Fractionation and Crystallization of Isotactic Poly(propylenes) Prepared with a Heterogeneous Transition Metal Catalysts

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Summary: A series of poly(propylenes) (PPs) were prepared by slurry polymerization using a $MgCl_2$-supported transition metal catalyst. Two different external donors (EDs) were used: diphenyl dimethoxysilane (DPDMS) and methylphenyl dimethoxysilane (MPDMS). The molecular weight (MW) of the PPs was controlled using molecular hydrogen that was used as a transfer agent. To obtain materials with differing molecular weight and similar tacticities, polymers were fractionated with prep-TREF. DSC analyses of blends of TREF fractions showed that the crystallization behaviour of the polymer blends are strongly affected by the configuration (tacticity) and MW of the PP.

Keywords: crystallization; poly(propylene); TREF

Introduction

The crystallinity of any polyolefin is an important parameter determining the properties of the material. For stereoregular isotactic polypropylenes (iPPs) the structural differences between materials affect crystallization and melting behavior. The effects of molecular weight (MW),[1–4] molecular weight distribution (MWD)[5] and tacticity[4,6–8] on crystallization have been reported. Results indicate that the rate of crystallization decreases markedly with increasing MW,[2] but the overall crystallization rate might rise because an increasing number of intramolecular folded chain nuclei could result in a higher nucleation density.[3] For the samples with similar MWs and different tacticities the linear crystal growth rate might increase by as much as three orders of magnitude when the isotacticiy (*mmmm* %) of iPP increases from 78.7 to 98.8%.[7,9] The degree of crystallinity of iPPs is reported to be (typically) in range of 40% to 70%.[10]

The effect of hydrogen on PP polymerization using Ziegler–Natta catalysts has long been of commercial interest. This is largely because hydrogen has been used as a standard MW modifier in industrial polyolefin production. In addition to acting as a powerful transfer agent, hydrogen is known to lead to an increase in activity[11,12] and a reduction in polymer MW. The magnitude of the increase in activity caused by the addition of hydrogen activation is dependent on the external donor (ED) used in the polymerization.[13,14] Chadwick[15] reported the combined effects of the ED and hydrogen concentration on the occurrence of regioirregular insertion and chain transfer.

Most commercial iPPs can, for practical purposes, be regarded as blends of materials differing with respect to MW, MWD and tacticity.[16–18] The molecular make-up of iPPs will differ, which will, in turn affect the crystallization and melting behavior of these polymers. The use of preparative temperature rising elution fractionation (p-TREF) allows the characterization of a given iPP in terms of molecular make-up.[19] The use of p-TREF also allows for the isolation of fairly well-defined iPP

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fractions of a given MW and tacticity, which in turn allows for the more detailed study of, for example, crystallization behavior of such materials. This paper reports the initial results of cocrystallization studies of iPP samples with varying MW (and narrow MWD) and tacticity.

Experimental Part

Propylene was obtained from Sigma-Aldrich and used without any further purification. Highly purity Argon and Hydrogen were obtained from Afrox (South Africa). Toluene (Sigma–Aldrich) was dried by refluxing over sodium/benzophenone and then distilled in an inert gas atmosphere. Triethylaluminum (TEA) was obtained from Sigma-Aldrich. A commercial Ziegler-Natta catalyst with 2.78 wt% Ti content was purchased from Star Chemicals & Catalysts Co. (China). The EDs, diphenyl dimethoxysilane (DPDMS) and methylphenyl dimethoxysilane (MPDMS) were obtained from Fluka and used as received.

All reactions were carried out in an inert gas atmosphere. The polymerization reactions were carried out in a 350 mL stainless steel Parr autoclave with a gas inlet and pressure gauge. Typically the reactor was charged with the catalyst (43 mg, Ti content 2.78 wt%), TEA (2 mmol, Al/Ti mole ratio 80) and ED (0.091 ml in the case of DPDMS and 0.072 mL in the case of MPDMS, Al/Si mole ratio 5) in toluene (25 mL). The catalyst solution was stirred for 5 min and the required amount of propylene was added. The reactor was pressurized with hydrogen (to the required pressure) and the reaction mixture stirred for 1 h at room temperature. The reaction was quenched by addition of 10% HCl/MeOH. The resulting polymer was isolated by filtration, washed several times with methanol, and subsequently dried under vacuum at 80 °C for 15 h, to yield about 3–5 g PP as a white powder. These polymers were characterized by HT GPC (Polymer Labs PL-GPC 220, flow rate of 1 mL/min in 1,2,4 trchlorobenzene as solvent stabilized with 2,6-di-tert-butyl-4-methylphenol at 140 °C), DSC (TA instruments Q100 DSC, 2nd heating cycle at 10 °C/min used for determination of Tm, Tc determined from first cooling cycle). ^{13}C NMR spectra were recorded at 120 °C on a Varian Unity Inova NMR spectrometer equipped with an Oxford magnet (14.09 T), operating at 600 MHz, using a 5 mm inverse detection PFG probe. Samples (60–80 mg) for ^{13}C NMR analyses were dissolved at 110 °C in a 9:1 mixture of TCB and benzene-d_6 (Bz_6). Polymers were also fractionated by preparative TREF (for reviews on the process see references,[19–23] the apparatus used was built in-house.[24])

Typically 3.0 g of polymer was introduced to a 1000 mL glass reactor containing 300 mL xylene stabilized with 0.06 wt% Irganox 1010. The polymer was dissolved at 130 °C for about 1.5 h. The hot polymer solution was mixed with preheated washed sea sand (Aldrich, as an inert support). The glass reactor was cooled from 130 °C to 20 °C at a rate of 1.5 °C/h. The solution–sand mixture was loaded into a steel elution column. Fractions of the polymer, with increasing crystallinity, were then eluted with xylene at set (increasing) temperatures. Typically fractions were isolated after elution at 6 temperatures (25, 60, 80, 100, 120 and 140 °C). Subsequently the polymer fractions were recovered by removing the xylene under reduced pressure and drying at 50 °C (vacuum oven). Fractions were characterized by the same techniques as the parent polymers. In some cases WAXD analyses were performed at iThemba LABS (South Africa) on a Bruker AXS D8 ADVANCE diffractometer at room temperature with filtered CuKα radiation. All samples were scanned at 2θ angles, ranging from 6° to 50°, with a sampling width of 0.02°, where 2θ is the diffraction angle.

Results and Discussion

The properties of iPPs prepared using a $MgCl_2$-supported transition metal catalyst with the two different EDs, DPDMS and MPDMS, in the presence of different amounts of hydrogen are summarized in Table 1. It is obvious that the use of hydrogen strongly affects polymer molecular weight. The presence of ED during the propylene polymerization (Table 1) also had a noticeable effect on the MW. The use of DPDMS resulted in somewhat higher MW than in the case of MPDMS which could be due to the increased steric hindrance afforded by the two phenyl groups on DPDMS.[14] It is postulated that the presence of these bulkier substituents on the DPDMS was be more effective in preventing 2, 1 coordination of the monomer, which often leads to chain termination in the presence of hydrogen.

Figure 1 gives a graphic representation of the effect that hydrogen has on the tacitity of the polymers prepared (results also given in Table 1); it is quite clear that the introduction of hydrogen noticably increases the overall tacticity in the absence of ED, and less so in the presence of ED. It is also clear that increasing the amount of hydrogen used has little or no further effect on the tacticity.

TREF fractionation for iPPs, Z4, Z5, Z8, Z9 and Z10 were carried out, and the fractions characterized fully. Figure 2 gives the TREF distribution profiles for polymers Z4 and Z5, as example. Subtle, but clear differences are visible, particularly w.r.t the soluble fractions, and the 120 °C and 140 °C fractions. This was in line with what was expected, as these polymers are different w.r.t tacticity, MW and MWD.

The characterization results of the fractions for these samples are summarized in Table 2 (the data for Z8 – Z10 is omitted for the sake of space). Other researchers have clearly demonstrated that for PP the TREF profiles qualitatively reflect the distribution of isotacticity, with isotacticity increasing almost linearly with the elution temperature.[21–23,31] Table 2 shows that both Z4 and Z5 samples are composed of fractions with very different tacticities, ranging from rather atactic (elution temperature 25 °C) to highly isotactic (elution temperature 140 °C).

An interesting outcome of this analysis is that the isotacticity of Z4 fractions are systematically slightly greater than those of Z5 fractions, at a given elution temperature. This is spite of the tacticity of the Z5 parent polymer being higher than that of the Z4 parent polymer (Table 1). For all

Table 1.
Results of propylene polymerizations carried out with DPDMS, MPDMS and various concentrations of hydrogen[a].

Runs	ED	H_2 (wt %)	M_w^d	M_w/M_n	*mmmm* %[e]	T_m (°C)	T_c (°C)	ΔH_m^f (J/g)	Xc (%)
Z13	None	0.0	388 428	11.4	55.0	158.8	116.2	62.7	30
Z14	None	0.2	215 397	5.9	86.0	157.5	119.8	90.5	43
Z15	None	0.6	137 965	5.6	87.0	156.4	118.7	83.9	40
Z16	None	1.4	97 587	9.3	88.0	157.1	121.3	88.3	42
Z6	DPDMS[b]	0.0	1 105 416	6.6	87.0	160.6	114.0	77.8	37
Z5	DPDMS	0.2	312 580	4.1	96.0	161.9	118.4	108.9	52
Z4	DPDMS	0.6	252 956	5.4	94.0	160.6	116.5	103.9	50
Z3	DPDMS	1.4	184 759	6.1	93.0	161.2	124.2	104.5	50
Z7	MPDMS[c]	0.0	1 047 184	4.6	86.0	158.5	114.1	89.5	43
Z8	MPDMS	0.2	228 960	6.4	94.0	162.0	124.4	103.9	50
Z9	MPDMS	0.6	164 327	5.4	97.0	161.1	122.4	118.6	57
Z10	MPDMS	1.4	147 528	6.0	96.0	160.4	121.6	110.0	53

[a] Propylene polymerization was carried out in toluene at room temperature for 1 h with different amounts of hydrogen.
[b] diphenyl dimethoxysilane (Al/Ti molar ratio 80).
[c] methylphenyl dimethoxysilane (Al/Ti molar ratios 80).
[d] Determined by GPC.
[e] Determined by ^{13}C NMR.
[f] Determined by DSC.

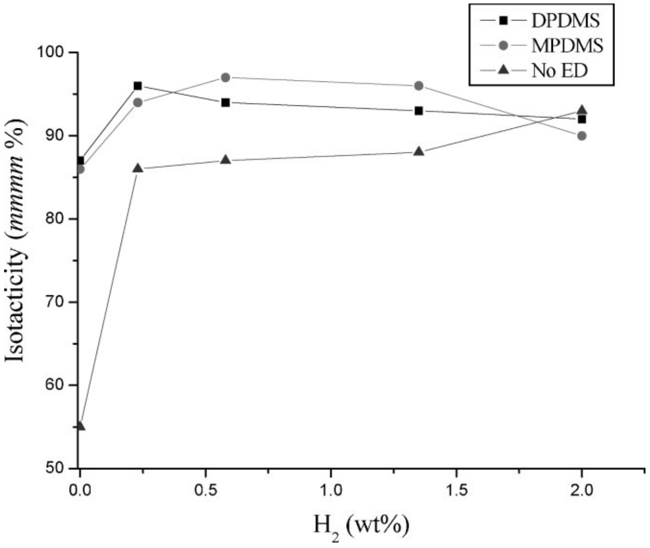

Figure 1.
The effect of hydrogen on the tacticity of PP (in presence and absence of ED).

the crystalline TREF fractions, WAXD analyses revealed only the presence of the α crystalline form. This is illustrated in Figure 3.

The results in Table 2 seem to indicate that tacticity alone does not determine the crystallizability of PP from solution, and that other factors may be involved. Crystallization may start due to immobilization of a given chain of sufficient regularity and length, and subsequent crystallization may then occur by chains that are chemically dissimilar.

The fact that we were able to synthesize a series of different propylene homopolymers, and then to fractionate these

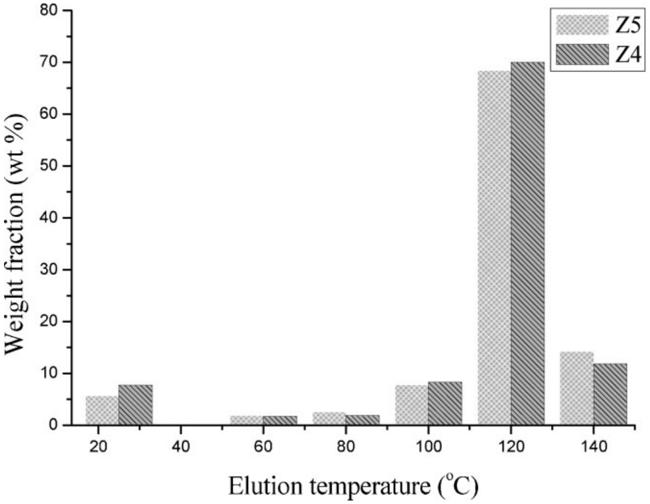

Figure 2.
The TREF fractionation data for polymers Z4 and Z5.

Table 2.
Fractionation data and analysis of the TREF fractions of polymers Z4 and Z5.

Runs	Fraction (T °C)	Weight (mg)	M_n	M_w/M_n	*mmmm* %	T_m (°C)	T_c (°C)	Xc (%)
Z5	25	168	299	33.4	–	–	–	–
	60	54	4 189	4.3	–	112	78	10
	80	75	1 968	5.9	63.0	129	96	19
	100	233	12 713	2.7	89.0	150–161	112	46
	120	2 053	72 523	2.9	96.0	161	118	49
	140	424	56 498	2.8	99.0	158	116	42
Z4	25	232	326	25.7	–	–	–	–
	60	52	1 578	10.4	–	114	84	12
	80	58	2 011	7.3	64.0	132	102	24
	100	251	9 726	2.6	93.0	148–157	111	44
	120	2 103	45 854	4.3	98.0	160	116	57
	140	356	52 131	3.6	99.0	158	114	49

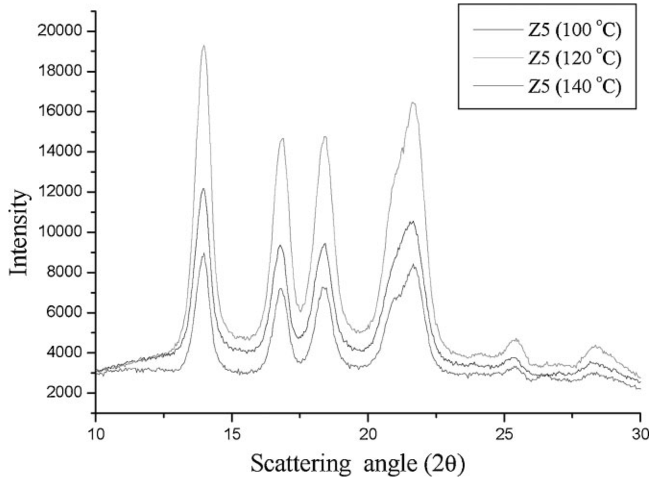

Figure 3.
Typical X-ray diffraction pattern of different fractions of the Z5 sample.

materials by preprative TREF meant that we could now select fractions isolated by these techniques and then blend them. In Table 3 we present data for individual fractions as well as data for fractions blended.

The fractions and blends given in Table 3 were selected based on their differences and similarities w.r.t molecular weight and tacticity. DSC scans are presented in Figure 4. As can be seen from Figure 4, all the blends showed only one melting

Table 3.
GPC, NMR and DSC results TREF fractions and their blends. Values in parentheses represent the temperature at which the fraction eluted.

Fractions	M_w	M_w/M_n	*mmmm* %	T_m (°C)	T_c (°C)	Xc (%)
Z4 $^{(120)}$	195 693	4.3	98.0	159.9	115.8	58
Z4 $^{(140)}$	142 342	3.6	99.0	157.8	114.1	49
Z4 $^{(120+140)}$	–	–	–	160.2	115.4	44
Z9 $^{(100)}$	25 918	2.4	93.0	149.5	113.0	42
Z10 $^{(110)}$	92 596	3.5	93.0	157.9	117.2	53
Z9 $^{(100)}$ + Z10 $^{(110)}$	–	–	–	155.8	115.5	46
Z8 $^{(80)}$	18 986	3.9	63.0	131.6	100.3	26
Z9 $^{(80)}$	14 126	3.3	80.0	134.3	102.8	26
Z8 $^{(80)}$ + Z9 $^{(80)}$	–	–	–	138.9	101.5	28

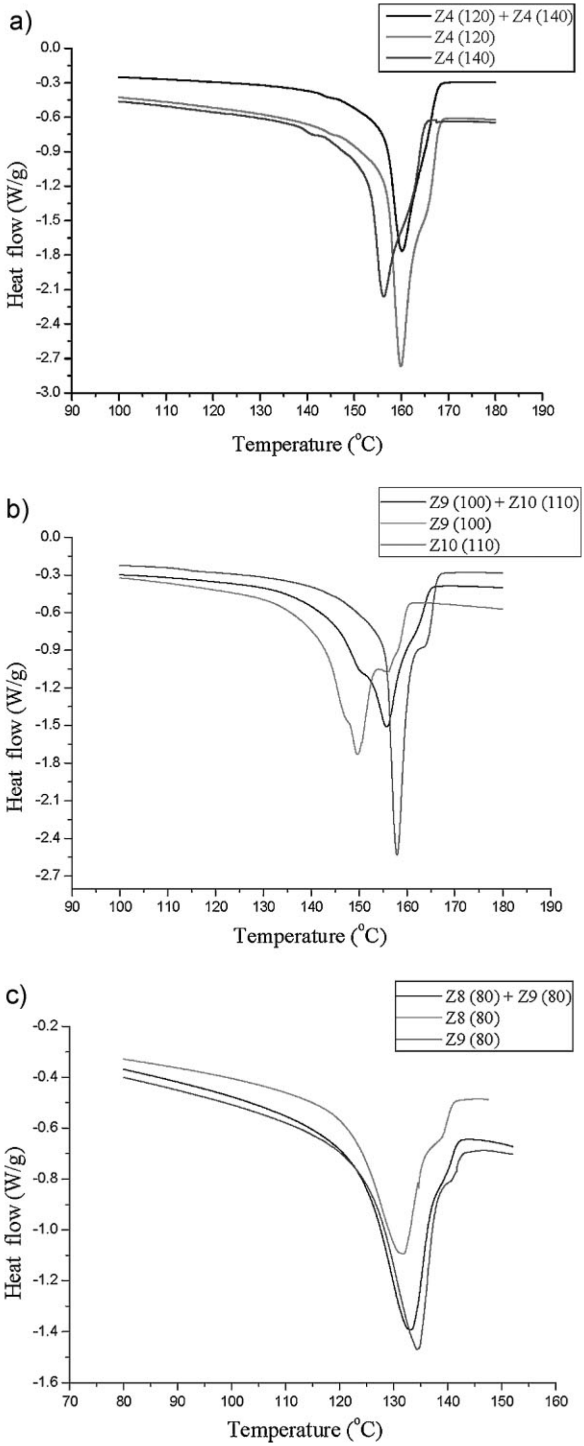

Figure 4.

DSC thermograms of selected TREF fraction blends: (a) and (b) polymers with same tacticities but different MWs, and (c) polymers with similar MWs but different tacticities.

peak, which indicates that that cocrystallization of the blends occurred. Although single melting peaks of blends are usually associated with a high extent of cocrystallization, two broad overlapping distributions of thicknesses of separate crystals, one from each component, could also lead to single broad endotherms.[37] Initial results here indicate that molecular weight appears to play some role in the crystallization of these blends in the bulk. When reasonably high molecular weight samples (Z4 $^{(120)}$ and Z4 $^{(140)}$) with similar tacticities are blended, the resultant blends melts at a similar (albeit slightly higher) temperature as the higher molecular weight fraction. With lower or intermediate molecular weight fractions (Z9 $^{(100)}$ and Z10 $^{(110)}$) we see a similar pattern, although the melting temperature is lower than that of the higher molecular weight material. In the case of two low molecular weight fractions with different tactcities, it is quite clear that the melting temperature of the blend is influenced by the material with the highest tacticity. What is interesting, though, is that the melting temperature of the blend is higher than that of either of the individual fractions. These are preliminary results, but we believe that these indicate that there are two variables that influence cocrystallization in the bulk, being the MW and tacticity. While this is intuitively obvious, it is not as clear-cut as to what effect the magnitude of the molecular weight (and differences in molecular weight of individual components) and variation in tacticity might have. A large number of experiments need to be conducted to investigate this matter, and much of this is at present under way in our laboratories.

Conclusion

By using transition metal catalyst systems it was possible to produce polymer samples of a wide variation in tacticity and MW. Preparative TREF allowed us to produce polymer fractions of well defined structure in terms of molecualr weight –and distribution, as well as tacticity. Moreover, X-ray diffraction showed only one crystal structure (α phase) for the more crystalline fractions of the PP samples. Furthermore, initial DSC results of different TREF fraction blends showed that the crystallization behavior of the polymer blends are strongly affected by the configuration (tacticity) and molecular weight of the PP.

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