Thermal behaviour of polypropylene fractions: 2. The multiple melting peaks

Ritva Paukkeri*
Department of Polymer Chemistry, University of Helsinki, PO Box 13, SF-00014 HY, Helsinki, Finland

and Arja Lehtinen
Neste Oy Chemicals, Polyolefins R&D, PO Box 320, SF-06101 Porvoo, Finland
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The appearance of double melting endotherms in dynamic d.s.c. runs of polypropylene fractions was studied with the aim of relating their appearance to the structure of the polymer. Fractions obtained by fractionation either according to stereoregularity or to molecular weight were investigated. Double peaks were detected for low molecular weight, non-isotactic fractions, as well as for low molecular weight fractions with isotacticities around 90%. Fractions consisted of pure α crystal form and those showing double melting endotherms had low average isotactic sequence lengths, generally below 80 propylene units. The occurrence of double-peak shapes was attributed to two different processes, one characteristic of highly stereoirregular material, and probably constituted by melting of two different crystalline species, and the other consisting of reorganization or recrystallization of less-ordered domains of crystalline material taking place during the melting scan.

(Keywords: isotactic PP; fractionation; differential scanning calorimetry; melting behaviour; stereoregularity; molecular weight)

INTRODUCTION

When the crystallization and melting behaviour of polypropylene fractions obtained either by fractionation according to molecular weight or isotacticity was studied, double peaks in the d.s.c. melting endotherms were detected for low molecular weight and non-stereoregular fractions[1]. Melting endotherms with multiple peak shapes have been reported by many authors and several reasons for their appearance have been proposed. Usually isothermally crystallized samples were examined using different crystallization temperatures. When the appearance of β-phase has been excluded, recrystallization or reorganization during the melting scan[2,3] and segregation during crystallization[4] have been suggested as possible causes of multiple endotherms. For syndiotactic polypropylene, double-peak shapes have been attributed to inhomogeneities in molecular weight[5].

In this work dynamic crystallization runs were applied to polypropylene fractions obtained by fractionation according to either stereoregularity or molecular weight. Utilizing structural analyses[1,6] made on the fractions obtained by fractionation according to stereoregularity, causes for the appearance of multiple melting peaks were sought. A set of fractions obtained by fractionation according to molecular weight was also submitted for [13]C n.m.r. sequence analysis with the aim of attaining a better understanding of the change in stereoregularity with molecular weight. Another objective was to separate the influence of molecular weight on the shape of melting endotherm from that of other parameters.

EXPERIMENTAL

The fractionation procedures and the structural characterization of the fractions have been described previously[1,6]. [13]C n.m.r. spectroscopic pentad distributions were determined for the fractions separated according to molecular weight using the procedure described in reference 6.

Wide-angle X-ray diffractograms were obtained on a Siemens diffractometer, model 500 using CuKα radiation with a wavelength of 1.54 Å. X-ray studies of selected fractions were performed either directly on the precipitated material or on hot-pressed films melted at 200–225°C and cooled to 40°C at a rate of 10°C min^{-1}.

D.s.c. runs were performed on a Mettler TA 4000 DSC 30 instrument. Before crystallization and melting experiments, samples were premelted in order to erase their thermal history and morphology. Samples (3 mg) were heated from 30 to 200°C at a rate of 10°C min^{-1}, cooled to 30°C at the same rate and reheated to 200°C. Reheating was performed at a rate of 10°C min^{-1} with the exception of some experiments in which the influence of heating rate on the melting endotherm was studied. Correspondingly, experiments were carried out to study the dependence of crystallization on cooling rate. The instrument was calibrated with water, indium and lead. Measurements were carried out under nitrogen atmosphere.

RESULTS AND DISCUSSION

Two endothermic peaks were detected in the d.s.c. melting curves of polypropylene fractions having low isotacticity

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and/or low molecular weight. An example of the typical change in the shape of melting endotherms of the fractions with increasing molecular weight and isotacticity is given in *Figure 1*. These fractions were obtained from a slurry polymerized sample (designated as sample B) by fractionation according to stereoregularity. The first fraction (B/1) had a considerably lower melting temperature (T_m), its second melting peak being in the same temperature range as the first melting peaks of the other fractions. Correspondingly, the first melting temperatures at 140–145°C were detected for the first few fractions of other samples obtained by fractionation according to stereoregularity (see *Table 1*). For the higher melting fractions showing double endotherms, it was the first melting temperature that formed a continuous line as a function of molecular weight with melting temperatures

of highly isotactic fractions showing single endotherms (see *Figure 2*: in this figure T_m is presented for all fractions of sample A, not only for the fractions submitted for n.m.r. sequence analysis).

The heating rate used in these melting runs was 10°C min⁻¹, which has been reported as an optimum rate to avoid reorganization or recrystallization influencing the shape and character of the melting endotherm of isotactic polypropylene[7]. Some selected low molecular weight fractions were submitted for WAXS analysis. These studies were performed on both precipitated fractions and melt-pressed films (an example is shown in *Figure 3*). No β-phase was found in either case. Thus, the source of double-peak shapes should be related to processes involving α crystals only. In the literature double melting endotherms have been attributed to

Table 1 Characteristics of some selected polypropylene fractions obtained by fractionation according to stereoregularity

Fraction	$\bar{M}_w$ ($\times 10^{-3}$)	$\bar{M}_w/\bar{M}_n$	mmmm (%)	rrrr (%)	Av.m-seq./ propylene units[a]	T_{m1}[b] (°C)	T_{m2} (°C)
A/1	34	3.5	57.4	5.1	9	139.9	151.6
A/2	42	3.9	53.3	9.5	9	145.6	156.4
A/6	87	2.3	93.6	0.1	68	159.1	166.6
A/9	135	2.2	95.9	0.0	123	163.7	–
A/11	192	2.4	96.4	0.0	137	164.4	–
A/14	323	2.6	97.0	0.0	159	166.2	–
A/15	749	3.7	97.5	0.0	196	168.7	–
B/1	22	3.1	73.0	3.8	21	145.5	154.9
B/8	79	2.2	77.5	3.2	27	154.9	164.2
B/13	116	2.3	82.0	2.0	21	159.1	166.7
B/14	228	2.6	93.4	0.8	80	165.0	–
B/16	317	2.8	93.6	1.0	83	165.0	–
B/18	651	3.2	98.1	0.0	265	167.5	–
C/1	61	3.7	61.6	6.2	10	143.0	154.9
C/2	126	4.6	46.9	10.5	9	141.4	154.2
C/6	120	2.5	81.7	2.6	31	160.9	167.6
C/8	192	2.4	93.0	0.8	86	164.1	–
C/11	241	2.3	95.2	0.0	99	165.9	–
C/12	308	2.3	97.7	0.0	195	167.5	–
C/13	380	2.5	98.1	0.0	255	169.3	–
D/1	27	3.0	67.1	4.3	10	139.8	150.6
D/2	56	4.2	46.0	9.5	6	140.4	151.7
D/4	103	4.8	53.3	15.9	11	150.6	160.6
D/11	178	2.5	96.1	0.3	113	162.1	–
D/13	225	2.5	96.9	0.0	108	163.0	–
D/15	562	3.1	98.2	0.0	272	165.4	–
E/2	37	4.0	83.0	1.5	26	145.5	156.4
E/9	73	2.0	96.0	0.0	147	161.2	–[c]
E/13	149	2.1	98.8	0.2	497	164.5	–
E/15	460	2.9	99.0	0.0	554	166.3	–
E/16	335	2.6	99.5	0.0	998	162.9	–
E/18	491	2.8	99.5	0.0	998	167.9	–

[a] Data from reference 6
[b] Melting temperatures for all fractions are presented in reference 1
[c] Shoulder on the right-hand side of the melting endotherm, peak temperature not detected

transitions between different modifications of α crystal form[8,9]. Two limiting structures, α_1 and α_2 forms, differing in degrees of disorder in the up- and down-positioning of the chains, have been postulated for the α crystal form[8,9]. The relative amounts of these two forms can be evaluated using an X-ray diffraction technique. Guerra *et al.*[9] have also proposed that a 'continuum' of different structures could exist instead of only two limiting forms co-existing in various ratios. This 'continuum' changes

from the limiting disordered modification α_1 to the limiting ordered modification α_2.

In this work the low molecular weight fractions showed double melting endotherms (see *Table 1*). These fractions consisted of about 15–22% of the materials and had mostly broad molecular weight distributions (*MWD*s), with the exception of fractions of sample B, and low
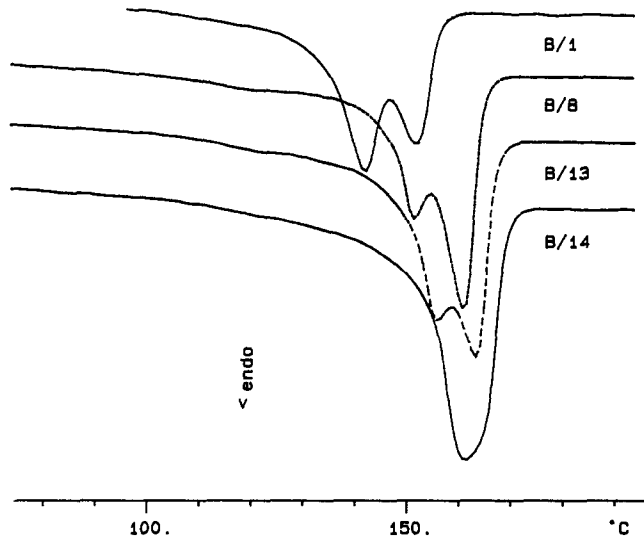

Figure 1 Melting endotherms of some polypropylene fractions obtained by fractionation according to stereoregularity (sample B)
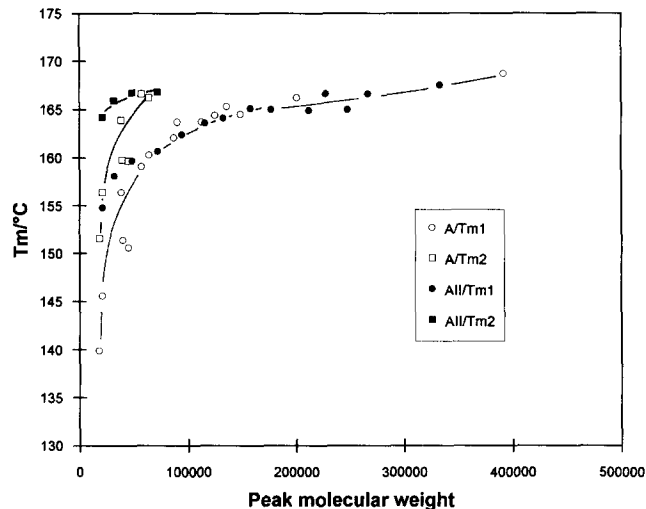

Figure 2 Correlation between melting temperatures and molecular weight for all the fractions of sample A: (○) T_{m1} and (□) T_{m2} of fractions obtained by fractionation according to stereoregularity; (●) T_{m1} and (■) T_{m2} of fractions obtained by fractionation according to molecular weight. T_{m1} is the first melting temperature of a double endotherm or the peak temperature of a single endotherm, and T_{m2} is the second melting temperature of a double endotherm
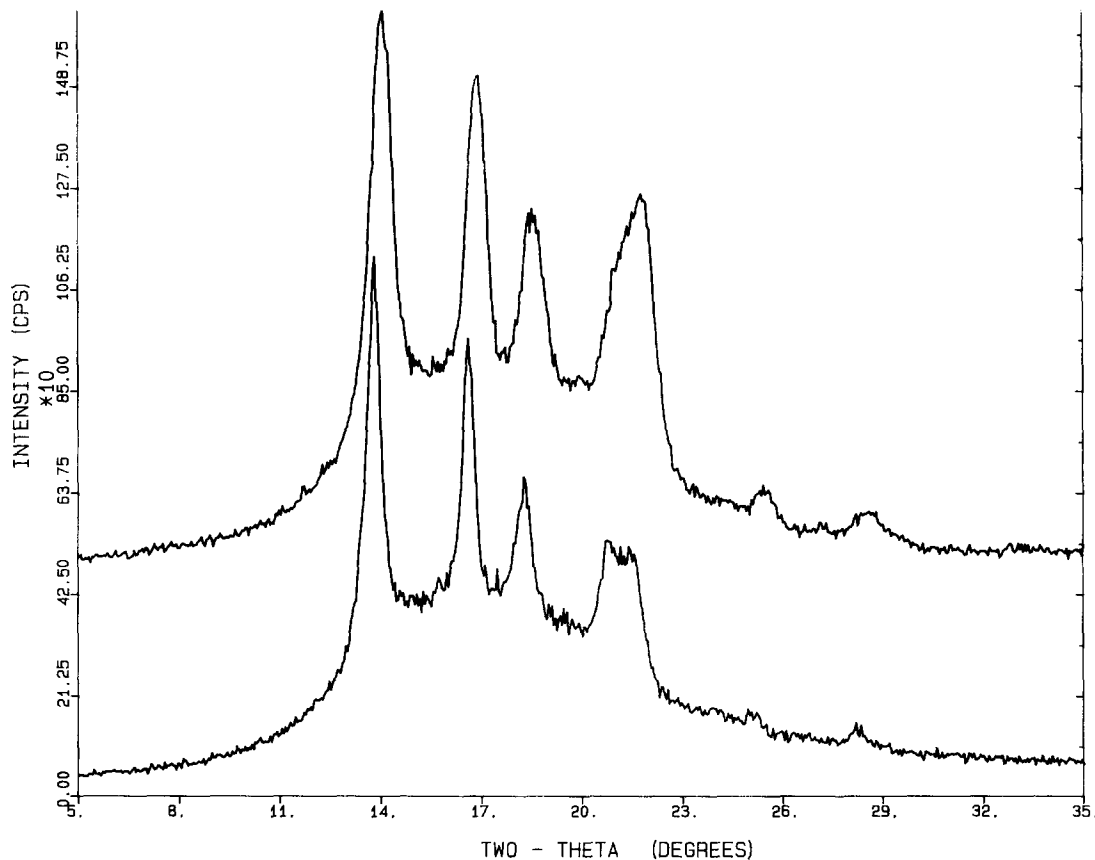

Figure 3 X-ray diffractograms of fraction C/1 ($\bar{M}_w = 61\,000$, 61.6% *mmmm*). The upper curve was measured for the precipitated fraction, the lower one for melt-pressed film

isotacticities. Depending on the sample studied, the molecular weight of the fraction was over 60 000–160 000 before a single melting endotherm was detected (*Figure 2*). However, no minimum value for isotactic pentad sequence content could be given for the appearance of a single melting peak. The fractions with low isotacticity also contained some syndiotactic material (for complete sequence analysis, see reference 6). The second melting peak disappeared when the average *m*-sequence length of the fraction was around 80 propylene units, except for fractions of sample E. These fractions had very low molecular weights and, for example, in the melting curve of fraction E/9 ($\bar{M}_w = 73\,000$) a shoulder on the right-hand side of the endotherm was still detected, though the average *m*-sequence length was 147 propylene units.

Despite the fractionation technique used, the short-chain fractions showed double melting endotherms (*Figure 2*). When fractionated according to molecular weight, sample A was divided into larger fractions (designated as AII fractions) than in fractionation according to stereoregularity[1]. Thus, the non-isotactic part, which consists of only around 5% of the material (according to [13]C n.m.r. spectroscopic analysis[1] the amount of isotactic *mm* triads was 95% in sample A), was not separated as well as in fractionation according to stereoregularity.

The first fractions of the AII series showing double

melting endotherms had higher melting temperatures than the first fractions obtained from the same sample by fractionation according to stereoregularity (*Table 2*). These fractions had narrow *MWD*s, thus excluding a lower molecular weight fraction[5] as a possible cause of the appearance of double-peak shapes. The [13]C n.m.r. spectroscopic pentad distributions in *Table 3* show that the defects in stereoregularity were also concentrated in low molecular weight fractions in this type of fractionation, long-chain fractions containing only *mmmrrmmm* propagation errors. Syndiotactic material was now more evenly distributed between the fractions with different molecular weights, and no link between syndiotactic content and the occurrence of double endotherm could be detected. Again the second melting peak disappeared when the average *m*-sequence length was high enough (over 84 propylene units).

As mentioned earlier, most authors have attributed the higher melting peak to material reorganized during the d.s.c. scan. A different explanation for the occurrence of double endotherms was suggested by Martuscelli *et al.*[10]. They proposed that the two melting peaks observed in their isothermally crystallized fractions with a lower degree of stereoregularity may be related to the existence of processes of primary and secondary crystallization in the samples. The higher melting temperature corresponded to the fusion of lamellar crystals formed during the process of primary crystallization, whereas the lower temperature corresponded to the fusion of crystals grown mainly in interfibrillar regions during the secondary crystallization process.

When the shapes of the melting endotherms of AII fractions were examined (*Figure 4*) it was observed that the size of the second melting peak decreased with increasing molecular weight (stereoregularity also increased slightly with increasing molecular weight). Correspondingly, when the influence of heating rate on the shape of these endotherms was studied, a very low heating rate increased the size of the second melting peak. When the heating rate was high (20°C min^{-1}) only the first melting peak was detected (*Figure 5*). Both these observations support the hypothesis that the second melting peak was caused by reorganization of less-ordered domains of crystalline material during the melting scan, whereas the lower temperature peak was the actual melting peak of the material crystallized in the dynamic crystallization run. Only the first melting peak was present when stereoregularity and the molecular weight of the fraction were high enough.

Table 2 Characteristics of fractions obtained from sample A by fractionation according to molecular weight

Fraction	$\bar{M}_w$ ($\times 10^{-3}$)	$\bar{M}_w/\bar{M}_n$	T_{m1} (°C)	T_{m2} (°C)
AII/1	33	2.5	154.8	164.2
AII/2	44	1.9	158.1	165.9
AII/3	63	1.7	159.7	166.7
AII/4	89	1.5	160.7	166.8
AII/5	118	1.6	162.4	–[a]
AII/6	141	1.5	163.6	–
AII/7	167	1.6	164.1	–
AII/8	207	1.7	165.1	–
AII/9	238	1.8	165.0	–
AII/10	302	2.0	164.9	–
AII/11	321	2.0	166.6	–
AII/12	347	2.0	165.0	–
AII/13	412	2.4	166.6	–
AII/14	526	2.5	167.5	–
AII/15	947	3.1	166.7	–

[a] Shoulder on the right-hand side of the melting endotherm, peak temperature not detected

Table 3 [13]C n.m.r. spectroscopic characterization of the fractions obtained from sample A by fractionation according to molecular weight

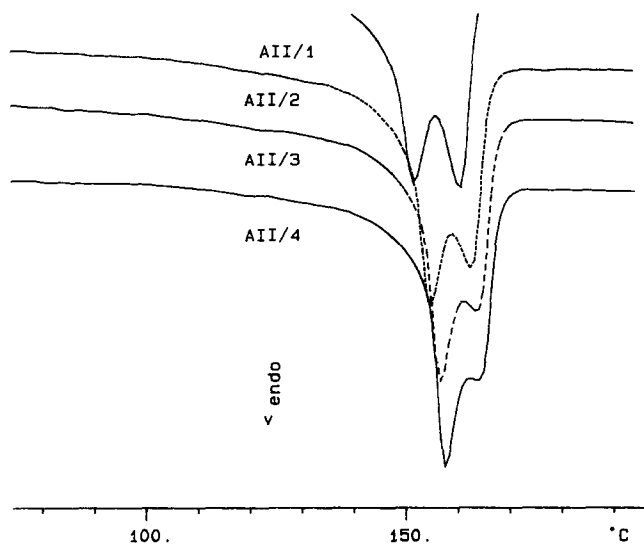| Fraction	*mmmm*	*mmmr*	*rmmr*	*mmrr*	*mmrm* and *rmrr* (%)	*rmrm*	*rrrr*	*mrrr*	*mrrm*	Av. *m*-seq./ propylene units[a]
AII/1	88.2	2.4	0.4	3.2	1.6	0.5	1.4	1.2	1.1	42
AII/4	94.0	1.6	0.2	1.9	0.6	0.0	0.7	0.5	0.5	84
AII/6	96.2	0.9	0.2	1.0	0.4	0.0	0.5	0.3	0.5	135
AII/8	96.9	1.0	0.0	1.1	0.2	0.0	0.3	0.0	0.5	180
AII/10	97.6	1.0	0.0	1.0	0.0	0.0	0.0	0.0	0.4	200
AII/13	97.9	0.6	0.1	0.7	0.1	0.0	0.2	0.0	0.4	233
AII/15	98.3	0.6	0.0	0.6	0.0	0.0	0.2	0.0	0.3	305

[a] Determined as in reference 6

Figure 4 Change in the shape of the melting endotherm with increasing molecular weight of the fractions. Fractions were obtained by fractionation according to molecular weight
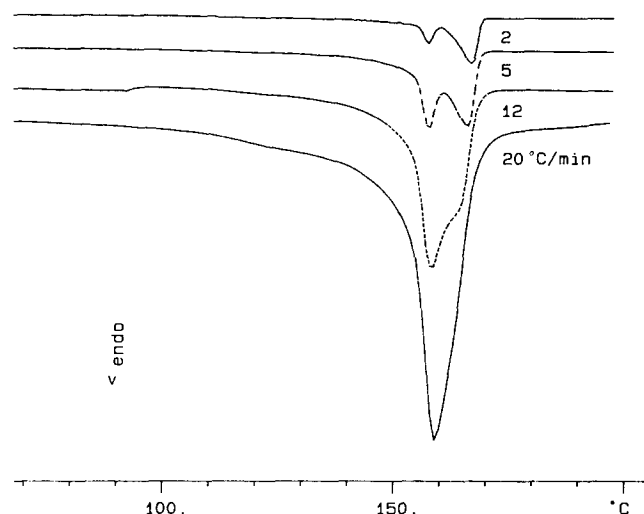

Figure 5 Influence of heating rate on the shape of the melting endotherm of a PP fraction obtained by fractionation according to molecular weight (fraction AII/4, $\bar{M}_w = 89\,000$, 94.0% *mmmm*)

Similar observations concerning the effect of heating rate on the shape of multiple melting endotherms of isothermally crystallized samples have been reported in the literature[2,11]. Yadav and Jain[2] obtained only a single melting peak by using very high heating rates. When the heating rate was lowered, more time was available for reorganization or recrystallization to take place, and the area of the second peak increased. Finally, when the heating rate was extremely low, most of the isothermally crystallized fraction underwent recrystallization and only the second peak was observed. Janimak *et al.*[11] also observed that the heat of fusion attributed to the lower melting peak materials increased with isotacticity, e.g. imperfect crystals with a relatively high isotacticity were less easy to anneal further (during the melting scan) compared with those with low isotacticity.

Fractions obtained by fractionation according to stereoregularity were tested similarly using different heating rates. Melting curves of the fractions showing melting temperatures comparable to the AII set of

fractions underwent a similar change in the shape of melting endotherm with the change in heating rate as the AII fractions. An example is shown in *Figure 6* for C/6 fraction ($\bar{M}_w = 120\,000$, 81.7% *mmmm*). Here again the second melting peak dominated at low heating rates. When the heating rate was increased, the amount of reorganization decreased and the first peak started to dominate.

The areas of individual peaks of a multiple melting endotherm were also influenced by the cooling rate used during crystallization (*Figure 7*). Now the lower melting peak was more pronounced, when lower cooling rates were applied and more time was available for organization in the crystallization step. Thus, no recrystallization occurred for the slowly (2°C min⁻¹) crystallized sample during the melting scan.

In contrast, the melting endotherms of the least isotactic fractions showing their first melting temperatures at 140–145°C were less sensitive to heating rate (*Figure 8*). Thus, the melting peak at 140–145°C may be
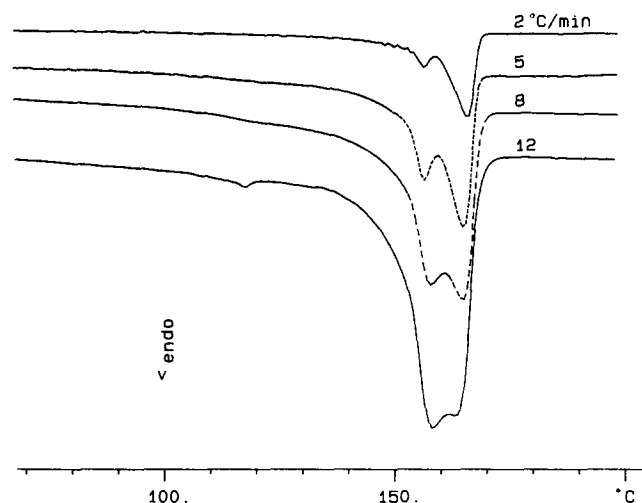

Figure 6 Influence of heating rate on the shape of the melting endotherm of a PP fraction obtained by fractionation according to stereoregularity (fraction C/6, $\bar{M}_w = 120\,000$, 81.7% *mmmm*)
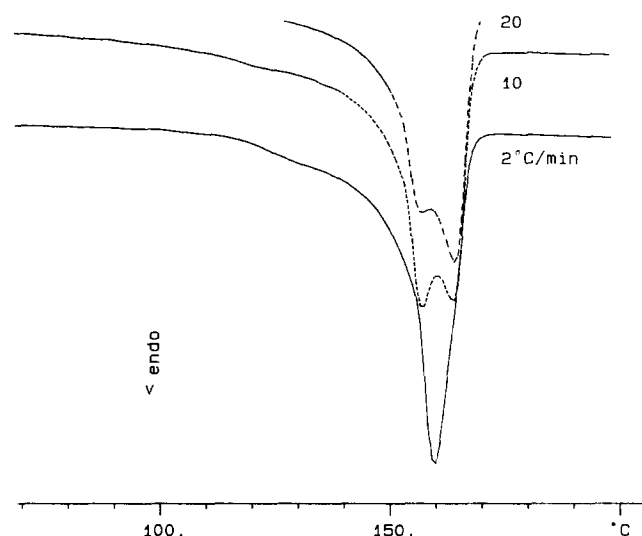

Figure 7 Influence of cooling rate on the shape of the melting endotherm of fraction C/6. The heating rate was 10°C min⁻¹
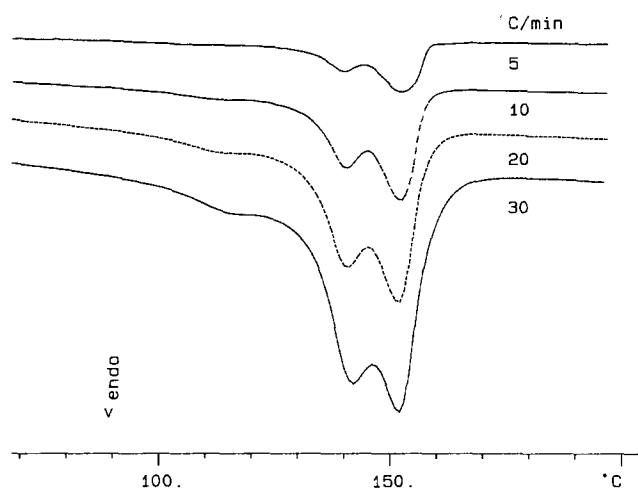
Figure 8 Influence of heating rate on the shape of the melting endotherm of a PP fraction obtained by fractionation according to stereoregularity (fraction C/1, $\bar{M}_w = 61\,000$, 61.6% *mmmm*)

CONCLUSIONS

The examination of the fractions isolated in this study provides a clearer view of the influence of molecular structure of the polymer on the occurrence of multiple melting endotherms. Multiple peaks in low molecular weight fractions were attributed to two distinct processes. One of these, appearing when isotacticity of the material was especially low, probably consisted of the melting of two different crystalline species, stable against the reorganization during the melting scan, whereas for the more isotactic fractions showing double melting endotherms, reorganization took place during the melting scan. When average isotactic sequence lengths of the fractions were high enough, usually around 80 propylene units, only a single peak was detected in the melting endotherms.

attributed to the melting of a separate, thermally more stable non-stereoregular fraction present in this material. Low first melting peaks of multiple endotherms were also detected by Passingham *et al.*[3] for some rapidly cooled polypropylenes. They explained the existence of the peak at 143°C by 'low conformational regularity', as detected by i.r. measurements. This material underwent a melting–recrystallization process during the melting scan. However, this material was highly isotactic, containing less than 2% of *racemic* dyads. Thus, the defects in crystalline structure caused by rapid cooling are not comparable to those caused by low isotacticity of the material.

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