Microstructural analysis of polypropylenes produced with heterogeneous Ziegler–Natta catalysts

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Microstructural analysis was carried out on five isotactic polypropylenes produced with different heterogeneous Ziegler–Natta catalyst systems and different polymerization processes. The samples were fractionated according to stereostructure using a direct extraction method. Pentad tacticities of unfractionated samples and selected fractions were determined by ^{13}C n.m.r. spectroscopy. I.r. isotacticities were also measured. Statistical analysis of the polymerization mechanism was carried out on the basis of the two-site model from the pentad tacticities, and average lengths of *meso* and *racemic* sequences were determined. In addition to atactic and isotactic materials produced at different catalytic sites, the polypropylene samples contained syndiotactic material as stereoblocks in isotactic chains. On the basis of the analysis carried out on the fractions, slight differences in the microstructure were found to exist between the samples produced by different processes and catalyst types. These differences have a significant effect on average sequence lengths.

(Keywords: isotactic polypropylene; Ziegler–Natta catalysts; fractionation; ^{13}C n.m.r.; tacticity)

INTRODUCTION

Polypropylenes produced with different polymerization processes and catalyst types have different processabilities and end-use properties. These differences in properties arise largely from differences in molecular structure, i.e. molecular weight distribution and stereostructure of the chain. However, processing conditions also have an effect. Since testing of end-use properties is expensive and requires large amounts of material, stereostructure analysis is often carried out, and the final properties are predicted on the basis of these results. Stereostructure analysis is most accurately performed by ^{13}C n.m.r. spectroscopy. This method gives the actual stereochemical order of the chain and provides useful information about the polymerization mechanism.

Several authors have studied the influence of catalyst type on stereostructure[1–3]. The influence of the polymerization process has not been so widely investigated. Usually the structure of the whole polymer has been studied. In some studies the polymer has been divided into heptane-soluble and heptane-insoluble fractions and these have been characterized separately[1,2]. Studies of these two fractions have increased our knowledge about the polymerization. Several statistical models have been used to describe the propagation (Bernoullian, first and second order Markovian, enantiomorphic etc.[4]). In many cases, at least two different types of active centres are needed to explain the results. The possibility of more than two types of active centre has also been proposed. Kakugo *et al.*[3] suggested that one atactic and two types of isospecific centres are present in their heterogeneous catalyst system. Kissin[5] proposed a continuous distribution of active centres with different stereospecificity.

In the case of continuous tacticity distribution, a separation of atactic and isotactic material simply by heptane extraction is not possible and a more thorough fractionation is required. In this work the polypropylene samples were divided into several fractions for the study of the tacticity distribution in molecular chains of various lengths. Polypropylenes were fractionated according to stereostructure using a solvent gradient direct extraction method. Molecular weights and molecular weight distributions of the whole samples and the fractions were determined using size exclusion chromatography (s.e.c.) and the whole polymers and selected fractions were submitted for ^{13}C n.m.r. sequence analysis. Sequence distributions were examined by determining average sequence lengths of *meso* and *racemic* additions and using statistical analysis. For statistical analysis 'the two-site model', a combination of Bernoullian and enantiomorphic models, was selected. I.r. isotacticities of the fractions were also determined and studied as a function of average sequence length.

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EXPERIMENTAL

Materials

The samples analysed in this study were isotactic polypropylenes produced by different processes and with different heterogeneous Ziegler–Natta catalyst systems (see *Table 1*). Four samples were commercially available film grades with a melt flow rate of around 3 g/10 min. The fifth sample was polymerized in a laboratory slurry process using a novel choice of an internal donor in the polymerization catalyst[6].

Fractionation

Samples of about 5 g were fractionated according to stereostructure using a direct extraction method[7,8]. The dissolution time per fraction was 15 min and 300 ml of solvent/non-solvent mixture was used per fraction. The amount of solvent in these mixtures varied from 40 to 77%. Xylene/ethyleneglycol monoethyl ether was used as the solvent/non-solvent pair and the fractionation temperature was 125°C. No removal of atactic material was carried out before fractionation. Fifteen fractions were first collected from each sample. If the last fraction contained more than 40% of the material, the fractionation was continued and the last fraction was divided into four further fractions. The recovery was 95–98% when 15 fractions were collected. After partial refractionation, the total recovery was 88–89%.

Analysis of polymers and their fractions

In determining catalyst residues, the contents of metallic elements were analysed using atomic absorption spectroscopy. X-ray fluorescence was used for Cl analysis. The molecular weights and molecular weight distributions of the whole samples and fractions were determined at 135°C using a Millipore Waters 150C ALC/GPC instrument. The solvent used was 1,2,4-trichlorobenzene (TCB) and three Tosoh TSK-Gel GMHXL-HT columns were applied. For n.m.r. measurements samples were dissolved at 110–160°C in a 9:1 mixture of TCB and hexadeuterobenzene. Proton decoupled (NOE) ^{13}C n.m.r. spectra were recorded at 150°C on a Jeol GSX-400 instrument operating at 100.4 MHz. A spectral width of 7000 Hz, an acquisition time of 1.198 s with 32 k data points, a relaxation time of 9.5 s and a 45° pulse of 9.3 μs were used to collect 2000 scans. All spectra were baseline corrected. Curve fitting was done using the NMR1 program supplied by New Methods Research. Lorenzian line shape function was fitted to the methyl carbon resonances. I.r. isotacticity was determined from melt pressed films with a thickness of 0.045 ± 0.005 mm on a Nicolet 510 FTIR spectrometer. Bands at 998 and 974 cm^{-1} were used as a measure of isotactic helix content and a reference, respectively. I.r. absorbance ratios, $A(998)/A(974)$, were calibrated with tacticity values obtained by n.m.r. spectroscopy[7,9].

RESULTS AND DISCUSSION

For structural analysis, five PP samples produced with different processes and catalyst systems (*Table 1*) were fractionated in 15–18 fractions using a solvent gradient extraction technique. Several fractions (each 1–8% by weight) were collected from the non-stereoregular, low-molecular-weight part of the polymer. Larger fractions were obtained from the high-molecular-weight material. The molecular-weight averages and molecular-weight distributions (MWDs) of the fractions were determined by s.e.c. (*Table 2*). Based on these analysis results and cumulative weight fractions, six to seven fractions of each sample were selected for the ^{13}C n.m.r. analysis. The characteristics of the whole polymers and their selected fractions are listed in *Table 2*. I.r. isotacticities were determined when possible (molecular weight and isotacticity high enough).

The first few fractions collected from each sample had a very low average molecular weight and a broad MWD (an example is shown in *Figure 1*). Pentad tacticities determined by n.m.r. spectroscopy (*Tables 3* and *4*) indicated that the high polydispersity was probably due to syndiotactic material present in these fractions. After about 10–15% of the polymer was collected, the non-stereoregular material had dissolved and the fractionation proceeded according to molecular weight. The high molecular weight fractions had lower polydispersities and only small differences could be observed in their stereostructure.

The change in the stereostructure with increasing molecular weight is presented in *Figure 2* for the fractions of sample B. After the first fractions, the number of propagation errors diminishes and in the spectrum of the last dissolved fraction only signals from the propagation error *mmrrmm* are observed. Characteristic for this sample was a relatively high stereoregularity of low-molecular-weight fractions. On the other hand, long chain molecules (fractions B/13, B/14 and B/16) still contained syndiotactic *rrrr* sequences, as well as traces of *rmmr* and *rmrr* sequences. Signals *rmmr* and *rmrr* indicate that propagation errors are grouped together in a 'blocky' manner. However, the actual length and position of these blocks within the chain cannot be determined; syndiotactic or heterotactic sequences can be located either in the chain ends or between isotactic sequences.

Chain defects in high-molecular-weight polymer may be explained by low internal donor concentration used

Table 1 Polymerization processes and catalyst types used in preparation of polypropylenes. Catalyst residues in polypropylene samples

Sample	Process	Catalyst system[a]	Ash (%)	Al ($mg\,kg^{-1}$)	Mg ($mg\,kg^{-1}$)	Ti ($mg\,kg^{-1}$)	Cl ($mg\,kg^{-1}$)
A	Gas-phase	HY	0.052	116	94	29	50
B	Slurry (lab. process)	HY	0.022	80	12	1	35
C	Bulk	HY	0.013	48	6	1	14
D	Slurry	LY	0.010	12	1	15	<10
E	Gas-phase	HY	0.013	45	12	3	40

[a] HY = $TiCl_3$ or $MgCl_2$-supported; LY = first generation catalyst system

in the polymerization catalyst. The appearance of these defects is still surprising when compared with the results of Busico *et al.*[2], who investigated the stereostructure of polypropylenes produced by several $MgCl_2$-supported catalyst systems with different Lewis bases. The heptane-insoluble fractions of those polypropylenes had similar stereochemical composition containing only *mmrrmm* defects, irrespective of which Lewis base was used in the polymerization catalyst, or even when no Lewis base was used as an internal donor.

The stereoregularities of the fractions from all five samples are summarized in *Tables 3* and *4* and in *Figure 3*. Because the fractions obtained from different samples had different polydispersities, the peak molecular weight $\sqrt{\bar{M}_n \bar{M}_w}$ was used in *Figure 3*. A common feature for all samples was that in addition to isotactic and atactic polymer they contained syndiotactic material. The

Table 2 Characteristics of polypropylene samples studied and the fractions selected for structural analysis

Sample	Fraction (wt%)	Cumulative fraction (wt%[a])	$\bar{M}_w \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$	I.r. isotacticity (%)
A			405	5.4	95.7
A/1	5.3	2.7	34	3.5	n.d.[b]
A/2	2.0	6.3	42	3.9	68.6
A/6	3.9	11.9	87	2.3	94.5
A/9	5.6	27.1	135	2.2	96.4
A/11	3.7	36.6	192	2.4	94.7
A/14	17.1	55.3	323	2.6	96.1
A/15	36.2	81.9	749	3.7	97.9
B			462	6.0	94.2
B/1	2.8	1.4	22	3.1	n.d.
B/8	2.1	12.7	79	2.2	79.9
B/13	1.8	21.3	116	2.3	87.9
B/14	14.9	36.2	228	2.6	91.9
B/16	4.4	58.5	317	2.8	91.4
B/18	36.6	81.7	651	3.2	95.4
C			355	4.7	92.7
C/1	8.5	4.3	61	3.7	64.5
C/2	3.0	10.0	126	4.6	56.9
C/6	4.9	17.5	120	2.5	91.4
C/8	5.8	27.9	192	2.4	93.0
C/11	5.9	44.2	241	2.3	95.3
C/12	21.9	58.1	308	2.3	96.1
C/13	29.3	83.7	380	2.5	98.5
D			386	5.6	95.7
D/1	4.7	2.4	27	3.0	n.d.
D/2	3.0	6.1	56	4.2	64.0
D/4	1.4	10.0	103	4.8	n.d.
D/11	7.0	31.0	178	2.5	94.7
D/13	4.9	43.1	225	2.5	94.9
D/15	43.6	74.0	562	3.1	94.3
E			397	5.5	96.3
E/2	1.6	8.3	37	4.0	74.1
E/9	1.9	19.5	73.	2.0	95.2
E/13	2.8	29.6	149	2.1	96.9
E/15	21.8	48.9	460	2.9	95.9
E/16	6.2	66.0	335	2.6	95.5
E/18	30.0	85.0	491	2.8	94.5

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

[b] n.d. = not determined

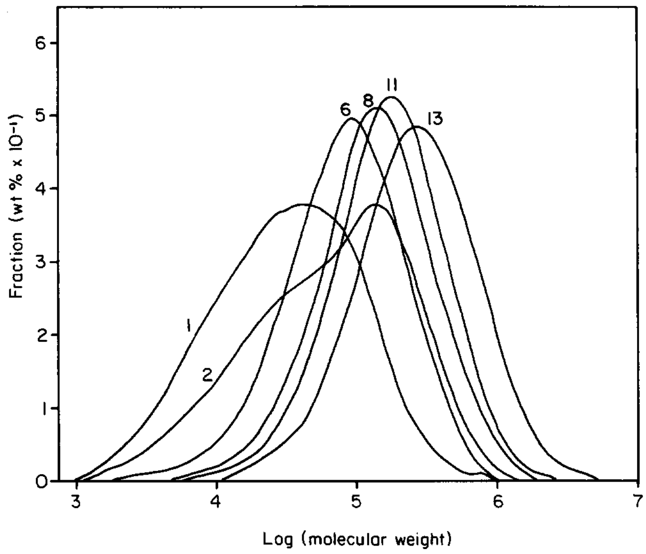

Figure 1 Molecular weight distribution curves of selected fractions of sample C

Table 3 Observed and calculated (in parentheses)[a] pentad tacticities of polypropylene A and its selected fractions

Sample	*mmmm*[b]	*mmmr*	*rmmr*	*mmrr*	*mmrm* + *rmrr*	*rmrm*	*rrrr*	*rrrm*	*mrrm*
A	0.925	0.021	0.003	0.020	0.009	0.000	0.007	0.006	0.009
	(0.925)	(0.019)	(0.001)	(0.021)	(0.002 + 0.006)	(0.003)	(0.007)	(0.006)	(0.010)
A/1	0.575	0.087	0.021	0.100	0.062	0.021	0.051	0.038	0.045
	(0.575)	(0.088)	(0.011)	(0.098)	(0.013 + 0.046)	(0.023)	(0.051)	(0.046)	(0.049)
A/2	0.533	0.093	0.017	0.104	0.058	0.008	0.095	0.047	0.045
	(0.533)	(0.094)	(0.008)	(0.100)	(0.010 + 0.047)	(0.016)	(0.095)	(0.047)	(0.050)
A/6	0.936	0.021	0.003	0.020	0.004	0.000	0.001	0.003	0.012
	(0.936)	(0.021)	(0.001)	(0.022)	(0.002 + 0.002)	(0.002)	(0.001)	(0.002)	(0.011)
A/9	0.959	0.016	0.000	0.017	0.000	0.000	0.000	0.000	0.008
	(0.959)	(0.016)	(0.000)	(0.017)	(0.000)	(0.000)	(0.000)	(0.000)	(0.008)
A/11	0.965	0.014	0.000	0.015	0.000	0.000	0.000	0.000	0.006
	(0.965)	(0.014)	(0.000)	(0.014)	(0.000)	(0.000)	(0.000)	(0.000)	(0.007)
A/14	0.970	0.012	0.000	0.012	0.000	0.000	0.000	0.000	0.006
	(0.970)	(0.012)	(0.000)	(0.012)	(0.000)	(0.000)	(0.000)	(0.000)	(0.006)
A/15	0.975	0.010	0.000	0.010	0.000	0.000	0.000	0.000	0.005
	(0.975)	(0.010)	(0.000)	(0.010)	(0.000)	(0.000)	(0.000)	(0.000)	(0.005)

[a] Based on two-site model. Optimum values of parameters for the calculation are listed in *Table 5*

[b] Relative error in the experimental values of *mmmm* pentads is below 0.5%, in other pentads up to 5%. The accuracy of three significant figures is applied because the pentad distributions presented here were used as initial values in calculating the parameters of the two-site model (see *Table 5*)

Table 4 Observed pentad distributions of polypropylenes B–E and their selected fractions

Sample	*mmmm*[a]	*mmmr*	*rmmr*	*mmrr*	*mmrm*+*rmrr*	*rmrm*	*rrrr*	*rrrm*	*mrrm*
B	0.888	0.029	0.005	0.029	0.010	0.000	0.016	0.009	0.014
B/1	0.730	0.065	0.000	0.087	0.032	0.000	0.038	0.016	0.032
B/8	0.775	0.044	0.000	0.061	0.036	0.000	0.032	0.024	0.028
B/13	0.820	0.050	0.015	0.056	0.022	0.000	0.020	0.000	0.017
B/14	0.934	0.019	0.002	0.019	0.004	0.000	0.008	0.004	0.010
B/16	0.936	0.018	0.002	0.020	0.003	0.000	0.010	0.001	0.010
B/18	0.981	0.006	0.001	0.008	0.000	0.000	0.000	0.000	0.004
C	0.896	0.029	0.002	0.028	0.007	0.000	0.017	0.008	0.013
C/1	0.616	0.062	0.023	0.083	0.058	0.021	0.062	0.032	0.043
C/2	0.469	0.099	0.000	0.130	0.084	0.000	0.105	0.051	0.062
C/6	0.817	0.046	0.006	0.055	0.000	0.000	0.026	0.026	0.024
C/8	0.930	0.022	0.000	0.026	0.001	0.000	0.008	0.002	0.011
C/11	0.952	0.020	0.000	0.018	0.000	0.000	0.000	0.000	0.010
C/12	0.977	0.010	0.000	0.010	0.000	0.000	0.000	0.000	0.003
C/13	0.981	0.008	0.000	0.008	0.000	0.000	0.000	0.000	0.003
D	0.903	0.023	0.004	0.022	0.012	0.000	0.018	0.007	0.011
D/1	0.671	0.066	0.043	0.059	0.053	0.000	0.043	0.029	0.036
D/2	0.460	0.092	0.040	0.115	0.067	0.015	0.095	0.060	0.056
D/4	0.533	0.054	0.000	0.095	0.041	0.048	0.159	0.037	0.033
D/11	0.961	0.017	0.000	0.012	0.000	0.000	0.003	0.001	0.006
D/13	0.969	0.018	0.000	0.010	0.000	0.000	0.000	0.000	0.003
D/15	0.982	0.007	0.000	0.009	0.000	0.000	0.000	0.000	0.002
E	0.921	0.016	0.006	0.019	0.011	0.000	0.011	0.006	0.010
E/2	0.830	0.067	0.000	0.065	0.008	0.000	0.015	0.000	0.015
E/9	0.960	0.013	0.000	0.019	0.000	0.000	0.000	0.000	0.008
E/13	0.988	0.004	0.000	0.004	0.000	0.000	0.002	0.000	0.002
E/15	0.991	0.004	0.000	0.004	0.000	0.000	0.000	0.000	0.001
E/16	0.995	0.002	0.000	0.002	0.000	0.000	0.000	0.000	0.001
E/18	0.995	0.002	0.000	0.002	0.000	0.000	0.000	0.000	0.001

[a] See footnote *b* in *Table 3*

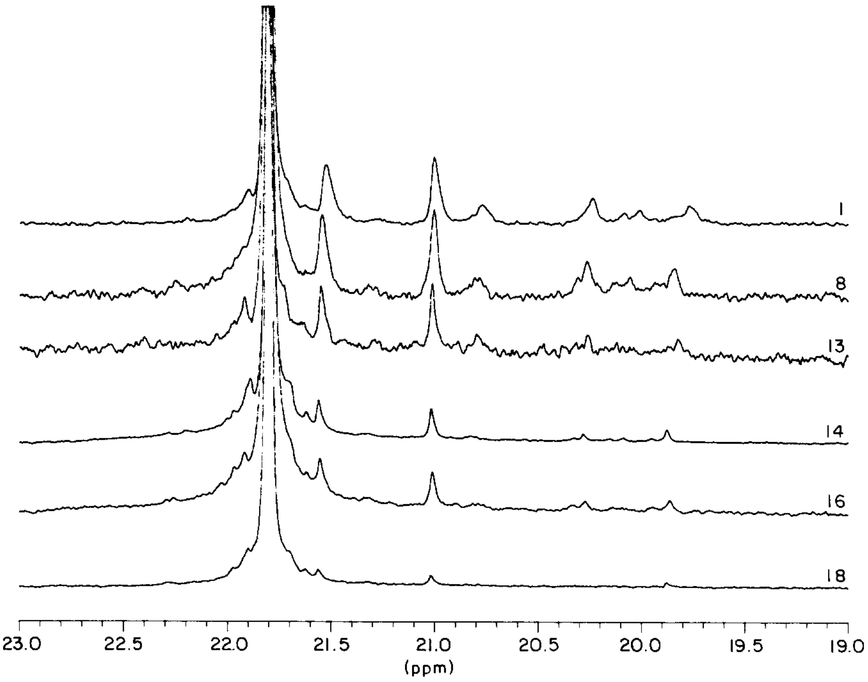

Figure 2 Change in the stereostructure with increasing molecular weight for selected fractions of sample B

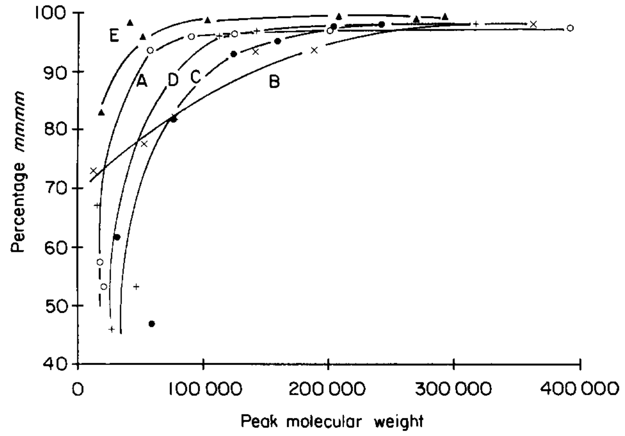

Figure 3 Pentad tacticities of polypropylene fractions as a function of molecular weight: ○, sample A; ×, sample B; ●, sample C; +, sample D; and ▲, sample E

percentage of syndiotactic sequences was not highest in the first fraction but reached a higher value after the first fraction had been collected (e.g. fractions A/2, C/2 and D/4). Since the easily dissolved syndiotactic material was not dissolved in the first solvent/non-solvent mixture, a stereoblock nature can be suggested for its structure. Syndiotactic sequences occur as blocks in the same chain with relatively long isotactic sequences, the latter making this material poorly soluble.

As mentioned before, sample B, which was made in a laboratory slurry process using an $MgCl_2$-supported high-yield catalyst, had several types of chain defects even in high-molecular-weight material. A similar feature was also observed for the relatively high-molecular-weight fractions of sample C. This bulk-polymerized sample had a slightly narrower MWD than the other samples and fractions with very low molecular weight were not obtained from it. The fractions of the two gas-phase polymerized samples, A and E, were non-isotactic only when the molecular weight was low, long polymer chains containing only *mmrrmm* propagation errors. Especially in the high-molecular-weight fractions of sample E, the amount of defects of any kind was barely detectable. Sample D was the only polypropylene produced by a first-generation catalyst system. The results obtained indicate that this catalyst type is also capable of producing stereoregular high-molecular-weight polymer.

A statistical analysis of the polymerization mechanism was carried out from the pentad tacticities based on the two-site model[10,11]. According to this model, polymer fractions consist of two parts: atactic material produced at a catalytic site obeying Bernoullian statistics, and isotactic material originating from an enantiomorphic site-model-controlled catalytic site. The optimum values of the three parameters of this model[10,11] were determined by an iterative fitting calculation (*Table 5*) and are defined as follows: α = probability of selecting a *d*(*l*)-unit at a *d*(*l*)-preferring site in the enantiomorphic-site propagation model; ω = weight fraction of the polymer produced at enantiomorphic sites; and σ = probability of selecting a *meso* dyad configuration in the Bernoullian model site. Pentad stereosequence distributions were calculated using the best-fitting values of α, ω and σ and compared with observed distributions. Because of the large number of fractions investigated in this study, calculated sequence distributions are presented only for one of the samples (sample A in *Table 3*).

Table 5 Optimum values of the parameters[a] for the two-site model[b]

Sample	α	ω	σ
A	0.990 (1)	0.97 (1)	0.31 (8)
A/1	0.934 (4)	0.81 (2)	0.29 (2)
A/2	0.921 (3)	0.81 (1)	0.17 (2)
A/6	0.990 (3)	0.99 (7)	0.49 (50)
A/9	0.991 (1)	1.00 (1)	–[c]
A/11	0.993 (1)	1.00 (1)	–
A/14	0.994 (1)	1.00 (1)	–
A/15	0.995 (1)	1.00 (1)	–
B	0.985 (1)	0.96 (1)	0.21 (4)
B/1	0.954 (3)	0.92 (2)	0.18 (6)
B/8	0.971 (3)	0.89 (2)	0.26 (5)
B/13	0.972 (5)	0.95 (2)	0.30 (13)
B/14	0.990 (2)	0.98 (1)	0.18 (22)
B/16	0.990 (1)	0.99 (1)	0.09 (4)
B/18	0.996 (1)	1.00 (1)	–
C	0.985 (1)	0.97 (1)	0.16 (2)
C/1	0.950 (5)	0.80 (2)	0.26 (3)
C/2	0.899 (9)	0.79 (4)	0.17 (4)
C/6	0.971 (8)	0.95 (4)	0.18 (14)
C/8	0.988 (1)	0.99 (1)	0.06 (8)
C/11	0.990 (1)	1.00 (1)	–
C/12	0.995 (1)	1.00 (1)	–
C/13	0.996 (1)	1.00 (1)	–
D	0.988 (1)	0.96 (1)	0.20 (3)
D/1	0.961 (9)	0.82 (4)	0.31 (8)
D/2	0.904 (9)	0.76 (4)	0.22 (4)
D/4	0.935 (10)	0.75 (4)	0.11 (4)
D/11	0.993 (1)	1.00 (1)	–
D/13	0.993 (1)	1.00 (5)	–
D/15	0.996 (1)	1.00 (1)	–
E	0.992 (1)	0.96 (1)	0.27 (8)
E/2	0.966 (7)	0.99 (8)	0.00 (96)
E/8	0.997 (1)	1.00 (1)	–
E/13	0.998 (1)	1.00 (1)	–
E/15	0.998 (1)	1.00 (1)	–
E/16	0.999 (1)	1.00 (1)	–
E/18	0.999 (1)	1.00 (1)	–

[a] α = probability of selecting a *d*(*l*)-unit at a *d*(*l*)-preferring site in the enantiomorphic-site propagation model; ω = weight fraction of the polymer produced at enantiomorphic sites; σ = probability of selecting a *meso* dyad configuration in the Bernoullian model site

[b] Standard deviation is given in parentheses: 0.990 (1) = 0.990 ± 0.001; 0.97 (1) = 0.97 ± 0.01

[c] Value not defined, because $\omega = 1$

For high-molecular-weight fractions, good fits between observed and calculated distributions were obtained. For low-molecular-weight fractions, the deviations were larger because these fractions contained syndiotactic material. Thus, on the basis of these results, long-chain isotactic material can be considered to be produced at isospecific active sites, as proposed in the two-site model. In contrast, the two-site model is inadequate for describing the stereocontrol in the polymerization of non-isotactic material.

A more detailed examination of the values of the parameters α, ω and σ shows that low-molecular-weight polymer produced at the Bernoullian sites was mainly syndiotactic (*Table 5*). For the high-molecular-weight fractions σ becomes poorly defined when ω approaches a value of 1 (see equations in refs 10 and 11). A comparison of the values of α for the fractions obtained from each sample confirms that the fractionation proceeded according to tacticity. Some differences in the values of α between the samples were also observed. The catalyst used in preparation of sample E contained isospecific sites capable of producing highly stereoregular polymer. Although sample D contained syndiotactic-rich

Table 6 Number-average sequence lengths of *meso* and *racemic* additions for the whole polymers and their fractions

Sample	Average sequence length/propene units[a]			
	m_{obsd}	m_{calcd}	r_{obsd}	r_{calcd}
A	62	62	2.5	2.5
A/1	9	9	2.5	2.6
A/2	9	8	3.2	3.2
A/6	68	71	2.1	2.0
A/9	123	121	2.0	2.0
A/11	137	138	2.0	2.0
A/14	159	163	2.0	2.0
A/15	196	202	2.0	2.0
B	43	44	2.9	2.9
B/1	21	16	2.8	2.8
B/8	27	19	2.7	2.8
B/13	21	26	2.6	2.7
B/14	80	79	2.7	2.8
B/16	83	88	2.9	3.0
B/18	265	268	2.0	2.0
C	52	50	3.0	3.0
C/1	10	10	2.6	2.9
C/2	9	7	3.0	3.1
C/6	31	26	3.1	2.9
C/8	86	76	2.7	2.6
C/11	98	102	2.0	2.0
C/12	195	211	2.0	2.0
C/13	255	261	2.0	2.0
D	51	53	3.0	3.1
D/1	10	12	2.7	2.7
D/2	6	6	2.9	3.0
D/4	11	10	3.7	4.5
D/11	113	136	2.6	2.5
D/13	108	154	2.0	2.0
D/15	272	265	2.0	2.0
E	57	61	2.7	2.8
E/2	26	28	2.8	2.4
E/8	147	121	2.8	2.4
E/13	497	497	3.0	3.0
E/15	554	570	2.0	2.0
E/16	998	998	2.0	2.0
E/18	998	998	2.0	2.0

[a] Observed (m_{obsd} and r_{obsd}) and calculated (m_{calcd} and r_{calcd}) number-average sequence lengths were obtained from observed and calculated pentad sequence distributions (see *Tables 3* and *4*)

short-chain polymer, its high-molecular-weight fractions had higher values of α than fractions from samples B and C with comparable cumulative weight fractions (e.g. fractions D/11, B/14 and C/8).

Average sequence lengths of *meso* and *racemic* additions were evaluated for each fraction from pentad tacticities[12,13]. The results are reported in *Table 6*. Average *meso* sequence length was defined as:

$$m=\frac{mmmm+3*\frac{1}{2}mrrr+2rmmr+\frac{1}{2}rmrm+\frac{1}{2}rmrr}{\frac{1}{2}rmrm+\frac{1}{2}rmrr+rmmr+\frac{1}{2}mmmr} \qquad (1)$$

and average *racemic* sequence length as:

$$r=\frac{rrrr+3*\frac{1}{2}mrrr+2mrrm+\frac{1}{2}rmrm+\frac{1}{2}mmrm}{\frac{1}{2}rmrm+\frac{1}{2}mmrm+mrrm+\frac{1}{2}mrrr} \qquad (2)$$

As the signals of *mmrm* and *rmrr* pentads overlap in the spectrum, and only the sum (*mmrm*+*rmrr*) is obtained, areas used for these two pentads in 'observed' sequence length calculations were attained by dividing the sum (*mmrm*+*rmrr*) into two equal parts. When theoretical sequence distributions were calculated using the parameters of the two-site model, separate values for *mmrm* and *rmrr* pentads were obtained. If the average sequence lengths obtained from the calculated pentad distributions (m_{calcd} and r_{calcd} in *Table 6*) are compared with 'observed' values (m_{obsd} and r_{obsd}), only slight deviations are noticed, indicating that the approximation made for 'observed' sequence lengths is valid.

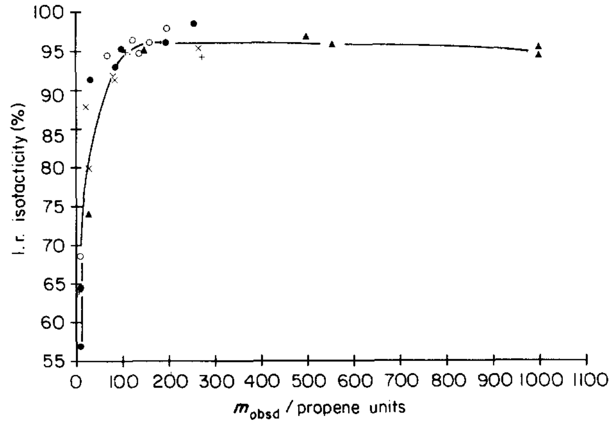

Figure 4 I.r. isotacticity values of the fractions as a function of observed average sequence length of *meso* additions (m_{obsd}). For symbols, see *Figure 3*

When average *meso* sequence lengths for fractions from different samples are compared, it is found that small differences in pentad tacticities have a remarkable effect on sequence lengths. Highly stereospecific sample E has an average *meso* sequence length four to five times larger for the last fractions than comparable fractions from other samples. Average lengths of *racemic* sequences vary in a limited range of 2 to 4.5. However, the average length of racemic sequences does not necessarily give the actual length of syndiotactic stereoblocks, because the *racemic* sequence lengths obtained now are mean values for mixtures of atactic, syndiotactic and low-molecular-weight isotactic materials or stereoblock polymer. Thus, the existence of longer syndiotactic sequences is still possible in low-molecular-weight fractions. For isotactic fractions containing only *mmrrmm* propagation errors, the sequence length of *racemic* additions approaches a value of 2.

In *Figure 4* i.r. isotacticity values from *Table 2* are presented as a function of 'observed' average sequence length of *meso* additions. A relatively good correlation between these two parameters is obtained, irrespective of the fact that the fractions from different samples have different molecular weights and molecular-weight distributions. The i.r. absorbance band at 998 cm^{-1}, which was used as a measure of isotactic helix content in these measurements, has been linked to regular 3_1 helices of 10–12 monomer units[14]. *Figure 4* shows that a constant level of i.r. isotacticity is obtained when m_{obsd} is above 80 propene units.

CONCLUSIONS

The fractionation method used in this study made it possible to divide the samples into several fractions differing in stereostructure. The influence of the polymerization process on the stereostructure and the nature of active centres could be evaluated on the basis of structural analyses carried out on the fractions.

Isotactic polypropylenes produced with heterogeneous Ziegler–Natta catalyst systems contain small amounts of atactic and syndiotactic material. At least part of the syndiotactic material exists as stereoblocks in the same chains with isotactic sequences. Although a first generation catalyst system produced material rich in atactic and syndiotactic polymer, it was stereospecific in producing long-chain isotactic polymer. Slight differences in stereoregularity were found between the samples produced by high-yield catalysts using different polymerization processes. Small amounts of chain irregularities significantly decreased the average *meso* sequence length.

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