Thermal behaviour of polypropylene fractions: 1. Influence of tacticity and molecular weight on crystallization and melting behaviour

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Five isotactic polypropylenes, produced by different polymerization processes and with different heterogeneous catalyst systems, were fractionated according to stereoregularity. One of the samples was also fractionated according to molecular weight, to obtain a set of narrow fractions of different molecular weights. Crystallization and melting behaviours of the whole samples and the fractions were studied as a function of tacticity and molecular weight. Crystallization and melting experiments were performed using d.s.c. For tacticity determinations $FTi.r.$ spectroscopy was applied. The thermal properties studied in this work were mostly dependent on tacticity and a linear correlation between crystallinity and i.r. isotacticity was found. In the main part of the molecular weight range studied ($\bar{M}_w \sim 22\,000$–$947\,000$) molecular weight had no or only a small influence on crystallization behaviour. In addition to detecting correlations between thermal properties and molecular structure, small differences between the samples produced with different processes and catalyst systems were also observed.

INTRODUCTION

The study of the thermal properties of polymers by calorimetric methods (d.s.c.) has become widespread during the last two decades. The simple and rapid operation and small sample masses make the study of crystallization and melting processes easy to accomplish by this method. The melting and crystallization behaviour of isotactic polypropylene crystallized in different ways has been widely studied[1–13]. Calorimetric properties have also been examined as possible indirect measures for tacticity of polymers with side-groups. Burfield et al.[1] studied thermal properties in an attempt to establish a calorimetric index for polypropylene isotacticity. They found correlations between both crystallization and melting properties and isotacticity, crystallization enthalpy being the most reproducible measure. Molecular weight also had some influence on crystallization and melting temperatures, especially melting temperature, which increased with increasing molecular weight. According to Martuscelli et al.[2,3], molecular weight distribution (MWD) affected crystallization rate. However, tacticity was one of the main factors determining this property. The fractions of varying stereoregularity used in these studies were obtained mainly by successive extractions with hydrocarbon solvents. More recent work

by Janimak et al.[5–8] utilized polypropylene fractions with similar molecular weights and MWDs but different isotacticities in examining the influence of isotacticity on crystallization and melting behaviour. Their studies included changes in the crystalline structures with changes in isotacticity, as well as the effect of isotacticity on linear crystal growth and morphology of the polymer.

The main aim of this work was to obtain a better understanding of the influence of both isotacticity and molecular weight on crystallization and melting behaviour. The samples investigated were high molecular weight polypropylenes and their fractions were obtained by fractionation according to either stereoregularity or molecular weight. In this paper their crystallization and melting temperatures and crystallinities measured by d.s.c. are correlated with i.r. isotacticity and molecular weight. A more detailed study of the multiple melting endotherms found for some fractions will be presented in the following paper.

EXPERIMENTAL

A series of fractions obtained by fractionation of five high molecular weight (melt flow rate ≈ 3 g/10 min) polypropylenes produced with different polymerization processes and different heterogeneous Ziegler–Natta catalyst systems (*Table 1*) was used in this study. All samples were

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Table 1 Polymerization processes and catalyst systems used in the production of the polypropylenes. ^{13}C n.m.r. spectroscopic triad tacticities of the samples

Sample	Catalyst system	Process	mm	mr (%)	rr
A	HY[a]	Gas-phase	94.9	3.0	2.1
B	HY	Slurry (lab. process)	92.2	3.9	3.9
C	HY	Bulk	92.7	3.5	3.8
D	LY[b]	Slurry	93.0	3.5	3.5
E	HY	Gas-phase	94.4	2.9	2.7

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

fractionated according to stereoregularity using a direct extraction method[14,15]. Fourteen fractions were first collected from each sample using a xylene/ethylene glycol monoethyl ether solvent system, and the undissolved residue was dissolved in decalin at 145°C. If the decalin-dissolved fraction contained more than 40% of the material, the fractionation was continued and the last fraction was divided into four further fractions. One of the samples (A) was also fractionated according to molecular weight using ethylene glycol monobutyl ether/diethylene glycol monobutyl ether as a solvent/non-solvent pair[15]. This fractionation was also carried out without first removing any atactic material. In fractionation according to molecular weight the fractionation temperature was 159°C and the total recovery was 97.0%.

The molecular weights and molecular weight distributions of the whole samples and their fractions were determined at 135°C on a Millipore Waters 150C ALC/GPC instrument. Three Tosoh TSK-Gel GMHXL-HT columns were applied and the solvent used was 1,2,4-trichlorobenzene (TCB). The ^{13}C n.m.r. spectroscopic pentad distributions were determined for some selected fractions obtained by fractionation according to stereoregularity, and they are reported elsewhere[14]. The ^{13}C n.m.r. spectroscopic triad tacticities presented here (*Table 1*) for the whole polymers were calculated from pentad tacticities. Infra-red isotacticities were determined from melt pressed films with a thickness of 0.050 ± 0.005 mm on a Nicolet 510 FTi.r. spectrometer. Bands at 998 and 974 were used in calculating the absorbance ratio (A_{998}/A_{974}). Infra-red absorbance ratios were calibrated with ^{13}C n.m.r. spectroscopic triad tacticities[15,16]. For some fractions of very low isotacticity or low molecular weight i.r. isotacticity values were not obtained, because the films prepared from them were too sticky or brittle to be measured. For some fractions the amount of the sample was not adequate for film pressing. Otherwise, two films were prepared from each fraction and the mean value for the absorbance ratio was calculated.

Crystallization times at 120°C were measured with a Perkin–Elmer DSC-7 instrument. Samples of 9–11 mg were melted at 225°C (5 min) and then cooled at a rate of 75°C min^{-1} to 120°C. The crystallization time was detected as the peak maximum.

Crystallization and melting temperatures and crystallinities were determined on a Mettler TA 3000 DSC 30 instrument. To obtain a similar thermal history for each sample, samples (3 mg) were first heated from 30 to 200°C at a rate of 10°C min^{-1} then cooled to 30°C at the same rate and reheated to 200°C. In both crystallization and melting experiments the peak temperatures were detected. In crystallinity calculations, a heat of fusion of 209 J g^{-1} was used for 100% crystalline material[17]. The instrument was calibrated with water, indium and lead. All measurements were conducted under nitrogen atmosphere.

RESULTS AND DISCUSSION

All five polypropylenes studied in this work were highly isotactic containing 92–95% *mm* triads (*Table 1*). Small structural differences between the samples could be observed; the gas phase polymerized grades (A and E) contained smaller amounts of syndiotactic triads than the other materials.

When these polypropylenes were fractionated according to stereoregularity using a xylene/ethylene glycol monoethyl ether solvent/non-solvent system, small fractions (0.8–8.5 wt%) were first collected (*Table 2*). These fractions had low isotactic contents and low molecular weights. *Figure 1* shows that after the non-stereoregular material had been dissolved, an almost constant value of i.r. isotacticity was obtained and fractionation proceeded mainly according to molecular weight.

In *Figure 2* i.r. isotacticity is represented as a function of molecular weight for the fractions of each sample. In *Figures 1* and *2*, as well as in other figures in this article, the peak value ($M_p = \sqrt{\bar{M}_n \bar{M}_w}$) was used for molecular weight in order to eliminate the influence of different polydispersities of the fractions. The first few fractions collected from each sample had broad molecular weight distributions (*Table 2*). This probably arose from syndiotactic material contained in these fractions (see ^{13}C n.m.r. spectroscopic pentad distributions in reference 14). The fractions of sample B, which was made in a laboratory slurry process, and the fractions from bulk polymerized sample C had low isotacticities compared to the fractions of the other samples. Even the higher molecular weight fractions of sample B had relatively low isotacticity values, i.r. isotacticities remaining below 90% up to $\bar{M}_w \sim 1 \times 10^5$.

Despite the fact that the properties measured by FTi.r. and ^{13}C n.m.r. spectroscopy are not the same, the former being related to isotactic helix content of the sample and only the latter measuring the actual stereochemical order of the chain, the i.r. isotacticities described now showed very similar trends as a function of molecular weight to the pentad tacticities reported earlier[14]. A close correlation also exists between the average isotactic sequence length, calculated from pentad distributions, and i.r. isotacticity, as reported in reference 14.

The crystallization curves in dynamic d.s.c. runs showed narrow peak shapes and only a single peak was obtained for each fraction. When the crystallization temperatures (T_c) were presented as a function of molecular weight (*Figure 3*), curves quite similar to those in *Figure 2* were attained. Differences between the samples and between the fractions of each sample were maintained, indicating that the T_c is mainly dependent on isotacticity. A non-stereoregular polymer hinders the crystallization of the first fractions of each sample, causing lowered T_cs. A slight decrease in T_c was observed for the last fractions of each sample. This is probably caused by the restricted mobility of very long chains in these fractions. Thus, molecular weight has a minor influence

Table 2 Characteristics of the fractions obtained by fractionation according to stereoregularity

Sample	Wt (%)	Cum. wt[a] (%)	$\bar{M}_w$ (×10^{-3})	$\bar{M}_w/\bar{M}_n$	I.r. isotacticity (%)	T_c (°C)	δH_c (J g^{-1})	T_{m1} (°C)	T_{m2} (°C)	t_{max} (min)
A[b]			405	5.4	95.7	111.8	92.1	163.7	–	0.6
A/1	5.3	2.7	34	3.5	n.d.[c]	101.8	48.0	139.9	151.6	n.d.
A/2	2.0	6.3	42	3.9	68.6	106.3	54.0	145.6	156.4	n.d.
A/3	0.8	7.8	102	5.2	81.8	110.5	69.7	150.6	159.7	n.d.
A/4	0.9	8.6	86	4.8	87.7	110.5	75.4	151.4	159.8	n.d.
A/5	0.9	9.5	62	2.6	92.1	113.1	84.8	156.4	163.9	0.8
A/6	3.9	11.9	87	2.3	94.5	111.9	94.3	159.1	166.6	n.d.
A/7	3.0	15.4	93	2.1	94.3	111.8	93.2	160.3	166.2	0.8
A/8	7.4	20.6	129	2.2	96.5	111.7	96.1	162.1	–	0.7
A/9	5.6	27.1	135	2.2	96.4	113.4	96.4	163.7	–	0.6
A/10	4.8	32.3	186	2.7	94.7	113.4	93.8	163.7	–	0.6
A/11	3.7	36.6	192	2.4	94.7	114.3	96.6	164.4	–	n.d.
A/12	2.7	39.7	226	2.3	96.0	114.1	95.7	164.5	–	0.5
A/13	5.7	43.9	206	2.3	94.3	113.5	94.9	165.3	–	n.d.
A/14	17.1	55.3	323	2.6	96.1	112.5	92.5	166.2	–	0.5
A/15	36.2[d]	81.9	749	3.7	97.9	112.3	96.8	168.7	–	0.6
B			462	6.0	94.2	108.3	93.9	167.1	–	1.4
B/1	2.8	1.4	22	3.1	n.d.	108.6	68.5	145.5	154.9	3.3
B/2	1.2	3.4	37	3.2	n.d.	106.7	58.9	143.9	154.9	n.d.
B/3	0.9	4.4	47	2.7	n.d.	107.5	51.6	145.0	156.7	3.1
B/4	2.8	6.3	99	4.0	n.d.	109.8	59.7	148.2	159.2	n.d.
B/5	0.8	8.2	50	2.4	75.0	111.8	67.8	151.4	161.7	n.d.
B/6	1.2	9.2	58	2.5	75.9	111.7	69.5	153.2	163.4	1.2
B/7	1.9	10.7	71	2.3	80.9	111.8	73.5	154.9	164.2	1.1
B/8	2.1	12.7	79	2.2	79.9	111.8	74.5	154.9	164.2	1.2
B/9	1.4	14.5	85	2.2	80.4	111.8	71.6	155.7	165.1	1.2
B/10	1.3	15.9	86	2.0	81.0	110.9	76.2	156.7	165.1	1.1
B/11	1.5	17.3	99	2.1	85.4	111.9	79.1	157.5	165.9	1.1
B/12	1.5	18.8	108	2.3	86.2	112.8	82.7	159.1	166.7	1.0
B/13	1.8	20.4	116	2.3	87.9	112.8	81.9	159.1	166.7	1.0
B/14	14.9	28.8	228	2.6	91.9	112.1	91.2	165.0	–	0.9
B/15	17.9	45.1	259	2.6	92.2	112.8	87.5	163.3	–	1.0
B/16	4.4	56.3	317	2.8	91.4	111.9	86.8	165.0	–	1.1
B/17	5.0	61.0	367	2.6	94.0	112.7	90.9	165.8	–	0.7
B/18	36.6[d]	81.7	651	3.2	95.4	111.9	89.6	167.5	–	1.0
C[b]			355	4.7	92.7	110.9	89.5	166.0	–	1.0
C/1	8.5	4.3	61	3.7	64.5	104.2	52.2	143.0	154.9	n.d.
C/2	3.0	10.0	126	4.6	56.9	101.7	40.3	141.4	154.2	n.d.
C/3	1.6	12.3	141	4.0	60.3	106.6	45.3	148.2	160.0	2.8
C/4	0.9	13.6	140	3.7	72.1	110.8	58.7	152.5	162.6	n.d.
C/5	1.0	14.6	103	3.0	n.d.	112.4	72.3	155.8	165.2	n.d.
C/6	4.9	17.5	120	2.5	91.4	113.4	87.5	160.9	167.6	0.9
C/7	5.0	22.5	169	2.4	92.4	112.5	88.0	161.8	167.7	0.7
C/8	5.8	27.9	192	2.4	93.0	113.6	91.7	164.1	–	0.7
C/9	6.5	34.1	176	2.1	93.9	113.3	94.2	164.2	–	0.6
C/10	4.0	39.3	229	2.3	94.5	113.3	96.7	165.1	–	0.6
C/11	5.9	44.2	241	2.3	95.3	113.3	93.8	165.9	–	0.6
C/12	21.9	58.1	308	2.3	96.1	112.4	93.2	167.5	–	0.6
C/13	29.3	83.7	380	2.5	98.5	114.2	97.2	169.3	–	0.6
C/14	1.1	98.9	126	2.2	n.d.	115.8	95.2	166.6	–	n.d.

Table 2 *continued*

Sample	Wt (%)	Cum. wt[a] (%)	$\bar{M}_w$ ($\times 10^{-3}$)	$\bar{M}_w/\bar{M}_n$	I.r. isotacticity (%)	T_c (°C)	δH_c (J g^{-1})	T_{m1} (°C)	T_{m2} (°C)	t_{max} (min)
C/15	0.6[d]	99.7	322	2.8	n.d.	115.0	87.3	165.1	–	n.d.
D[b]			386	5.6	95.7	110.8	94.4	165.4	–	0.6
D/1	4.7	2.4	27	3.0	n.d.	101.4	61.1	139.8	150.6	n.d.
D/2	2.8	6.1	56	4.2	64.0	103.0	48.3	140.4	151.7	n.d.
D/3	1.8	8.4	96	5.5	64.6	106.5	52.1	146.7	157.3	2.0
D/4	1.4	10.0	103	4.8	n.d.	108.9	62.3	150.6	160.6	n.d.
D/5	1.1	11.3	125	5.4	n.d.	109.0	71.7	153.1	161.4	n.d.
D/6	2.0	12.9	75	2.8	91.4	112.3	90.0	156.4	164.7	0.7
D/7	2.6	15.2	76	2.7	91.4	111.7	91.6	157.9	165.5	0.6
D/8	1.9	17.4	89	2.7	92.1	112.5	91.9	158.8	165.5	0.6
D/9	3.4	20.1	104	2.4	94.1	112.3	92.7	159.7	165.6	0.7
D/10	5.8	24.6	141	2.3	93.8	112.5	97.7	161.3	–	0.6
D/11	7.0	31.0	178	2.5	94.7	112.5	94.9	162.1	–	0.6
D/12	6.2	37.6	193	2.6	95.3	112.5	96.8	162.9	–	0.7
D/13	4.9	43.1	225	2.5	94.9	112.5	97.3	163.0	–	0.6
D/14	6.6	48.8	277	2.6	95.2	112.5	95.5	163.8	–	0.6
D/15[e]	43.6	74.0	562	3.1	94.3	112.5	97.4	165.4	–	0.6
D/16	3.7	97.6	531	2.9	94.1	112.4	98.0	169.5	–	0.5
D/17	0.4	99.6	505	2.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
D/18	0.2	99.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
E[b]			397	5.5	96.3	111.0	92.7	163.7	–	0.8
E/1	7.5	3.8	46	4.6	76.1	103.3	56.3	142.1	152.2	–
E/2	1.6	8.3	37	4.0	74.1	108.2	59.7	145.5	156.4	2.1
E/3	1.1	9.7	45	3.0	n.d.	112.4	81.7	153.8	162.2	0.7
E/4	0.8	10.7	50	2.6	n.d.	113.2	85.0	155.5	163.1	n.d.
E/5	1.2	11.7	48	2.4	94.4	114.4	94.4	157.0	164.6	0.5
E/6	1.3	13.0	51	2.1	95.3	115.1	95.4	158.7	165.4	0.4
E/7	2.1	14.7	59	2.1	95.1	114.2	97.0	159.5	165.5	0.5
E/8	2.8	17.1	60	2.1	96.4	114.3	96.0	160.4	–	0.5
E/9	1.9	19.5	73	2.0	95.2	114.4	96.8	161.2	–	0.4
E/10	1.7	21.2	73	2.1	95.4	114.5	96.1	161.2	–	0.5
E/11	2.7	23.4	78	2.2	94.6	113.9	98.1	160.5	–	0.4
E/12	3.4	26.5	133	2.1	96.5	114.3	99.0	163.6	–	0.4
E/13	2.8	29.6	149	2.1	96.9	115.1	98.2	164.5	–	0.4
E/14	7.0	34.5	160	2.1	97.2	114.1	93.6	165.4	–	0.5
E/15[e]	21.8	48.9	460	2.9	95.9	113.9	99.4	166.3	–	0.5
E/16	6.2	62.9	335	2.6	95.5	114.0	97.3	162.9	–	0.4
E/17	3.9	68.0	282	2.5	96.1	113.8	98.8	167.1	–	0.5
E/18	30.0	85.0	491	2.8	94.5	113.1	98.7	167.9	–	0.5

[a] $\Sigma w_{i-1} + \frac{1}{2} w_0 = 0$
[b] Characterization of the whole polymer was carried out on precipitated material
[c] n.d. = Not determined
[d] Dissolved in decalin
[e] Fractions 15–18 were obtained by refractionation of the last fraction collected in the original fractionation

on T_c in the high molecular weight region. Crystallization enthalpy (δH_c) is also mainly dependent on isotacticity (see Table 2), as reported earlier by Burfield et al.[1].

Burfield et al. also observed a different crystallization behaviour between polymers produced by conventional and supported catalysts. Polymers produced with

supported catalysts showed lower T_cs. As possible explanations for these differences they suggested variations in the distribution of stereochemical defects, unsaturated chain ends produced by supported catalysts, lower molecular weight and narrower MWD of polymers made by supported catalysts and smaller amounts of catalyst
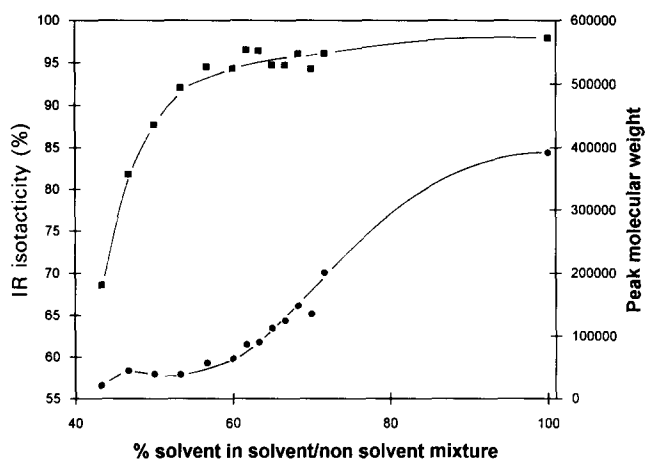
Figure 1 Change in isotacticity (■) and molecular weight (●) of the fractions with increasing solvent content in the solvent/non-solvent system used in the fractionation (sample A, fractionated according to stereoregularity at 125°C)
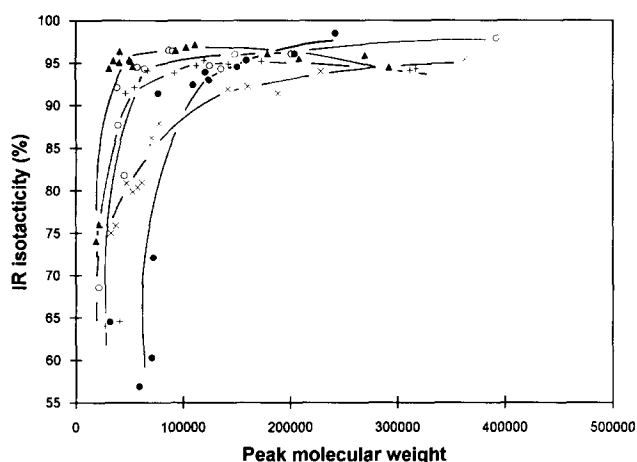

Figure 2 Infra-red isotacticity *versus* molecular weight for the fractions obtained by fractionation according to stereoregularity: (○) fractions of sample A; (×) sample B; (●) sample C; (+) sample D; (▲) sample E

residues in these polymers. In this work the crystallization temperatures of the unfractionated commercial samples were similar for both the sample D produced with a first-generation catalyst system and the samples produced with supported catalysts (*Table 2*). In contrast to the conventional catalyst polymerized samples of Burfield *et al.*, sample D contained very small amounts of catalyst residues[14] because of the washing step after polymerization.

In contrast to the results of Burfield *et al.*, the high molecular weight fractions of sample D (together with the fractions of sample B, which was also polymerized with a slurry process) showed somewhat lower T_cs compared to fractions of samples A, C and E. If the possible explanations listed above are considered, i.r. isotacticities of the fractions of sample D are comparable to the isotacticities of the fractions of samples A, C and E (*Table 2*). Also, the distribution of stereodefects, as determined by n.m.r. spectroscopy[14] in the long-chain fractions of sample D, was similar to that of the other samples. In any case, the differences in T_cs observed between the fractions of samples produced by the two types of catalysts were small compared to those found by Burfield *et al.*[1], who registered an average difference

of 8°C between T_c values of samples made by conventional and supported catalysts.

The conclusion on the influence of both parameters, molecular weight and isotacticity on T_c by examining the fractions obtained by fractionation according to stereoregularity, was confirmed by the analysis of the narrow *MWD* fractions reported in *Table 3*. These fractions, obtained from sample A by fractionation according to molecular weight, had almost similar i.r. isotacticities, ranging from only 92 to 96% (see *Figure 4*), and molecular weights in the range of 33 000–947 000. Crystallization temperatures of these fractions lay within 2.5°C, despite the differences in molecular weight. The influence of isotacticity is noted if, for example, T_cs of fractions A/1 ($T_c = 101.8°C$) and AII/1 ($T_c = 111.7°C$) are compared: a difference of around 10°C exists, though molecular weights of these two fractions are almost similar.

In addition to their different isotacticities, the two fractions mentioned above had different polydispersities distinguishing them. An idea of the influence of polydispersity on T_c can be obtained when, for example, unfractionated sample A is compared with its fraction having an analogous molecular weight and i.r. isotacticity (fraction AII/13, *Table 3*). The fraction with narrow *MWD* has somewhat higher T_c compared to the unfractionated sample.

Correspondingly, narrowing of *MWD* raises melting temperature (T_m) (see fraction AII/13 in *Table 3* and compare also the T_m values of the whole samples and their fractions with analogous molecular weights in *Table 2*). However, it should be noted that real isotacticity, as measured by n.m.r. spectroscopy[14,18] is higher for long-chain fractions than for unfractionated polymers. Thus, the small increase observed in T_c and T_m values might be caused partly by increased isotacticity.

Melting temperature was found to be mainly dependent on isotacticity, but now the influence of molecular weight was also obvious (*Tables 2* and *3*). Though isotacticity was the main parameter determining the peak temperature (compare, for example, T_ms of fractions A/1 and AII/1), the peak shape was strongly dependent on molecular weight. The fractions of AII series with $\bar{M}_w$ values below 89 000 showed double peaks in their melting endotherms, despite their high i.r. isotacticity values. For the fractions obtained by fractionation according to stereoregularity
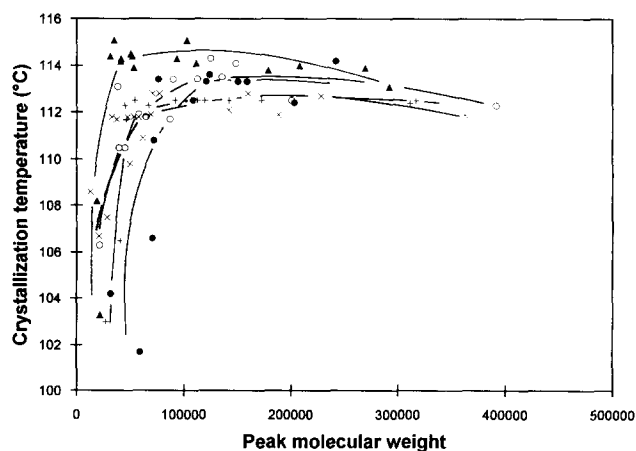

Figure 3 Crystallization temperature *versus* molecular weight for the fractions obtained by fractionation according to stereoregularity. Symbols as in *Figure 2*

Table 3 Characteristics of the fractions obtained by fractionation according to molecular weight
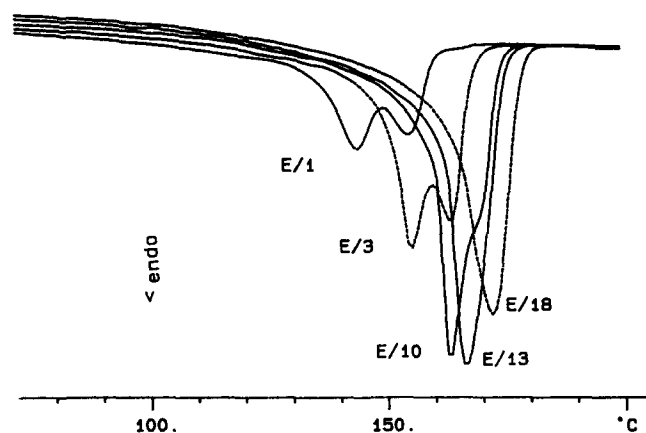
Sample	Wt (%)	Cum. wt[a] (%)	$\bar{M}_w$ ($\times 10^{-3}$)	$\bar{M}_w/\bar{M}_n$	I.r. isotacticity (%)	T_c (°C)	T_{m1} (°C)	T_{m2} (°C)	Cryst. (%)	t_{max} (min)
A[b]			405	5.4	95.7	111.8	163.7	–	47.3	0.6
AII/1	7.7	3.8	33	2.5	n.d.[c,d]	111.7	154.8	164.2	42.7	1.1
AII/2	6.8	11.1	44	1.9	n.d.	112.8	158.1	165.9	43.5	0.8
AII/3	4.8	16.9	63	1.7	92.7	112.8	159.7	166.7	47.2	n.d.
AII/4	5.9	22.2	89	1.5	92.0	112.6	160.7	166.8	44.5	0.7
AII/5	3.5	26.9	118	1.6	93.5	113.4	162.4	–	47.0	n.d.
AII/6	4.5	30.9	141	1.5	93.0	112.6	163.6	–	44.7	n.d.
AII/7	4.0	35.2	167	1.6	92.7	113.3	164.1	–	45.8	0.7
AII/8	3.3	38.8	207	1.7	93.1	112.3	165.1	–	45.9	n.d.
AII/9	4.4	42.6	238	1.8	96.2	112.5	165.0	–	49.4	n.d.
AII/10	8.3	48.9	302	2.0	94.2	114.3	164.9	–	45.1	0.4
AII/11	6.9	56.6	321	2.0	95.9	111.9	166.6	–	46.6	n.d.
AII/12	7.4	63.7	347	2.0	94.0	112.6	165.0	–	45.6	n.d.
AII/13	10.1	72.5	412	2.4	95.8	113.5	166.6	–	46.1	0.5
AII/14	6.7	80.9	526	2.5	93.8	112.5	167.5	–	46.3	n.d.
AII/15	15.6	92.0	947	3.1	95.8	113.3	166.7	–	45.8	1.0

[a] $\Sigma w_{i-1} + \frac{1}{2} w_i$
[b] Characterization of the whole polymer was carried out on precipitated material
[c] n.d. = Not determined
[d] [13]C n.m.r. spectroscopic triad isotacticity of the fraction AII/1 was 91.0%[18]
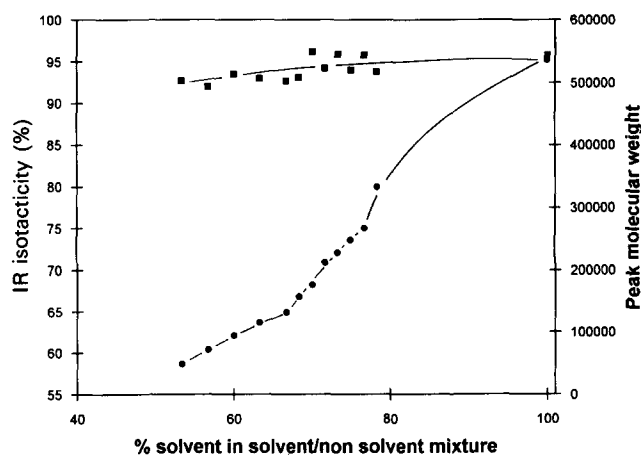
Figure 4 Change in isotacticity (■) and molecular weight (●) of the fractions with increasing solvent content in the solvent/non-solvent system used in fractionation (sample A, fractionated according to molecular weight at 159°C)

Figure 5 Melting endotherms of some fractions of sample E obtained by fractionation according to stereoregularity

the appearance of double peaks was dependent on stereoregularity. For example, all the fractions of sample C with weight average molecular weights below 169 000 showed double peaks, but for sample E only fractions with $\bar{M}_w$ below 73 000 had double melting endotherms. An example of the change in the shape of melting endotherms of the fractions with increasing isotacticity and molecular weight is presented in *Figure 5*. The double peaks of these fractions, consisting of pure α crystal form as determined by WAXS[18], were probably caused in most cases by reorganization[2,9] of the less ordered domains of the crystalline material during the d.s.c. scan. For the most stereoirregular fractions having their first melting peaks at 140–145°C the first melting peak was less sensitive to recrystallization. For

these fractions existence of two distinctly melting crystalline species can be suggested. These phenomena and the factors in molecular structure responsible for them will be discussed more thoroughly in the following paper in this series[18].

Crystallinity, as determined from the area of a melting endotherm, was not significantly influenced by molecular weight (*Table 3*). In contrast, a close correlation between i.r. isotacticity and crystallinity was found (*Figure 6*). This is reasonable, because a stereoregular chain structure is required for crystallizability. Earlier, Burfield *et al.*[1] presented log(δH_m) as a function of log (100 *mm*) (δH_m = enthalpy of fusion and *mm* = n.m.r. spectroscopic triad isotacticity) and found a good correlation. A linear correlation between i.r. index and heat of fusion has also been reported for syndiotactic polypropylene by Haftka and Könnecke[19].
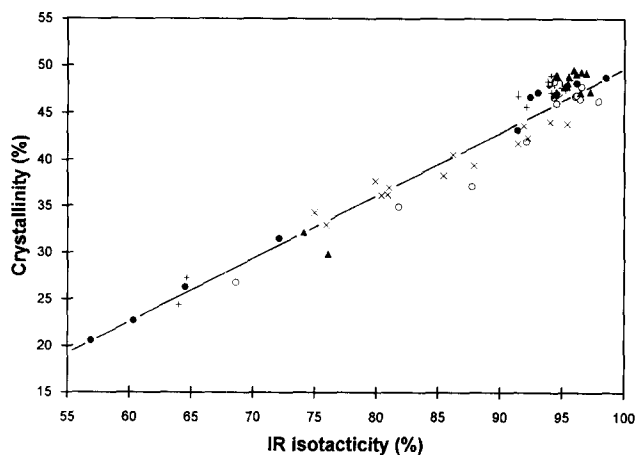
Figure 6 D.s.c. crystallinity *versus* i.r. isotacticity for fractions obtained by fractionation according to stereoregularity. Symbols as in *Figure 2*

Figure 7 Isothermal crystallization (at 120°C) of the fractions obtained by fractionation according to stereoregularity. Symbols as in *Figure 2*

Crystallization rates of the fractions in isothermal crystallization were also determined. Considering the parameters influencing the overall crystallization rate, according to the literature heterogeneous nucleation dominates and crystallization occurs on catalyst residues, dust particles and other impurities. Crystal growth rate is constant at a given temperature and depends only on the temperature[10,11]. The overall kinetics of crystallization is also influenced and controlled by the concentration and distribution of defects that are present along the polymer chains[2].

Fractions were preheated for 5 min at 225°C to erase their previous thermal history. Crystallization times were detected at 120°C as the peak maxima. The limitations of the instrument used must also be considered: because of the low maximum controlled cooling rate attained with the instrument $(75°C \, min^{-1})$ an error up to $[(T_m - 120°C)/75°C]min$ may be added to the crystallization times measured in this work. The crystallization times measured are presented as a function of molecular weight in *Figure 7*. The simultaneous change in isotacticity with increasing molecular weight can be found in *Figure 2* and *Table 2*. Isotacticity was the dominating parameter determining the crystallization rate as well. Differences between the fractions of different samples were also observed. Fractions of the slurry polymerized sample B had distinctly longer crystallization times compared to, for example, fractions of sample E. Differences in crystallization rates between the fractions of these two samples correspond to differences in i.r. isotacticity as presented in *Figure 2* and *Table 2*. These differences in isotacticity were also observed in n.m.r. spectroscopic experiments[14], long-chain fractions of sample B containing higher amounts of defects than comparable fractions from other samples. N.m.r. spectroscopic analyses also showed that no head-to-head irregularities were present in these fractions, excluding them as a possible cause of differences in crystallization times. All the fractions were treated similarly in the fractionation step and thus differences in morphology did not result in variations in crystallization rates either.

The influence of molecular weight on crystallization rate was examined using fractions isolated by fractionation according to molecular weight (*Table 3*). The short-chain fractions had somewhat increased crystallization times, still being short compared to the crystallization times of non-stereoregular fractions with low molecular weights
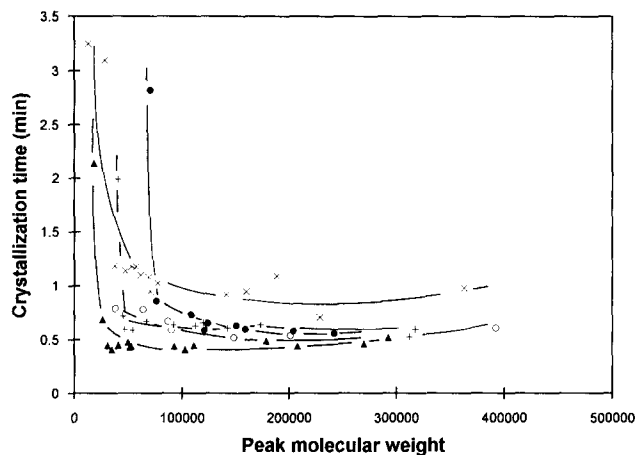
(*Table 2*). A slight increase in crystallization time was also observed for the very high molecular weight fraction AII/15 $(M_w = 947\,000)$. Thus, isotacticity was the main parameter determining crystallization rate, but molecular weight had its minor crystallization rate decreasing effect both near the lower and upper limits of the molecular weight range studied in this work.

When the influence of *MWD* on crystallization time is considered, contradictory results have been reported for so-called controlled rheology polymers in the literature. These polymers have a narrow *MWD* as a result of, for example, peroxide degradation, and both faster[12] and slower[13] crystallization rates as compared to broad *MWD* polymers have been reported for them. In this work no significant differences were observed for the crystallization rates of the whole samples and their narrow fractions having comparable molecular weights and isotacticities (*Tables 2* and *3*). Only sample B polymerized in the laboratory had a distinctly longer crystallization time than its comparable fractions, but this can be explained by morphology effects. Crystallization time was measured directly for reactor powder, and not for precipitated polymer, as in the case of commercial samples (originally obtained in pelleted form) and the fractions.

CONCLUSIONS

The fractions isolated in this work, either according to stereoregularity or molecular weight, provided an opportunity to study the effects of both isotacticity and molecular weight on thermal properties of polypropylene. In the molecular weight range studied $(M_w = 22\,000-947\,000)$ isotacticity was the main parameter determining T_c and T_m and crystallinity, as well as the crystallization rate in isothermal crystallization. Molecular weight had a less pronounced effect on crystallization rate, but almost no influence on crystallinity. In contrast, the shape of melting endotherms was clearly influenced by molecular weight in the low molecular weight region.

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