9. Now the amount of polypropylene was around 10 g in each fractionation, whereas the amount of solvent/non-solvent mixture was retained at 300 ml per fraction. Fractionations were performed on a reactor powder without first precipitating the samples, as was previously done with the pelleted polypropylenes[9]. The recoveries in the fractionations were 96.4–100.0% (note that the recoveries were slightly increased by the antioxidant added in the washing step after precipitation).

### *Analysis of polypropylenes and their fractions*

The differential scanning calorimetry (d.s.c.) and size exclusion chromatography (s.e.c.) methods used in the characterization of the unfractionated polymers and their fractions have been described earlier[9,10]. The n.m.r. procedure applied for the unfractionated samples H and I and their fractions was the one described in ref. 9. $^{13}C$ n.m.r. spectra of samples F and G and their fractions were recorded at 140°C on a Varian Unity-400 instrument operating at 100.577 MHz. In these measurements, a relaxation time of 6.0 s and a 45° pulse of 8.0 $\mu$s were used, the other parameters being the same as described for the JEOL GSX-400 instrument in ref. 9. For samples F and G, the curve fitting was done using Varian software.

## RESULTS AND DISCUSSION

### *Fractionation*

The isotacticities of the three samples polymerized by a catalyst system with only Al alkyl as a co-catalyst were high; the heptane insolubles of these samples varied between 95 and 97% (*Table 1*). The addition of an external donor raised the amount of heptane insolubles, whereas the overall productivity was decreased.

The four polypropylenes were fractionated under similar conditions using a solvent gradient extraction method. Already the different solubilities of the samples in the fractionation step can be taken as an indication of their different stereoregularities. Sample I, even though it had the lowest molecular weight, was poorly soluble and, for example, only 20% of it was dissolved when the percentage of solvent in the solvent/non-solvent mixture was 67% (fraction I/11). For sample G, only 57% of solvent was needed to dissolve the same percentage of the material (fraction G/6) (see *Table 2*). Thus, the solubility in fractionation was dependent on the polymerization process, and the addition of external donor lowered the solubility. When compared with the fractionations of the commercial samples[9], which were originally obtained in a pelleted form and precipitated for the fractionation, the solubilities were lower now because of the restricted solvent diffusion into the reactor powder.

### *Thermal analysis*

As was reported in ref. 10, crystallization and melting properties are mainly dependent on isotacticity, and they can be used as rough estimates for it. Some differences in crystallization and melting temperatures and enthalpies were found to exist between the fractions of the four samples studied in this work (*Table 2*). Those differences were especially pronounced for the crystallization temperatures ($T_c$) (*Figure 1*). Fractions of samples F and G, which were polymerized with 2,2-diisobutyl-1,3-dimethoxypropane as an internal donor in their catalyst system,

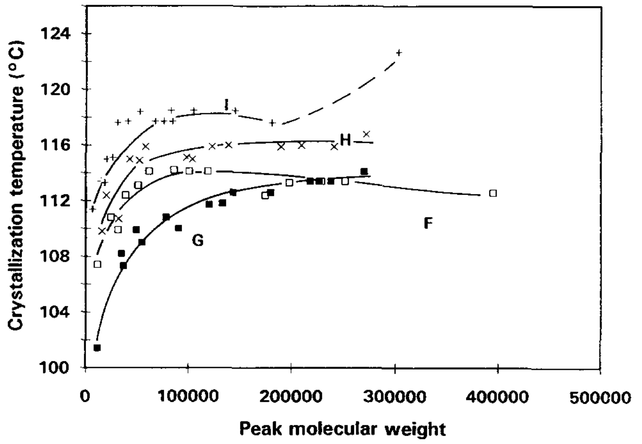

**Figure 1** Crystallization temperature of the fractions as a function of peak molecular weight $(\bar{M}_w\bar{M}_n)^{1/2}$: (■) sample G; (□) sample F; (×) sample H; and (+) sample I

**Table 1** Catalyst systems and polymerization processes used in preparation of the polypropylenes. Product characterization of the polypropylenes

| PP code | Process | R in internal donor[a] | External donor | Activity (kg PP/g catalyst) | Melt flow rate (g/10 min) | Total $C_7$-insolubles (%) |
|---|---|---|---|---|---|---|
| F | Slurry | i-$C_4H_9$ | None | 15.7 | 3.2 | 96.2 |
| G | Bulk | i-$C_4H_9$ | None | 36.3 | 3.4 | 97.1 |
| H | Slurry | n-$C_6H_{13}$ | None | 10.2 | 3.8 | 95.1 |
| I | Slurry | n-$C_6H_{13}$ | CMMS[b] | 5.6 | 4.3 | 97.2 |

[a] $R_2C(CH_2OCH_3)_2$
[b] Cyclohexylmethyldimethoxysilane

**Table 2** Characteristics of the unfractionated polypropylenes and their fractions[a]

| Sample | Solvent (%) | Cumulative fraction (wt%)[b] | $\bar{M}_w/10^3$ | $\bar{M}_w/\bar{M}_n$ | $T_c$ (°C) | $\delta H_c$ (J g$^{-1}$) | $T_{m1}$ (°C) | $T_{m2}$ (°C) | Crystallinity (%) |
|---|---|---|---|---|---|---|---|---|---|
| **F** | | | **516** | **7.8** | **114.0** | **92.7** | **161.3** | – | **46.0** |
| **F/1** | **40.0** | **1.0** | **22** | **3.4** | **107.4** | **57.0** | **138.9** | **149.8** | **27.9** |
| **F/2** | **43.3** | **3.6** | **46** | **3.6** | **110.8** | **64.4** | **145.5** | **155.5** | **31.6** |
| F/3 | 46.7 | 5.9 | 58 | 3.4 | 109.9 | 59.1 | 144.7 | 154.7 | 28.3 |
| F/4 | 50.0 | 8.0 | 65 | 2.8 | 112.4 | 70.2 | 149.7 | 158.8 | 34.9 |
| F/5 | 53.3 | 10.2 | 86 | 2.9 | 113.1 | 71.8 | 151.4 | 159.7 | 34.7 |
| **F/6** | **56.7** | **12.2** | **108** | **3.1** | **114.1** | **72.1** | **152.2** | **160.5** | **34.5** |
| F/7 | 60.0 | 14.2 | 100 | 2.6 | 114.1 | 76.4 | 153.0 | 161.4 | 38.3 |
| F/8 | 61.7 | 17.5 | 144 | 2.8 | 114.2 | 84.6 | 155.5 | 161.3 | 41.0 |
| F/9 | 63.3 | 23.0 | 177 | 3.1 | 114.1 | 85.2 | 156.3 | n.p.[c] | 41.5 |
| **F/10** | **65.0** | **30.0** | **198** | **2.8** | **114.1** | **85.0** | **158.0** | – | **41.2** |
| **F/11** | **66.7** | **39.8** | **325** | **3.4** | **112.4** | **88.5** | **159.6** | – | **43.5** |
| F/12 | 68.3 | 50.0 | 362 | 3.4 | 113.3 | 87.0 | 159.6 | – | 42.4 |
| F/13 | 70.0 | 56.5 | 412 | 3.3 | 113.4 | 90.0 | 160.4 | – | 44.6 |
| F/14 | 71.7 | 61.1 | 472 | 3.5 | 113.4 | 87.8 | 160.4 | – | 43.4 |
| **F/15** | **Decalin** | **77.9** | **862** | **4.8** | **112.6** | **91.8** | **162.8** | – | **44.2** |
| F/16 | Decalin | 96.1 | 745 | 4.9 | n.d.[d] | n.d. | n.d. | n.d. | n.d. |
| **G** | | | **415** | **4.6** | **109.8** | **86.7** | **162.2** | – | **42.4** |
| **G/1** | **40.0** | **1.2** | **23** | **3.7** | **101.4** | **43.7** | **134.0** | **145.6** | **20.2** |
| **G/2** | **43.3** | **5.0** | **67** | **3.7** | **108.3** | **61.5** | **144.8** | **155.6** | **30.2** |
| G/3 | 46.7 | 8.9 | 68 | 3.3 | 107.3 | 54.8 | 144.0 | 154.8 | 26.0 |
| G/4 | 50.0 | 11.5 | 83 | 2.8 | 109.9 | 65.7 | 148.9 | 158.9 | 32.2 |
| **G/5** | **53.3** | **14.2** | **91** | **2.7** | **109.0** | **68.8** | **149.7** | **158.8** | **33.7** |
| G/6 | 56.7 | 18.0 | 127 | 2.6 | 110.8 | 75.1 | 153.9 | 161.3 | 36.5 |
| G/7 | 60.0 | 22.4 | 141 | 2.4 | 110.0 | 73.9 | 153.9 | 161.3 | 38.2 |
| **G/8** | **61.7** | **28.3** | **192** | **2.5** | **111.7** | **85.9** | **156.4** | **n.p.** | **41.7** |
| G/9 | 63.3 | 35.5 | 210 | 2.5 | 111.8 | 81.9 | 157.2 | – | 41.8 |
| G/10 | 65.0 | 42.6 | 228 | 2.5 | 112.6 | 82.4 | 158.8 | – | 41.9 |
| **G/11** | **66.7** | **50.7** | **287** | **2.5** | **112.6** | **89.1** | **160.4** | – | **43.3** |
| G/12 | 68.3 | 61.1 | 344 | 2.5 | 113.4 | 87.9 | 161.3 | – | 43.7 |
| G/13 | 70.0 | 72.3 | 358 | 2.5 | 113.4 | 90.7 | 162.1 | – | 44.8 |
| **G/14** | **71.7** | **81.3** | **382** | **2.6** | **113.4** | **91.2** | **163.7** | – | **45.4** |
| G/15 | Decalin | 92.6 | 470 | 3.0 | 114.1 | 92.0 | 165.4 | – | 44.3 |
| **H** | | | **367** | **6.0** | **115.6** | **89.4** | **161.2** | – | **45.0** |
| **H/1** | **40.0** | **1.0** | **31** | **3.7** | **109.8** | **64.3** | **141.4** | **151.5** | **32.4** |
| **H/2** | **43.3** | **3.8** | **36** | **3.3** | **112.4** | **73.4** | **148.9** | **158.0** | **36.3** |
| H/3 | 46.7 | 6.6 | 56 | 3.1 | 110.7 | 65.8 | 148.1 | 157.2 | 32.3 |
| H/4 | 50.0 | 9.0 | 73 | 3.0 | 115.0 | 78.1 | 152.2 | 160.5 | 35.9 |
| H/5 | 53.3 | 11.8 | 80 | 2.4 | 114.9 | 78.5 | 153.0 | 161.4 | 34.8 |
| **H/6** | **56.7** | **15.0** | **87** | **2.3** | **115.9** | **80.2** | **155.5** | **161.4** | **37.8** |
| H/7 | 60.0 | 19.0 | 148 | 2.3 | 115.1 | 80.5 | 155.5 | 161.3 | 39.9 |
| H/8 | 61.7 | 23.4 | 160 | 2.4 | 115.0 | 82.1 | 157.1 | – | 39.8 |
| **H/9** | **63.3** | **27.3** | **199** | **2.6** | **115.9** | **89.1** | **158.8** | – | **42.7** |
| H/10 | 65.0 | 31.7 | 227 | 2.7 | 116.0 | 88.4 | 158.7 | – | 43.4 |
| **H/11** | **66.7** | **41.2** | **317** | **2.8** | **115.9** | **91.9** | **161.3** | – | **45.3** |
| H/12 | 68.3 | 54.4 | 358 | 2.9 | 116.0 | 94.7 | 161.2 | – | 45.7 |
| H/13 | 70.0 | 64.3 | 421 | 3.1 | 115.9 | 95.3 | 162.9 | – | 45.7 |
| **H/14** | **71.7** | **70.7** | **507** | **3.5** | **116.8** | **95.3** | **163.7** | – | **46.1** |
| H/15 | Decalin | 86.8 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| **I** | | | **302** | **4.7** | **114.0** | **95.5** | **162.9** | – | **46.8** |
| I/1 | 40.0 | 0.4 | 10 | 2.5 | 111.4 | 65.8 | 141.8 | n.p. | 32.8 |
| **I/2** | **43.3** | **1.4** | **25** | **2.8** | **113.4** | **75.6** | **148.0** | **156.4** | **37.7** |
| I/3 | 46.7 | 2.7 | 28 | 2.5 | 113.3 | 74.1 | 148.0 | 156.4 | 36.7 |
| **I/4** | **50.0** | **3.8** | **28** | **1.9** | **115.0** | **78.0** | **150.5** | **158.9** | **38.5** |

*continued*

**Table 2** *continued*

| Sample | Solvent (%) | Cumulative fraction (wt%)[b] | $\bar{M}_w/10^3$ | $\bar{M}_w/\bar{M}_n$ | $T_c$ (°C) | $\delta H_c$ (J g$^{-1}$) | $T_{m1}$ (°C) | $T_{m2}$ (°C) | Crystallinity (%) |
|---|---|---|---|---|---|---|---|---|---|
| I/5 | 53.3 | 5.2 | 36 | 1.9 | 115.1 | 80.1 | 151.3 | 159.7 | 40.5 |
| I/6 | 56.7 | 6.6 | 42 | 1.9 | 117.6 | 82.9 | 153.8 | 160.5 | 40.8 |
| I/7 | 60.0 | 8.3 | 57 | 2.0 | 117.7 | 84.3 | 156.2 | 161.3 | 43.9 |
| I/8 | 61.7 | 11.3 | 74 | 2.0 | 118.4 | 89.0 | 157.1 | – | 44.4 |
| **I/9** | **63.3** | **14.8** | **92** | **1.9** | **117.7** | **85.9** | **158.8** | - | **44.1** |
| I/10 | 65.0 | 18.1 | 108 | 2.0 | 117.7 | 90.5 | 158.7 | - | 44.6 |
| I/11 | 66.7 | 20.2 | 121 | 2.1 | 117.7 | 88.8 | 159.5 | - | 43.8 |
| I/12 | 68.3 | 21.7 | 122 | 2.2 | 118.5 | 87.8 | 160.4 | - | 45.3 |
| I/13 | 70.0 | 24.8 | 155 | 2.2 | 118.5 | 91.7 | 161.2 | - | 46.6 |
| **I/14** | **71.7** | **32.1** | **223** | **2.4** | **118.5** | **94.9** | **162.9** | - | **45.9** |
| **I/15** | **73.3** | **45.7** | **294** | **2.7** | **117.6** | **95.9** | **163.7** | - | **46.5** |
| **I/16** | **Decalin** | **75.8** | **552** | **3.3** | **122.7** | **96.5** | **166.2** | - | **47.9** |
| I/17 | Decalin | 98.8 | n.d.[d] | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |

[a] Samples selected for the sequence analysis are emphasized with bold characters

[b] $\Sigma w_{i-1} + \frac{1}{2} w_i$, $w_0 = 0$

[c] n.p. = shoulder on the right-hand side of the melting endotherm, peak temperature not detected

[d] n.d. = not determined

**Table 3** Observed pentad tacticities of the unfractionated polypropylenes and their selected fractions[a]

| Sample | mmmm | mmmr | rmmr | mmrr | mmrm + rmrr | rmrm | rrrr | mrrr | mrrm |
|---|---|---|---|---|---|---|---|---|---|
| F | 87.3 | 4.9 | 0.0 | 3.3 | 1.2 | 0.0 | 1.1 | 0.7 | 1.5 |
| F/1 | 57.9 | 10.9 | 0.9 | 9.9 | 5.8 | 1.1 | 5.1 | 3.4 | 5.0 |
| F/2 | 55.1 | 10.6 | 0.8 | 11.4 | 5.9 | 0.8 | 6.0 | 4.1 | 5.3 |
| F/6 | 72.7 | 6.8 | 0.9 | 7.5 | 3.9 | 0.0 | 3.4 | 1.9 | 2.9 |
| F/10 | 84.8 | 5.0 | 0.0 | 4.6 | 1.8 | 0.0 | 1.5 | 0.7 | 1.6 |
| F/11 | 94.4 | 2.1 | 0.0 | 2.1 | 0.2 | 0.1 | 0.2 | 0.0 | 0.9 |
| F/15 | 96.6 | 1.4 | 0.0 | 1.4 | 0.0 | 0.0 | 0.0 | 0.0 | 0.6 |
| G | 82.3 | 3.1 | 0.6 | 4.3 | 2.4 | 0.6 | 2.6 | 1.8 | 2.3 |
| G/1 | 44.5 | 12.4 | 1.7 | 11.8 | 8.9 | 2.1 | 7.6 | 5.6 | 5.4 |
| G/2 | 44.7 | 12.1 | 1.4 | 13.1 | 7.6 | 1.3 | 8.8 | 5.4 | 5.6 |
| G/5 | 45.7 | 11.0 | 1.1 | 13.4 | 7.3 | 0.7 | 9.2 | 4.9 | 6.7 |
| G/8 | 67.7 | 9.5 | 0.5 | 8.4 | 2.4 | 0.6 | 4.3 | 2.5 | 4.1 |
| G/11 | 90.2 | 2.2 | 0.3 | 2.6 | 2.0 | 0.0 | 0.9 | 0.4 | 1.4 |
| G/14 | 95.4 | 2.1 | 0.0 | 1.6 | 0.2 | 0.0 | 0.0 | 0.0 | 0.7 |
| H | 93.2 | 2.1 | 0.2 | 2.5 | 0.4 | 0.0 | 1.0 | 0.4 | 0.2 |
| H/1 | 51.1 | 10.3 | 0.5 | 11.4 | 7.2 | 0.7 | 7.4 | 4.1 | 7.3 |
| H/2 | 64.8 | 7.7 | 1.0 | 8.8 | 4.2 | 0.4 | 5.2 | 3.4 | 4.5 |
| H/6 | 81.6 | 4.5 | 0.6 | 4.6 | 2.0 | 0.5 | 2.6 | 1.3 | 2.3 |
| H/9 | 88.5 | 2.9 | 0.7 | 3.3 | 0.8 | 0.0 | 1.1 | 0.9 | 1.8 |
| H/11 | 94.5 | 1.9 | 0.0 | 1.9 | 0.2 | 0.0 | 0.6 | 0.1 | 0.8 |
| H/14 | 96.3 | 1.5 | 0.0 | 1.3 | 0.0 | 0.0 | 0.0 | 0.0 | 0.9 |
| I | 94.4 | 1.5 | 0.1 | 1.5 | 0.5 | 0.0 | 0.9 | 0.4 | 0.7 |
| I/2 | 71.3 | 6.9 | 1.1 | 7.0 | 3.6 | 0.0 | 4.4 | 2.4 | 3.3 |
| I/4 | 62.3 | 7.3 | 0.5 | 10.4 | 4.0 | 0.0 | 6.1 | 4.7 | 4.7 |
| I/9 | 86.4 | 3.7 | 0.4 | 3.8 | 1.2 | 0.0 | 1.6 | 1.2 | 1.7 |
| I/14 | 95.3 | 1.9 | 0.0 | 1.9 | 0.0 | 0.0 | 0.0 | 0.0 | 0.9 |
| I/15 | 97.0 | 1.2 | 0.0 | 1.2 | 0.0 | 0.0 | 0.0 | 0.0 | 0.6 |
| I/16 | 98.5 | 0.6 | 0.0 | 0.6 | 0.0 | 0.0 | 0.0 | 0.0 | 0.3 |

[a] Relative error is below 0.5% for mmmm pentads, up to 5% for other pentads

showed lower $T_c$ than the fractions of samples H and I, for which the internal donor was 2,2-dihexyl-1,3-dimethoxypropane. Surprisingly, the fractions of sample G, which was polymerized with a bulk process, has lower $T_c$ and thus probably lower isotacticities than the fractions of the slurry-polymerized sample F with comparable molecular weights. In contrast, the shift between the curves of samples H and I is logical: the addition of an external donor raises the isotacticity of sample I, causing higher $T_c$ values for its fractions.

The crystallization enthalpies ($\delta H_c$) are considerably lowered for the fractions of samples F and G (*Table 2*). Over 60% of sample G had to be collected before the $\delta H_c$ of the fractions reached the value of $90\,J\,g^{-1}$. High-molecular-weight fractions of samples H and I reach the level of commercial samples[10] in their $\delta H_c$ values. Sample I, which was polymerized with a catalyst system having both internal and external donors, had very small amounts of non-isotactic polymer because none of its fractions has a $\delta H_c$ value below $74\,J\,g^{-1}$. In general, based on the $\delta H_c$ measurements and excluding the bulk-polymerized sample G, the polypropylenes made by the new type of catalyst contained lower amounts of very non-isotactic material than the commercial samples. On the other hand, the $\delta H_c$ values of the long-chain material of samples F and G did not reach the values of commercial samples, indicating an increased frequency of defects in those chains. Similar features can be observed when the crystallinities of the fractions are considered (*Table 2*; for commercial samples, see ref. 10.)

### *Microtacticity*

For the determination of the actual chain stereoregularity, six fractions were selected from each sample on the basis of their cumulative weight fractions and molecular weights for $^{13}C$ n.m.r. sequence analyses. The results of these determinations are presented in *Table 3*. A mutual comparison of the sequence distributions of the four samples shows similar features as already observed in the d.s.c. analyses. Fractions of the slurry-polymerized sample F showed higher tacticities than fractions of sample G, which was polymerized with the same catalyst system using a bulk process. This difference cannot only be due to the fact that some atactic material soluble in the reaction medium was removed from the slurry-polymerized polymer, but was left in the bulk-polymerized sample; the fractionation took place according to stereoregularity, and the very non-isotactic material was removed from sample G when the first fractions were collected. However, its fractions with weight-average molecular weights of $(1-3)\times 10^5$ still contained large amounts of chain defects as compared to the fractions of sample F. The types of chain defects seem to be similar in both slurry and bulk polymerizations: in addition to the defect mmmrrmmm characteristics for catalyst- and site-controlled isotactic propagation, some syndiotactic material (rrrr and mrrr pentads) and up to 9% of pentad rmrr (and/or mmrm) were detected (see *Figure 2*). The high amount of mrrr pentads as compared to rrrr sequences, as well as the appearance of syndiotactic material and rmrr pentads only together with mmmr, mmmr and mrrm pentads, indicate that these defects exist as short blocks in isotactic chains. If the heterogeneity between separate chains is considered, it can be assumed that the material is quite homogeneous: for example, the molecular-weight distributions of most fractions of sample G are quite narrow, being around 2.5. It means that there cannot be large variations in tacticity either, because solubility in fractionation is dependent only on these two parameters.

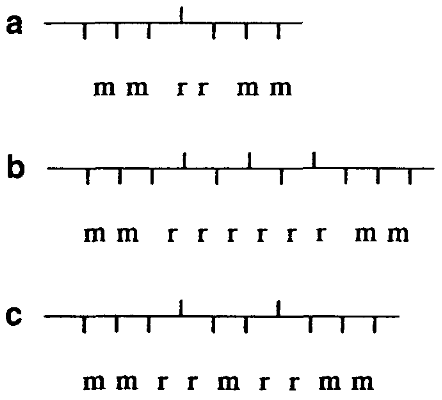

**Figure 2** Some possible structures for the defects in isotactic propagation

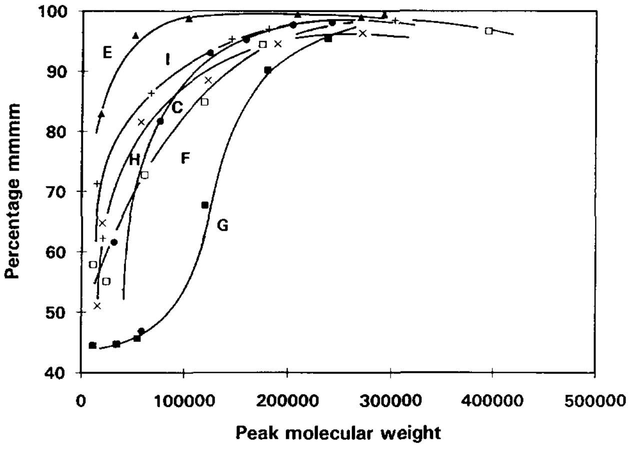

**Figure 3** Pentad tacticities of selected fractions as a function of molecular weight: (■) sample G; (□) sample F; (×) sample H; (+) sample I; (●) sample C; and (▲) sample E

Thus, the differences observed in stereoregularities between the fractions of samples F and G could be due to kinetic reasons: high monomer concentration favours the formation of non-isotactic material. Correspondingly, Pino *et al.*[11], for example, have observed for polymerization carried out in n-heptane with a $MgCl_2/TiCl_4/AlR_3$ catalyst that the dependence of the polymerization rate on monomer concentration was slightly larger for atactic than for isotactic polymer. In general, the change in polymerization temperature has a similar effect on tacticity. Coutinho *et al.*[12], for example, observed a loss of stereospecificity with increase in polymerization temperature. They suggested that the loss of stereocontrol on monomer insertion might be due to the increased vibration level of the catalytic complex.

Some non-isotactic material with a comparably high molecular weight was also found in the bulk-polymerized sample C analysed earlier in our laboratory[9], even though the catalyst system used in the production of this sample obviously contained an external donor (e.g. fraction C/2 had a $\bar{M}_w$ of 126000 and its mmmm fraction was only 46.9%). However, this sample contained 4.2% of n-heptane-soluble short-chain material ($\bar{M}_w = 29\,000$)[13]. It means that only a part of the material produced in non-isospecific centres grow longer. Concerning the high-molecular-weight non-isotactic material, it could be suggested that the 'extra' non-isotactic material, as compared to the slurry-polymerized sample, is not necessarily produced by aspecific sites having higher propagation rates, but it could be formed because the isospecific centres allow the formation of defects more easily. The increased chain transfer reaction to monomer caused by increased monomer concentration[14] can be suggested as one of the reasons for the narrow molecular-weight distribution (*MWD*) of the bulk-polymerized sample.

Based on the sequence analysis, the stereoregulating ability of the catalyst with 2,2-$R_2$-1,3-dimethoxypropane as an internal donor is better for R = n-hexyl than for R = i-butyl. The addition of an external donor raises the stereospecificity of the catalyst. As mentioned before, the very non-stereoregular material was absent on the basis of the $\delta H_c$ measurements carried out on the fractions of sample I. This might be taken as an indication of the external donor deactivating first the most aspecific centres. This explanation is also supported by the lowered productivity for the catalyst system used in the preparation of sample I (*Table 1*). On the other hand, the amount of very non-isotactic material was low in sample H as well, and the isotacticities of long-chain fractions of sample I were higher than those of sample H. Thus, it is probable that the external donor also increases the isospecificity of more isospecific active centres.

Fractions of samples H and I also contained chain defects similar to those observed for samples F and G. Only the frequency of defects varied from one sample to another. The amount of clustered errors (*Figures 2b* and *2c*) is largest in the fractions of sample G. If, for example, fractions with $\bar{M}_w$ around 200 000 are compared, most racemic units in fraction G/8 belong to blocks of defects, while in fraction I/14 only isolated mmmrrmmm defects exist. When samples H and I are compared, it can be stated that the addition of an external donor decreases the amount of both clustered and isolated defects. In commercial samples[9] similar types of defects were usually detected, but blocky defects were concentrated in the few most easily dissolving fractions that usually included less than 10% of the whole sample. Only in the bulk-polymerized sample were traces of clustered defects detected in the $\bar{M}_w$ range $(1\text{–}2) \times 10^5$.

In general, the amount of defects, and conversely the amount of isotactic mmmm pentads, is most informative when different samples are compared. *Figure 3* represents the isotactic pentad fractions of the four samples studied in this work as a function of peak molecular weight. Commercial grades C (bulk-polymerized) and E (gas-phase-polymerized) are also included. A complete sequence analysis for the fractions of these two samples, both polymerized with $MgCl_2$-supported high-yield catalyst systems, can be found in ref. 9. Cumulative weight fractions are not presented in the figure, but, for example, the fractions of sample G had mmmm fractions below 46% still when 14% of the material was collected (fraction G/5). In contrast, for example, less than 9% of sample E had an mmmm pentad fraction lower than 80%.

The influence of chain defects is clearly observed in the melting peaks of the fractions. As was observed earlier for the commercial polypropylenes[10,15], fractions with clustered defects showed double melting peaks due to some reorganization during the melting scan. Fractions of samples F–H showed double melting peaks up to $\bar{M}_w = (1.5\text{–}1.9) \times 10^5$ (*Table 2*), while fractions of sample I showed single melting peaks after $\bar{M}_w = 60\,000$. Fractions containing isolated mmmrrmmm defects showed single melting peaks, probably because this kind of defect can be easily incorporated in the crystalline structure.

### *Statistical analysis*

Statistical analysis was also applied to the $^{13}C$ n.m.r. sequence distribution data. Several models suggesting multiple catalytic sites, each producing different components, have been suggested in the literature[16–19]. The components of these models have different stereoregularities, and usually broad *MWD*s are also attributed to several catalytic sites. Statistical analysis of the data obtained in this work was performed using combinations of Bernoullian (B)[20] and enantiomorphic-site (E)[21] reaction probability models. Either two-site (E/B) or three-site (E/E/B and E/B/B) models were applied.

The optimum values of the parameters of these combined models were obtained by iterative fitting calculation. The parameters and the observed and calculated pentad distributions are listed in *Table 4* for selected fractions of sample F. When the two-site model (E/B) was applied, an $\alpha$ value of 0.98 and $\sigma$ of 0.22 were obtained, indicating that the enantiomorphic site was highly isospecific, and the Bernoullian site produced mainly syndiotactic polymer. These values are comparable to those obtained for commercial polypropylenes, when the two-site model was applied to each fraction separately[9]. When a three-site model with one enantiomorphic and two Bernoullian sites (E/B/B) was applied, a slightly better fit between observed and calculated distributions was obtained (*Table 4*). Now the values of the parameters indicated that one highly isospecific, one completely syndiospecific and one aspecific site were present. Weight fractions of the material produced in the syndiospecific sites ($B_1$) were below 4% for each fraction. Based on this model, the non-isotactic material was mainly produced in the atactic sites ($B_2$). According to any of these three models, the last fractions of sample F only contained material produced in the enantiomorphic, highly isospecific sites.

Distinctly best fit between experimental and calculated values was obtained when the E/E/B model with two enantiomorphic and one Bernoullian site was applied. The parameters of the model indicated an appearance of one type of highly isospecific enantiomorphic ($E_1$), one less-isospecific enantiomorphic ($E_2$) and an aspecific, mainly syndiotactic, Bernoullian site (B). Now the weight fractions of the material produced in the aspecific sites were below 10% for each fraction. For samples H and I the Bernoullian sites were completely syndiotactic (*Table 5*) and the amount of material produced in these sites was below 6% for each fraction (*Table 6*). Thus, the heterotactic material was produced in the less-isospecific enantiomorphic sites, and there were no purely atactic-producing (Bernoullian) centres on the catalyst surface. Non-Bernoullian distributions for atactic polypropylene have also been detected by other authors[22], but usually one type of atactic and one or more types of isotactic centres are thought to be present[11,13].

One difference between the observed and calculated sequence distributions is in the amount of rmrm pentad. This pentad is present only in the spectra of the first two fractions according to experimental observations, but

**Table 4** Observed and calculated sequence distributions for selected fractions of sample F, and optimum values of the parameters for the multiple-site models[a]

| | | Model | | |
|---|---|---|---|---|
| | Observed | E/B | E/B/B | E/E/B |
| F/1 | | | | |
| mmmm | 57.9 | 61.7 | 58.5 | 57.8 |
| mmmr | 10.9 | 3.3 | 6.6 | 10.2 |
| rmmr | 0.9 | 1.0 | 2.3 | 1.0 |
| mmrr | 9.9 | 4.6 | 6.2 | 10.4 |
| mmrm + rmrr | 5.8 | 7.1 | 9.1 | 5.0 |
| rmrm | 1.1 | 1.9 | 4.5 | 1.9 |
| rrrr | 5.1 | 11.5 | 5.5 | 5.2 |
| mrrr | 3.4 | 6.6 | 4.2 | 3.3 |
| mmrm | 5.0 | 2.3 | 3.1 | 5.2 |
| F/2 | | | | |
| mmmm | 55.1 | 59.1 | 55.8 | 55.0 |
| mmmr | 10.6 | 3.2 | 6.9 | 10.6 |
| rmmr | 0.8 | 1.0 | 2.4 | 1.0 |
| mmrr | 11.4 | 4.7 | 6.4 | 10.9 |
| mmrm + rmrr | 5.9 | 7.8 | 9.7 | 5.4 |
| rmrm | 0.8 | 2.1 | 4.8 | 2.1 |
| rrrr | 6.0 | 12.6 | 6.4 | 5.9 |
| mrrr | 4.1 | 7.2 | 4.4 | 3.7 |
| mrrm | 5.3 | 2.3 | 3.2 | 5.4 |
| F/6 | | | | |
| mmmm | 72.7 | 72.3 | 73.0 | 72.6 |
| mmmr | 6.8 | 3.6 | 4.9 | 6.7 |
| rmmr | 0.9 | 0.6 | 1.3 | 0.6 |
| mmrr | 7.5 | 4.4 | 4.7 | 6.9 |
| mmrm + rmrr | 3.9 | 4.5 | 5.2 | 3.1 |
| rmrm | 0.0 | 1.2 | 2.6 | 1.2 |
| rrrr | 3.4 | 7.1 | 3.5 | 3.3 |
| mrrr | 1.9 | 4.1 | 2.4 | 2.1 |
| mrrm | 2.9 | 2.2 | 2.4 | 3.5 |
| F/10 | | | | |
| mmmm | 84.8 | 85.0 | 84.8 | 84.6 |
| mmmr | 5.0 | 3.9 | 3.7 | 4.3 |
| rmmr | 0.0 | 0.2 | 0.5 | 0.3 |
| mmrr | 4.6 | 4.1 | 3.6 | 4.4 |
| mmrm + rmrr | 1.8 | 1.3 | 2.1 | 1.5 |
| rmrm | 0.0 | 0.4 | 1.0 | 0.6 |
| rrrr | 1.5 | 1.9 | 1.5 | 1.2 |
| mrrr | 0.7 | 1.1 | 1.0 | 0.9 |
| mrrm | 1.6 | 2.1 | 1.8 | 2.2 |
| F/11 | | | | |
| mmmm | 94.4 | 89.5 | 92.7 | 94.4 |
| mmmr | 2.1 | 4.0 | 2.8 | 2.0 |
| rmmr | 0.0 | 0.0 | 0.0 | 0.1 |
| mmrr | 2.1 | 4.0 | 2.8 | 2.0 |
| mmrm + rmrr | 0.2 | 0.2 | 0.1 | 0.2 |
| rmrm | 0.1 | 0.1 | 0.1 | 0.1 |
| rrrr | 0.2 | 0.1 | 0.0 | 0.1 |
| mrrr | 0.0 | 0.1 | 0.1 | 0.1 |
| mrrm | 0.9 | 2.0 | 1.4 | 1.0 |
| F/15 | | | | |
| mmmm | 96.6 | 89.5 | 92.7 | 96.5 |
| mmmr | 1.4 | 4.0 | 2.8 | 1.4 |
| rmmr | 0.0 | 0.0 | 0.0 | 0.0 |
| mmrr | 1.4 | 4.0 | 2.8 | 1.4 |
| mmrm + rmrr | 0.0 | 0.2 | 0.1 | 0.0 |
| rmrm | 0.0 | 0.1 | 0.1 | 0.0 |
| rrrr | 0.0 | 0.1 | 0.0 | 0.0 |
| mrrr | 0.0 | 0.1 | 0.1 | 0.0 |
| mrrm | 0.6 | 2.0 | 1.4 | 0.7 |
| $E_1$ component, $\alpha$ | | 0.978 | 0.985 | 0.993 |
| $E_2$ component, $\alpha$ | | | | 0.87 |
| $B_1$ component, $\sigma$ | | 0.22 | 0.00 | 0.16 |
| $B_2$ component, $\sigma$ | | | 0.52 | |
| F/1 $\omega(E_1)$ | | 0.69 | 0.60 | 0.25 |
| $\omega(E_2)$ | | | | 0.66 |
| $\omega(B_1)$ | | 0.31 | 0.04 | 0.09 |
| $\omega(B_2)$ | | | 0.36 | |
| F/2 $\omega(E_1)$ | | 0.66 | 0.57 | 0.20 |
| $\omega(E_2)$ | | | | 0.70 |
| $\omega(B_1)$ | | 0.34 | 0.04 | 0.10 |
| $\omega(B_2)$ | | | 0.39 | |
| F/6 $\omega(E_1)$ | | 0.81 | 0.77 | 0.54 |
| $\omega(E_2)$ | | | | 0.40 |
| $\omega(B_1)$ | | 0.19 | 0.02 | 0.06 |
| $\omega(B_2)$ | | | 0.21 | |
| F/10 $\omega(E_1)$ | | 0.95 | 0.91 | 0.76 |
| $\omega(E_2)$ | | | | 0.22 |
| $\omega(B_1)$ | | 0.05 | 0.01 | 0.02 |
| $\omega(B_2)$ | | | 0.08 | |
| F/11 $\omega(E_1)$ | | 1.00 | 1.00 | 0.95 |
| $\omega(E_2)$ | | | | 0.05 |
| $\omega(B_1)$ | | 0.00 | 0.00 | 0.00 |
| $\omega(B_2)$ | | | 0.00 | |
| F/15 $\omega(E_1)$ | | 1.00 | 1.00 | 1.00 |
| $\omega(E_2)$ | | | | 0.00 |
| $\omega(B_1)$ | | 0.00 | 0.00 | 0.00 |
| $\omega(B_2)$ | | | 0.00 | |

[a] $\alpha$ = probability of selecting a *d*(*l*) unit at a *d*(*l*)-preferring site in the enantiomorphic-site propagation model; $\sigma$ = probability of selecting a *meso* dyad configuration in the Bernoullian model site; $\omega(i)$ = weight fraction of the material produced in site *i*

**Table 5** Optimum values of the parameters[a] $\alpha$ and $\sigma$ for the E/E/B model[b]

| | F | G | H | I |
|---|---|---|---|---|
| $\alpha(E_1)$ | 0.993(5) | 0.993(10) | 0.992(3) | 0.996(4) |
| $\alpha(E_2)$ | 0.87(2) | 0.88(3) | 0.82(3) | 0.17(3)[c] |
| $\sigma(B)$ | 0.16(4) | 0.19(3) | 0.03(6) | 0.00(8) |

[a] $\alpha$ = probability of selecting a *d*(*l*) unit at a *d*(*l*)-preferring site in the enantiomorphic-site propagation model; $\sigma$ = probability of selecting a *meso* dyad configuration in the Bernoullian model site

[b] Standard deviation in parentheses: $0.993(5) = 0.993 \pm 0.005$; $0.87(2) = 0.87 \pm 0.02$

[c] $1 - 0.17 = 0.83$

**Table 6** Weight fractions of the materials produced in $E_1$ and B sites according to the E/E/B model[a]

| Fraction | $\omega(E_1)$ | $\omega(B)$ |
|---|---|---|
| F/1 | 0.25(8) | 0.09(2) |
| F/2 | 0.20(8) | 0.10(2) |
| F/6 | 0.54(6) | 0.06(1) |
| F/10 | 0.76(6) | 0.02(1) |
| F/11 | 0.95(6) | 0.00(1) |
| F/15 | 1.00(6) | 0.00(1) |
| G/1 | 0.00(12) | 0.18(3) |
| G/2 | 0.00(12) | 0.18(3) |
| G/5 | 0.02(11) | 0.18(3) |
| G/8 | 0.40(10) | 0.06(2) |
| G/11 | 0.89(12) | 0.02(2) |
| G/14 | 0.98(13) | 0.00(2) |
| H/1 | 0.28(4) | 0.06(2) |
| H/2 | 0.50(4) | 0.04(1) |
| H/6 | 0.77(3) | 0.02(1) |
| H/9 | 0.88(3) | 0.01(1) |
| H/11 | 0.97(3) | 0.00(1) |
| H/14 | 1.00(3) | 0.00(1) |
| I/2 | 0.56(5) | 0.03(1) |
| I/4 | 0.42(6) | 0.05(2) |
| I/9 | 0.80(4) | 0.01(1) |
| I/14 | 0.95(4) | 0.00(1) |
| I/15 | 0.98(4) | 0.00(1) |
| I/16 | 1.00(3) | 0.00(1) |

[a] Standard deviation in parentheses: $0.25(8) = 0.25 \pm 0.08$

traces of this pentad are found in calculated distributions of high-molecular-weight fractions. The equal amount of calculated mmmr and mmrr pentads indicates that those pentads arise from mmmrrmmm type of defect, and the structure mmmrmmm, which is forbidden for the catalyst-site-controlled propagation, is not included.

The optimum values of the parameters for the E/E/B model for all four samples are listed in *Tables 5* and *6*. *Table 5* shows that the values of $\alpha(E_1)$ and $\alpha(E_2)$ are similar for all samples. Only sample I, which was polymerized by a catalyst system containing an external donor, had a slightly increased $\alpha(E_1)$ value. Thus, according to the E/E/B model, the external donor acts by raising the isospecificity of isospecific active centres. On the other hand, the isospecificity of $E_2$ sites was lowered in samples H and I, and, as was mentioned before, the Bernoullian sites produced purely syndiotactic material.

As was mentioned before, the amount of material produced in the syndiospecific Bernoullian sites (B) was low for samples H and I. In contrast, almost 20% of the first fractions of the bulk-polymerized sample G was produced in the Bernoullian sites. The amounts of material produced in the two types of enantiomorphic sites differed from one sample to another. The fractions G/1, G/2 and G/5 contained around 80% of material produced in the less-isospecific ($E_2$) sites, whereas, for example, only the first fraction of sample H was mainly produced in these sites.

Even though an excellent agreement was obtained between experimental and calculated values when the E/E/B model was applied, some caution is needed when this model is thought to describe a real propagation reaction. Based on the results obtained now and those previously obtained for commercial samples[9,13], high-molecular-weight fractions contain small amounts of syndiotactic material. Thus, it is probable that syndiotactic chains are not produced by syndiospecific centres originally present on the catalyst surface and remaining unchanged throughout the chain growth. Syndiotactic material is more likely produced when an active centre (reversibly) 'switches' from isospecific to syndiotactic, thus producing a syndiotactic block or chain end in an originally isotactic chain. The E/E/B model cannot separate these blocks from syndiotactic material produced in syndiospecific centres originally present on the catalyst surface. The positioning of heterotactic material in the most non-isotactic polymer, whether it exists as blocks along isotactic chains or as separate chains, remains unsolved as well. This kind of situation might be better described using 'consecutive' models introduced recently for elastomeric polypropylenes by Cheng *et al.*[24].

## CONCLUSIONS

The analyses performed now support our previous results[10], according to which d.s.c. methods can be used for the evaluation of polymer isotacticity. The values obtained by d.s.c. correlated well with the $^{13}C$ n.m.r. pentad tacticities.

The novel catalyst type studied in this work produced material with the conventional stereostructure arising from a catalyst-site-controlled propagation mechanism. The stereospecificity of this catalyst type was high even without external donors, but it was further raised by the addition of a small amount of an external donor. The increase in isotacticity was probably due to both external donor selectively poisoning the most atactic centres and increasing the isotacticity of more isospecific centres. Slight differences in polymer stereoregularity were also detected depending on which alkyl group (i-butyl or n-hexyl) was used in the internal donor, 2,2-dialkyl-1,3-dimethoxypropane.

Defects in isotactic propagation were qualitatively similar for samples made by different catalysts, and only the frequency of defects and the amount of occurrence of clustered defects varied from one sample to another. When compared with polypropylenes produced with a catalyst system containing both internal and external donors, the high-molecular-weight material produced with the new catalyst type still contained more defects in chain stereostructure. The polymerization process seemed to influence remarkably the polymer stereoregularity, the bulk process favouring the formation of non-isotactic material. These differences in stereoregularities are thought to be due to kinetic factors.

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