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Obtaining the γ phase in isotactic polypropylene: effect of catalyst system and crystallization conditions

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Abstract

Five samples of isotactic polypropylene, iPP, and two copolymers of iPP with 1-hexene, synthesized with different catalyst systems, both heterogeneous and homogeneous, have been studied in order to analyse the effect of the catalyst system, the presence of comonomer units and the crystallization conditions on the phase structure of iPP and, in particular, on the amount of γ modification obtained. Minor amounts, if any, of γ modification are present in iPP samples synthesized with highly isospecific Ziegler–Natta catalysts and crystallized from the melt at different cooling rates, ranging from 100 to 3°C/min. On the contrary, considerable amounts of the γ form have been obtained both in samples prepared with catalysts of very low isospecificity or in those prepared with homogeneous metallocene catalysts. It has been shown that the relative proportion of the α and γ modifications can be controlled just by changing the crystallization conditions. A clear influence of the presence of comonomer units on favouring the formation of the γ phase has not been ascertained. Moreover, attempts to deduce the γ content from the d.s.c. melting patterns have been unsuccessful, since the two modifications exhibit very similar melting temperatures.

Keywords: Isotactic polypropylene; Copolymers with 1-hexene; α and γ modifications

1. Introduction

The polymorphic behaviour of isotactic polypropylene (iPP) is well documented [1–3]. The monoclinic α form is by far the most common [1–4], being found in all kinds of solution-crystallized iPP samples and also in most melt-crystallized specimens. The hexagonal β modification appears only under special crystallization conditions or in the presence of selective β nucleating agents [1–3,5–8]. The triclinic γ form has been found in the case of low-molecular weight iPP, crystallization under high pressure, in copolymers or in those samples prepared with homogeneous metallocene catalysts [1–3,9–15]. The γ form seems to be favoured by the presence of defects in the iPP chain. In addition, fast quenching of iPP leads to a phase of intermediate order, whose structure is still under controversy [1–3,16–20].

Since conventional supported Ziegler–Natta (ZN) catalysts usually lead to high molecular weights and high stereoregularities, only traces of the γ form are obtained in such cases under normal crystallization conditions. It has been shown [1,10] that the diffractograms corresponding to the α and γ modifications are very similar and only the region around $2\theta = 18–21°$ is appropriate for the differentiation between the two phases. Thus, the α form presents a diffraction at 18.6°, while the γ one shows a peak at $2\theta = 20.1°$. The rest of the diffractogram is very similar for the two modifications.

We are presently carrying out a comparative study of the properties of iPP-based samples synthesized with different catalyst systems, including heterogeneous ZN catalysts of different generations and homogeneous metallocene systems.

The purpose of this work is to analyse the effect of the catalyst system, the presence of comonomer units and the crystallization conditions on the phase structure of iPP and, in particular, on the amount of γ modification obtained.

2. Experimental

Five different types of catalysts have been used in obtaining the samples. Types A, B and C are heterogeneous ZN catalysts based on the system $MgCl_2/TiCl_4$, activated by $AlEt_3$. The difference is that type A does not have any

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Table 1
Results of the characterization of the different polymer samples

Sample	Catalyst	1-Hexene (mol%)	$[\eta]_v$	M_n	M_w/M_n	II	[mmmm]	T_m^a (°C)
PPML83	A	0	—	—	—	0.42	0.65	134
PPF08	B	0	—	47900	6.5	0.93	0.85	159
PHF24	B	4.7	—	—	—	—	0.77	147
PP1901	C	0	0.75	29900	6.1	0.92	0.82	156
PPZ02	D	0	0.58	35160	1.8	—	0.94	143
PPZ19	E	0	0.64	38600	1.9	—	0.93	145
PHZ431	E	2.6	0.52	31480	1.9	—	0.91	121

[a]Peak melting temperature after crystallization from the melt at 100°C/min

kind of donor while type B includes diisobutyl phthalate as internal donor and phenyltriethoxysilane as external donor, and type C includes 2,2-dicyclopentyl-1,3-dimethoxy propane as internal donor [21] and without external donor. Type D is an homogeneous metallocene catalyst of *rac*-ethylene-bisindenyl-zirconium dichloride, $Et(Ind)_2ZrCl_2$, activated by methylaluminoxane, MAO. Finally, type E consists also of $Et(Ind)_2ZrCl_2$ activated with a suitable Al*i*-But_3/MAO mixture [22].

These types of catalysts have been used to prepare the iPP homopolymers and the iPP–1-hexene copolymers indicated in Table 1. The comonomer compositions and the isotactic pentad fractions, [mmmm], were determined from the n.m.r. spectra in solutions of $C_2D_2Cl_4$. The isotactic content, II, corresponds to the weight fraction of the insoluble part of the polymer in boiling heptane. Intrinsic viscosities, $[\eta]_v$, were determined in 1,2-dichlorobenzene, DCB, at 135°C. Molecular weights were measured by g.p.c. in solutions of DCB at 135°C. Table 1 shows the results for the different samples. Some of them were not fractionated for II measurement because they have been prepared by using the above-mentioned single-site catalyst $Et(Ind)_2ZrCl_2$.

Wide-angle x-ray diffraction, WAXD, patterns were recorded at room temperature using a Philips diffractometer with a Geiger counter, connected to a computer. Ni-filtered Cu Kα radiation was used. The diffraction scans were collected over a period of 15 min between 2θ values of about 5 and 35° using a sampling rate of 1 Hz. The initial films for WAXD were prepared in a Collin press by cooling from the melt under a little pressure. The cooling process was carried out by quenching to room temperature (cooling rate of about 100°C/min) or by slow cooling at the inherent rate of the press (approximately at 3°C/min). Selected specimens were also crystallized by cooling from the melt at controlled rates in a Mettler FP82HT hot stage.

Calorimetric analyses were carried out in a Perkin-Elmer DSC7 calorimeter, connected to a cooling system and calibrated with different standards. About 7 mg of sample were used, and the heating rate was 10°C/min. The peak melting temperatures of the different samples after crystallization from the melt at 100°C/min are shown in the last column of Table 1.

3. Results and discussion

Since the diffractograms corresponding to the α and γ forms of iPP are rather similar, the determination of the relative proportion of both phases is not straightforward, and several methods have been proposed [10,23]. We have used a deconvolution procedure, after subtraction of the amorphous component. For that purpose, we acquired the diffraction pattern of an elastomeric polypropylene sample, obtained with an unbridged 'oscillating' metallocene catalyst [24,25]. No crystallinity has been detected in this sample by d.s.c., or by x-ray diffraction, as observed in the middle diffractogram of Fig. 1. A certain proportion of this amorphous pattern has been subtracted from the profiles

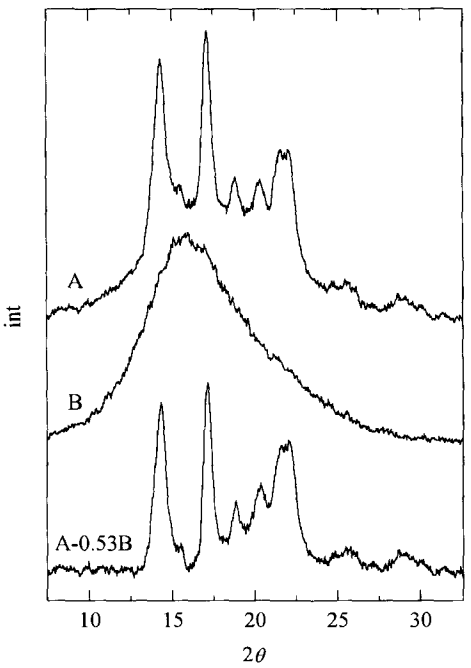

Fig. 1. X-ray diffraction profiles showing the procedure for obtaining the 'pure crystalline' diffractogram. (A) Actual sample (PPML83-d); (B) totally amorphous sample (elastomeric polypropylene), and difference A–0.53B, representing the 'pure crystalline' profile. A and B are normalized to the same total area, so that the x-ray degree of crystallinity of A is 0.47.

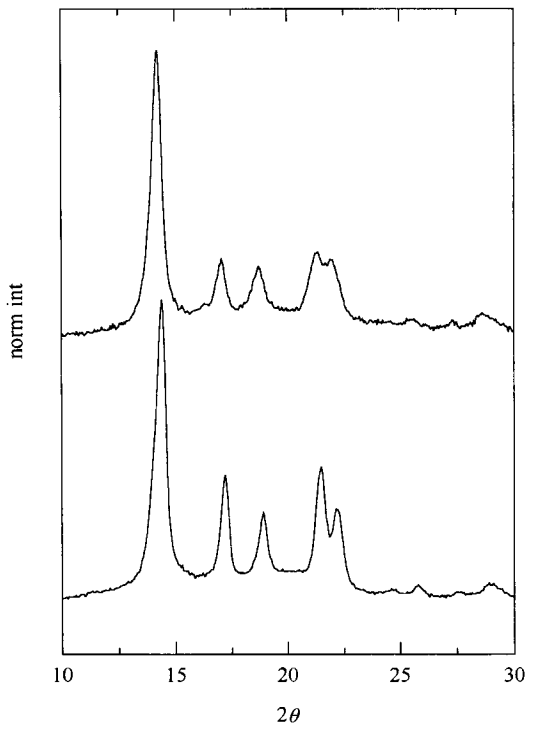

Fig. 2. X-ray diffractograms corresponding to homopolymer PP1901 crystallized from the melt at different cooling rates: 100°C/min (upper) and 3°C/min (lower).

of the different sample preparations and, assuming a simple two-phase model, the corresponding 'pure crystalline' diffractogram can be deduced when a flat background is obtained, as depicted in Fig. 1. Since all the original diffractograms were normalized to the same total intensity, the estimation of the x-ray crystallinity is straightforward.

Subsequently, the crystalline diffractograms were deconvoluted by using Pearson VII profiles for the crystalline diffractions. The proportion of the two modifications is obtained from the relative areas of the diffractions at $2\theta = 18.7$ and 20.2°. Evidently, the results will change slightly if a different method or different profiles for the fitting are applied, since the diffractions overlap. Moreover, we are assuming with this procedure that, in the samples with 100% of α or γ modification, the relative areas of the diffractions at 18.7 and 20.2°, respectively, in relation to the total crystalline area, are the same in both cases (we were unable to prove this point since we have not got pure modifications of both in any sample).

It is known that obtaining significant amounts of γ modification is rather difficult in the case of iPP samples of high isotacticity obtained with heterogeneous catalysts. Thus, Fig. 2 shows the diffractograms of two specimens of sample PP1901, obtained with catalyst C. These diffractograms show the diffractions corresponding to the α form of iPP. The presence of a peak at 20.1°, arising from the γ phase, cannot be totally disregarded, but it is inside the noise level (an upper limit of 15% of γ content is deduced, as indicated in Table 2). The total crystallinity of these specimens is rather high (see also Table 2) and the crystallites for specimen PP1901-b seem to be large, as expected, judging from the width of the reflections. Similar arguments apply for sample PPF08 (see Table 2), obtained with catalyst B, which displays a slightly higher isotacticity than polymer PP1901.

The presence of comonomer units have been reported to favour the formation of the γ modification. We have studied, in a previous paper [26], several copolymers of iPP and 1-hexene obtained with a catalyst of type B. The reported diffractograms of the quenched samples did not show any clear indication of the γ modification, although the crystallinity levels obtained for high comonomer contents preclude any precise conclusion. We have focused our attention, therefore, on the copolymer with the smaller comonomer content: 4.7 mol% of 1-hexene. The diffractograms for a quenched and a slowly crystallized specimen of this copolymer, named PHF24, are shown in Fig. 3. No clear indication of the γ modification can be deduced from these diffractograms. A peak at 20.1° may be present, although in a minor proportion. We also studied, in a previous paper [27], several fractions of copolymer PHF24, obtained by extracting with octane at different temperatures. The diffractograms of these fractions, with varying comonomer contents, stereoregularity and molecular weight, and crystallized from the melt, did not show a clear indication of the presence of γ form.

The situation is much different for the iPP sample obtained with catalyst A. This sample, PPML83, has a rather small isotactic content (see Table 1). Fig. 4 shows the

Table 2
X-ray crystallinity, f_c, and γ phase content, f_γ, for the iPP samples crystallized from the melt at different cooling rates

Specimen	Cooling rate (°C/min)	f_c^a	f_γ^b
PPML83-a	100	0.52	0.25
PPML83-b	10	0.47	0.44
PPML83-c	5	0.52	0.57
PPML83-d	1.5	0.47	0.67
PPF08-a	100	0.67	< 0.10
PPF08-b	3	0.70	< 0.20
PHF24-a	100	0.29	< 0.20
PHF24-b	3	0.42	< 0.30
PP1901-a	100	0.72	< 0.10
PP1901-b	3	0.74	< 0.15
PPZ02-a	100	0.60	~0.15
PPZ02-b	10	0.59	0.39
PPZ02-c	5	0.60	0.50
PPZ02-d	1.5	0.58	0.57
PPZ19-a	100	0.55	~0.15
PPZ19-b	16	0.57	0.36
PPZ19-c	8	0.56	0.41
PPZ19-d	4	0.55	0.48
PPZ19-e	1.5	0.51	0.58
PHZ431-a	100	0.50	< 0.3
PHZ431-b	3	0.50	~0.7

[a]Estimated error, ± 0.05
[b]Estimated error, ± 0.10

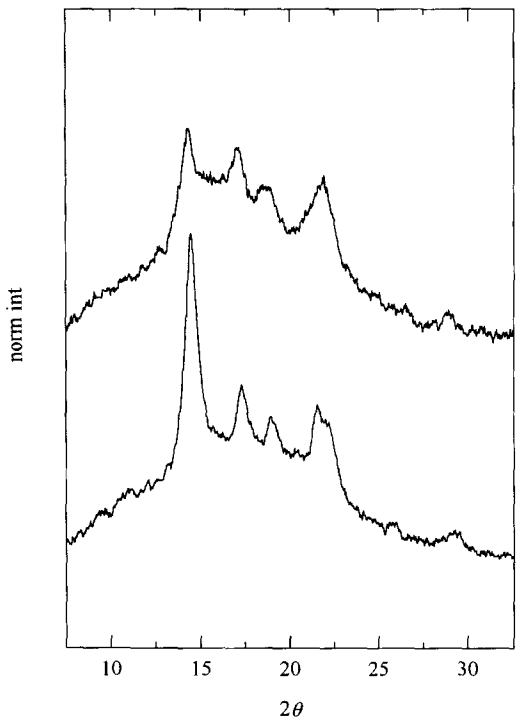

Fig. 3. X-ray diffractograms corresponding to copolymer PHF24 crystallized from the melt at different cooling rates: 100°C/min (upper) and 3°C/min (lower).

WAXD patterns corresponding to specimens of sample PPML83 prepared at different cooling rates. A clear peak of varying intensity can be observed at around 20.2°, indicating that the γ content increases as the cooling rate decreases, since this diffraction increases in intensity while the one at $2\theta = 18.7°$, arising from the α phase, diminishes. Thus, only a minor amount of the γ modification is present in the quenched sample, while it represents the major proportion for the specimen crystallized at the smallest rate.

The results of Table 2 indicate that the estimated content of the γ modification for sample PPML83 increases markedly as the cooling rate decreases, and the proportion between the two modifications can be controlled, therefore, by the crystallization conditions.

The remaining three samples have been synthesized with metallocene-based catalysts. Homopolymer PPZ02 was obtained with catalyst D. The corresponding results for the crystallinity and the γ content are also presented in Table 2. It is observed that the fractions of γ form for this polymer are slightly smaller than those for sample PPML83, for the same cooling rate.

We have also analysed a sample, PPZ19, synthesized with catalyst E, similar to catalyst D, but activated with Al*i*But$_3$, thus exhibiting a significantly higher activity (2.3 times higher). Fig. 5 shows the diffractograms of different specimens of this sample. The results of crystallinity and γ content (see Table 2) are practically identical to those for sample PPZ02, i.e. a higher yield of polymer is obtained

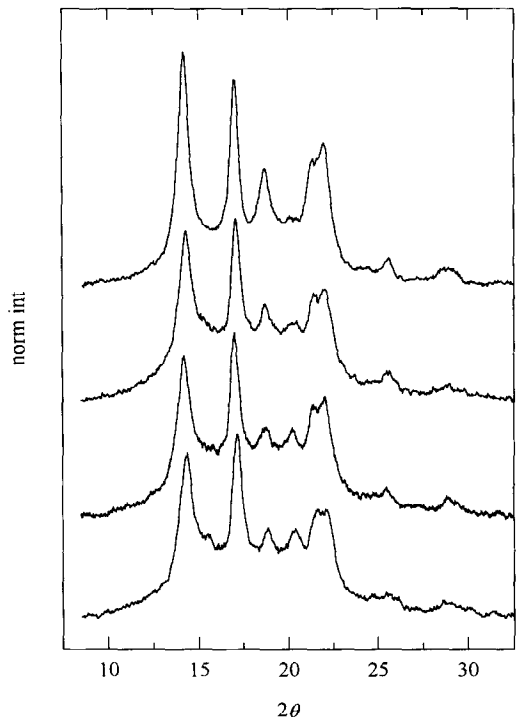

Fig. 4. X-ray diffractograms corresponding to homopolymer PPML83 crystallized from the melt at different cooling rates. From top to bottom: 100, 10, 5 and 1.5°C/min.

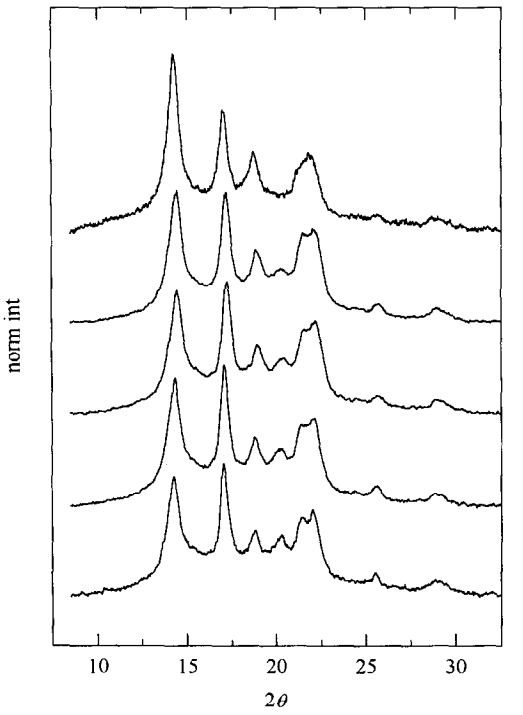

Fig. 5. X-ray diffractograms corresponding to homopolymer PPZ19 crystallized from the melt at different cooling rates. From top to bottom: 100, 16, 8, 4 and 1.5°C/min.

with catalyst E without a change in the properties analysed in this paper.

The last sample, PHF431, is a copolymer of iPP and 1-hexene, also prepared with the metallocene-based catalyst E. The diffractograms of two specimens of this copolymer are shown in Fig. 6. The noise level is rather high, due to the limited amount of sample. Nevertheless, the diagram for the slowly crystallized specimen shows a prominent peak around 20.2°, i.e. the γ form is predominant in this specimen. Regarding the quenched specimen, the amount of γ modification does not appear to be significantly different than the corresponding amount for homopolymer PPZ19, even though the molecular weight of the copolymer is slightly smaller. It seems, therefore, that the presence of comonomer units has not increased the ability to produce the γ phase by very much.

The influence of the cooling rate on the total crystallinity seems to be rather small, since the values for any particular sample are within the experimental error (see Table 2), and only in the case of copolymer PHF24 was a significantly smaller crystallinity obtained for the quenched specimen.

The effect of the cooling rate on the proportion of γ modification can be observed in Fig. 7, where the γ contents have been plotted against the logarithm of the cooling rate for three of the samples. Since the number of data points is very limited, and considering the experimental uncertainty, any conclusion from these results is rather speculative. A single line has been drawn through all the data points in Fig. 7, but it seems that different lines are obtained, the

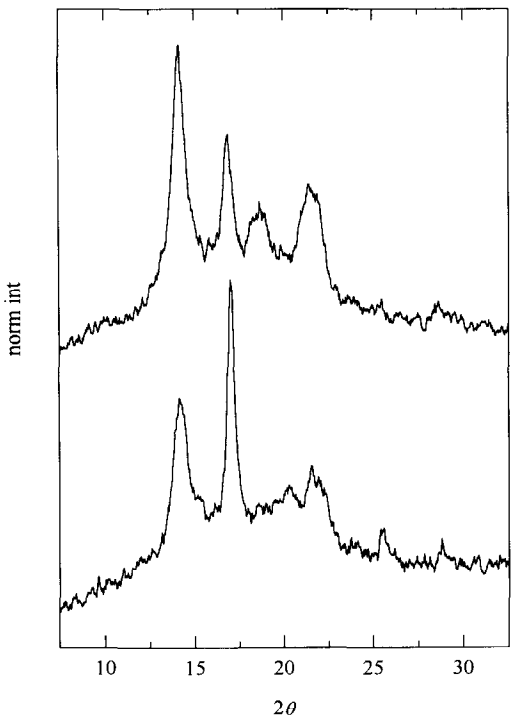

Fig. 6. X-ray diffractograms corresponding to copolymer PHZ431 crystallized from the melt at different cooling rates: 100°C/min (upper) and 3°C/min (lower).

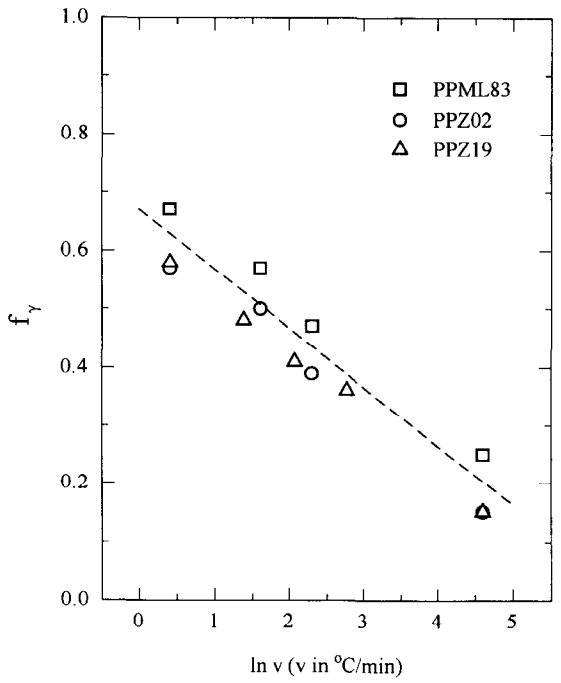

Fig. 7. Plot of the γ phase content as a function of the logarithm of the cooling rate for the indicated samples.

ordinate depending on the kind of sample, showing its higher or lower tendency to produce the γ phase. Of course, the molecular weight of the sample will also play an important role on the ability to produce the γ modification. In fact, a metallocene iPP sample with $M_w = 18\,000$ has been reported [28] to produce 100% γ form when isothermally crystallized at high temperatures (in that paper, progressively lower proportions of γ form were obtained when lowering the crystallization temperature).

The right-hand side of Fig. 7, corresponding to very high cooling rates, may present a discontinuity due to the formation of the disordered phase obtained by fast quenching of iPP. We have not found any indication of this phase in this study (the highest cooling rate has been around 100°C/min).

We plan to extend these investigations to other iPP samples, trying to get a better picture of the ability to produce the γ modification. It seems from Fig. 7 that any iPP sample will be able to give this modification: it is just a matter of diminishing the cooling rate (or the molecular weight), and the more steric defects present in a given sample, the less we need to diminish the cooling rate. This is the case of iPP samples of very low isotactic content or those synthesized with metallocene catalysts, where the errors, although not very numerous, are evenly distributed, and considerable amounts of γ phase are obtained at moderate cooling rates. On the contrary, iPP samples of high stereoregularity from heterogeneous catalysts need extremely low cooling rates. We plan to carry out such experiments, keeping the samples under vacuum or in inert atmosphere to prevent the degradation of the samples in the very long times required. Moreover, isothermal

experiments are also planned, since the isothermal crystallization at progressively higher temperatures will also give higher amounts of γ form.

We have also analysed these samples by d.s.c., trying to get another estimation of the γ content from the melting patterns. Fig. 8 shows the melting curves corresponding to sample PPZ02 crystallized from the melt at three different cooling rates. It is evident from these patterns that the melting temperatures of both the α and γ modifications are very similar and their relative content cannot be determined by d.s.c. The peak melting temperature of the slowly crystallized specimen (with more γ form) is slightly higher than the one for the quenched sample. It has been reported [28] that the α form is the one that melts at higher temperature. However, a slower crystallization will produce thicker crystals, with higher melting temperatures, which could explain the d.s.c. results. Moreover, recrystallization phenomena may be present in the d.s.c. experiments. We plan to analyse these aspects by real-time synchrotron experiments.

The peak melting temperatures of the different samples, quenched from the melt, are shown in the last column of Table 1. Besides the molecular weight, three other variables influence the melting temperatures: [mmmm] content, comonomer content and kind of catalyst (distribution of errors). Regarding the heterogeneous catalysts, a decrease of 25°C is found when comparing homopolymer samples PPF08 and PPML83, mainly due to their very different [mmmm] content. However, the decrease of the peak melting temperature caused by the presence of comonomer (sample PHF24) is rather small, since, for heterogeneous catalysts, the comonomer units (and any kind of error, including tacticity errors) are concentrated in the lower molecular weights, and the higher molecular weight chains have a content smaller than average, thus leading to longer sequences free of defects.

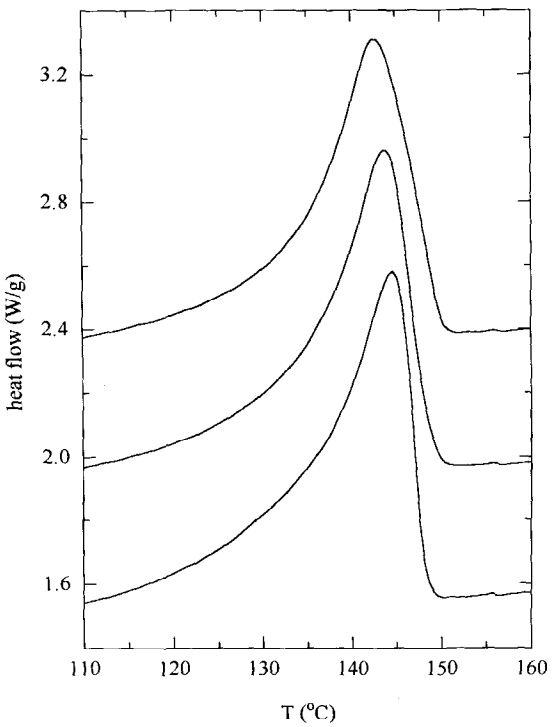

Fig. 8. D.s.c. melting curves corresponding to sample PPZ02 crystallized from the melt at different cooling rates. From top to bottom: 100, 20 and 3°C/min.

The errors are much more evenly distributed in the samples synthesized with homogeneous catalysts, in such a way that samples PPZ02 and PPZ19 display lower melting temperatures than PPF08 or PP1901, even though those have a higher [mmmm] content. For the same reason, a considerable decrease of the melting temperature is found for copolymer PHZ431, with only a 2.6 mol% comonomer content, but with a distribution presumably more random than that for copolymer PHF24. A similar behaviour is found in ethylene copolymers, when comparing samples prepared with heterogeneous and homogeneous catalysts [29,30].

4. Conclusions

Minor amounts, if any, of γ modification are present in iPP samples synthesized with highly isospecific ZN catalysts and crystallized from the melt at different cooling rates, ranging from 100 to 3°C/min. On the contrary, considerable amounts of the γ form have been obtained both in samples prepared with catalysts of very low isospecificity or in those prepared with homogeneous metallocene catalysts. It has been shown that the relative proportion of the α and γ modifications can be controlled just by changing the crystallization conditions.

A clear influence of the presence of comonomer units on favouring the formation of the γ phase has not been ascertained. Moreover, attempts to deduce the γ content from the d.s.c. melting patterns have been unsuccessful, since the two modifications exhibit very similar melting temperatures.

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