Melting behaviour of controlled rheology polypropylene

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The melting behaviour of reactor-made isotactic polypropylene (PP) and various controlled rheology polypropylene (CR-PP) samples crystallized under both isothermal and non-isothermal conditions were studied by differential scanning calorimetry and the crystal structure of isothermally crystallized samples at 120°C was investigated using wide angle X-ray diffraction. Multiple endotherms were observed dependent on the molecular weight of the samples, heating rate and cooling rate, and method of crystallization. Recrystallization or reorganization occurred more easily for low molecular weight samples and also for fast cooled samples during the reheating and the melting process. The isothermally crystallized CR-PPs produced by peroxide controlled degradation showed a small melting endotherm peak at ~143°C which is probably connected to the β form crystal, while unreacted PP showed the α form crystal only. The small endotherm peak was more prominent in one CR-PP sample of intermediate molecular weight. Attempts were made to explain this behaviour through the observed maximum in the half-time of crystallization *versus* molecular weight plot.

(Keywords: polypropylene; controlled rheology polypropylene; crystallization; melting endotherm; crystalline form; peroxide degradation)

INTRODUCTION

Polypropylene (PP) is a widely used versatile commodity polymer with a number of desirable properties. Commercial PP polymerized with conventional Ziegler–Natta catalysts has a high molecular weight and broad molecular weight distribution. The resulting high melt viscosity and elasticity limit its efficient processing in certain applications exhibiting, for example, draw resonance in fibre spinning. For the purpose of improving application and processing characteristics, the molecular weight and molecular weight distribution of the polymer can be modified under controlled conditions. This is the so-called controlled rheology polypropylene (CR-PP). CR-PP can be prepared in several ways. Controlled degradation of PP through the action of peroxides—known as 'viscbreaking'—is the most widely used approach, although thermo-oxidative degradation during extrusion has also been used[1]. The low molecular weight and narrow molecular weight distribution of CR-PP resins yield several rheological advantages during melt processing resulting from their combined high flowability and low elasticity.

Multiple crystalline forms have been observed for isotactic PP. Padden and Keith[2] classified its spherulites into four types. Keith *et al.*[3] and Turner-Jones *et al.*[4] classified the type I and II spherulites into the α form crystal (monoclinic) as described by Natta and Corradini[5], while types III and IV were categorized as the β form (hexagonal). A γ form was also observed[6,7], possessing a triclinic unit cell, but this has been obtained in the bulk only at high pressures[6] or for low molecular weight PP[7]. CR-PP shows some interesting and quite different morphological features. Awaya[8] reported a large variety of morphologies which do not belong to Padden and Keith's classification[2], including the formation of flower-like spherulites from PPs of high melt flow index (MFI = 120 g per 10 min at 230°C) that was isothermally crystallized at 150°C for more than 40 h. The appearance of radial cracks in the outer regions of these spherulites would suggest the presence, or, even the predominance of lower molecular weight PP in these regions. Altendorfer and Seitl[9] also observed the formation of different morphological structures in CR-PP injection moulded specimens.

The properties of polymer products are known to be affected by their morphology. Often, morphological features can be deduced from the melting behaviour of the polymers. The melting behaviour of PP has been studied by many investigators[10–16]. A common finding of these studies is the observation of multiple fusion endotherms under certain conditions due to the presence of the various crystal forms and spherulitic structures discussed above. Although CR-PP is commonly used in many applications, its thermal behaviour has only been marginally studied[10]. Thus, it is among the objectives of this study to examine the melting behaviour of various CR-PP resins of different molecular weight and molecular weight distribution and to relate it to the morphological features of samples crystallized under both isothermal and non-isothermal conditions.

EXPERIMENTAL

Materials

Unstabilized PP (nominal MFI = 0.8 g per 10 min at 230°C and 2.16 kg) was supplied by Shell Chemical Company in powder form. Three samples of CR-PP with different degrees of degradation were prepared by the *in*

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situ peroxide degradation oven technique described in our previous work[17]. PP powder was mixed with acetone containing the required amount of initiator at room temperature and the acetone was removed by applying vacuum. The degradation reaction on thin cold-pressed films (<1 mm thick) was carried out in a nitrogen circulated oven at 210°C for 3 min. The initiator used was Lupersol 130 (Atochem N. America) at three different concentrations based on the PP resin. The molecular weight and molecular weight distribution of the unreacted (sample A) and the three CR-PP samples (B, C and D) as determined in 1,2,4-trichlorobenzene by high temperature size exclusion chromatography (s.e.c.), Du Pont 900, are shown in *Figure 1* and *Table 1*, where the peroxide concentration used to prepare the CR-PP samples is also indicated. Due to their small sample size, MFI measurements were not possible for the CR-PP samples. However, based on previous data[17], their MFIs (g per 10 min) are estimated as follows: sample B, 20; sample C, 200; sample D, 500.

Thermal analysis

A Perkin-Elmer differential scanning calorimeter (DSC-4) was used in these experiments. Each sample was flushed with nitrogen for 10 min at 40°C and heated up to 200°C at a heating rate of 20°C min^{-1}. Samples were kept for 10 min at this temperature to erase any previous thermal history. For the isothermal crystallization experiments, the samples were rapidly cooled from 200°C to the crystallization temperature of 120°C; after 30 min, the samples were rapidly cooled to 40°C and reheated immediately at various heating rates. Non-isothermally crystallized PP was prepared by cooling the sample from 200 to 40°C at various cooling rates; melting endotherms were then obtained by heating at 20°C min^{-1}. Sample sizes were kept within narrow limits (5 ± 0.5 mg) since large variations in sample weight are known to affect the reproducibility of the data. Differential scanning calorimetry (d.s.c.) samples were chosen from several different locations of the reacted samples to eliminate possible non-uniformity. The reported data are the average of two to five determinations. The data were quite reproducible.

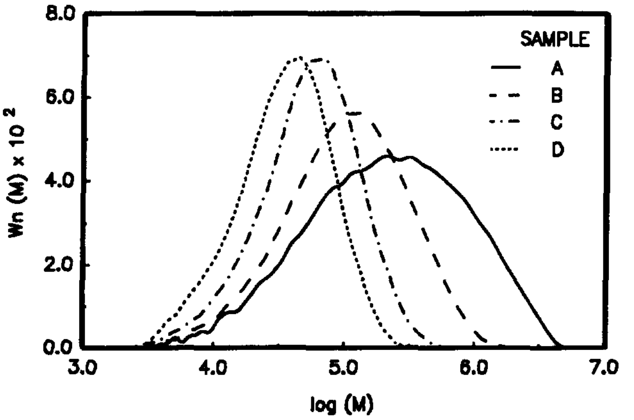

Figure 1 Molecular weight distribution by high temperature s.e.c. of unreacted PP (sample A) and CR-PP (samples B, C and D)

X-ray analysis

X-ray diffraction measurements were carried out with a General Electric XRD-6 X-ray diffractometer with CuKα radiation (Ni filter) at 30 kV and 15 mA. The samples were thin films (0.3 mm thick).

RESULTS AND DISCUSSION

Isothermally crystallized PP

Melting behaviour. Earlier studies[13] on the melting behaviour of reactor made isotactic PP that has been isothermally crystallized in the temperature range 105–125°C indicated that the d.s.c. curve has either two endotherms or may be resolvable into two. This phenomenon was attributed to crystal imperfections. The melting behaviour of samples A–D, which were isothermally crystallized at 120°C, at various heating rates are represented by the d.s.c. curves shown in *Figure 2*. Multiple endotherm peaks are sometimes observed depending on the heating rates. The observed peaks are labelled as T_1, T_2 and T_3 corresponding to their ascending order of appearance with temperature. Peaks T_1, T_2 and T_3 are observed, respectively, at ~143, 155–161 and 161–165°C depending on the molecular weight of the sample and the heating rate.

The total area of the melting peaks, i.e. the heat of fusion, is found to be more or less independent of the heating rate for all samples and is ~96 J g^{-1}. This observation suggests that the crystallinity of the sample is not affected by the heating rate, at least in the range studied. It is observed that with decreasing heating rate the area under peak T_3 (A_3) increases at the expense of the area under peak T_2 (A_2) and at high heating rates A_3 disappears completely. *Figure 3* shows clearly the effect of the heating rate on A_3. The increase of A_3 with decreasing heating rate suggests that recrystallization or reorganization of crystals originally formed during the isothermal crystallization occurs during melting. Generally. it has been shown[11–13] that peak T_2 represents the melting of crystals formed during isothermal crystallization, and peak T_3 is due to the melting of crystals formed by recrystallization or reorganization of the original crystals during heating. It has been also reported by various investigators[12–14] that recrystallization or reorganization can occur during melting of metastable crystals. At low heating rates metastable crystals have enough time to change into stable crystals by

Table 1 Molecular weight and molecular weight distribution of unreacted PP and CR-PP samples

Sample	Description	M_n	M_w	M_z	M_w/M_n
A	Unreacted PP MFI = 0.8	6.4×10^4	3.86×10^5	12.0×10^5	6.0
B	CR-PP 0.1 wt% peroxide	4.8×10^4	1.53×10^5	3.43×10^5	3.2
C	CR-PP 0.3 wt% peroxide	3.3×10^4	7.1×10^4	1.24×10^5	2.1
D	CR-PP 0.7 wt% peroxide	2.3×10^4	4.5×10^4	7.8×10^4	2.0

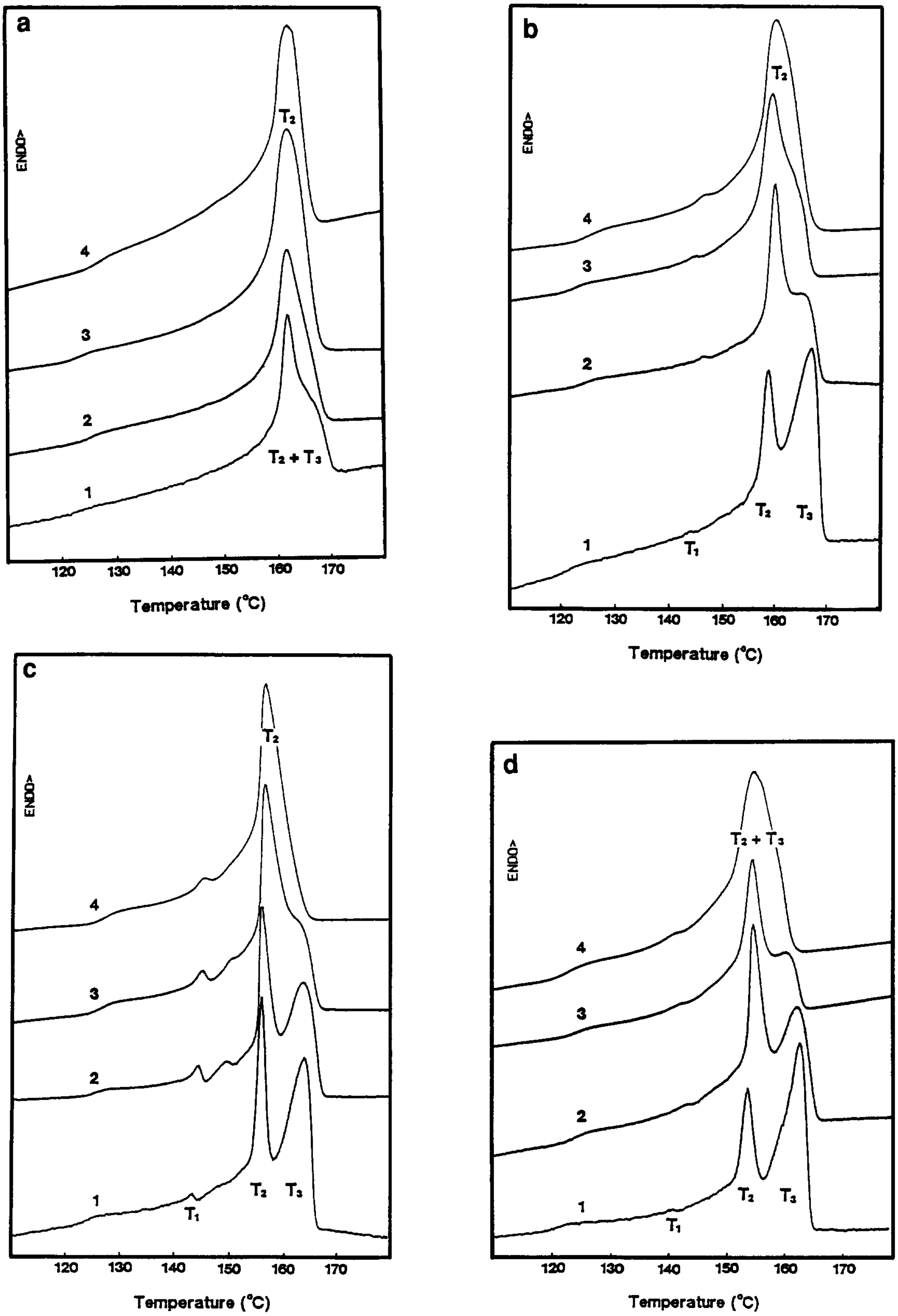

Figure 2 Effect of heating rate on the melting behaviour of the isothermally crystallized samples: (a) sample A (unreacted PP); (b) sample B (CR-PP); (c) sample C (CR-PP); and (d) sample D (CR-PP). Curves 1, 2, 3 and 4 correspond to heating rates of 3, 5, 10 and 20°C min^{-1} respectively

recrystallization or reorganization. However, as the heating rate increases, less and less time is available for recrystallization or reorganization. Consequently, at high heating rates, only one endotherm peak, peak T_2, is observed in agreement with the present results.

The area under peak T_3, A_3, strongly depends not only on the heating rate but also on the molecular weight as shown in *Figures 2* and *3*. The lower molecular weight samples, such as B, C and D, should experience more recrystallization or reorganization during melting due to differences in the high mobility of the macromolecules in the molten state. The latter is related to the degree of entanglement and heavily depends on the presence of long chains which exceed a critical chain length. Peroxide

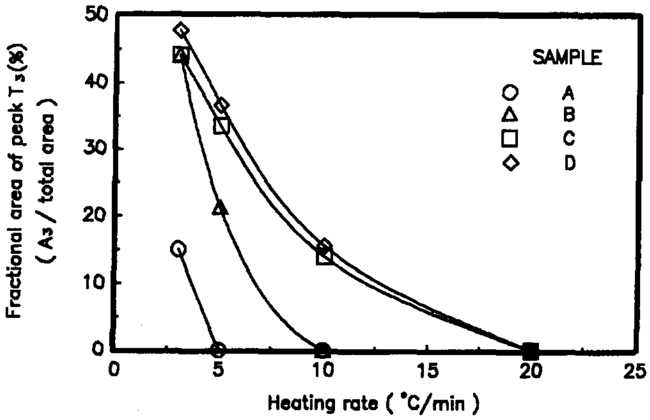

Figure 3 Effects of heating rate on the fractional area of peak T_3 (defined as A_3/total area) for isothermally crystallized samples A, B, C and D

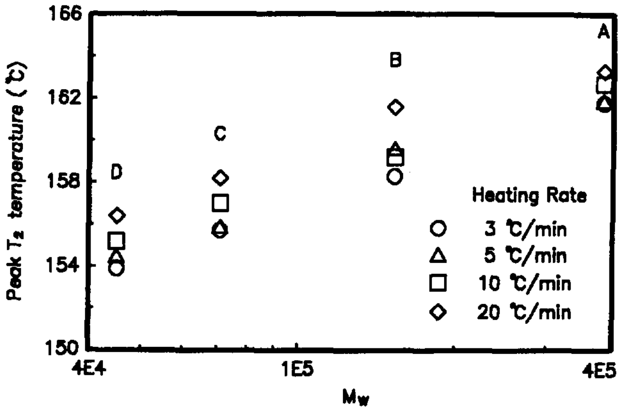

Figure 4 Dependence of peak T_2 temperature on molecular weight for isothermally crystallized samples A, B, C and D

initiated PP degradation has been known as a random chain scission reaction, to reduce the number of long chains significantly as shown in *Figure 1* and to result in less entanglement and higher mobility of the molecules. Thus, recrystallization or reorganization of lower molecular weight samples can occur more easily and faster during melting. The observed effects of heating rate and molecular weight can be summarized by stating that molecular reorganization will occur if the ratio of $t_{exp}/t(M)$ is greater than unity, where t_{exp} is the inverse of the heating rate and $t(M)$ is a measure of the time needed for molecular reorganization which is molecular weight dependent.

The temperature at which peak T_2 occurs is shown in *Figure 4* as a function of molecular weight and heating rate. The peak T_2 temperature increases with molecular weight at all heating rates in agreement with previous results[14]. *Figure 4* also shows the effect of heating rate on the peak T_2 temperature. It appears that heating rate affects the location of peak T_2 more significantly at lower molecular weights. For example, in sample A the maximum difference between the peak T_2 temperatures at different heating rates is ~1°C, while for sample D it is ~3°C.

Presence of different crystal forms. *Figure 5* shows the melting behaviour of each sample at the slow heating rate of 5°C min^{-1}. It is interesting to note that sample C shows a distinct small melting peak, whereas samples B and D show a trace of a very weak melting peak at ~143°C. This peak is not present in the unreacted sample A having the highest molecular weight and broadest molecular weight distribution, and is only observed in the CR-PP samples, suggesting the presence of different melting species. It is well known that isotactic PP can crystallize into more than one crystal form (α, β and γ) and generally the melting points of the β and γ form crystals are reported in the literature to occur in the above temperature region depending on the crystallization conditions and heating rates[6,15]. In order to study their crystal structures, X-ray diffraction patterns were taken for samples A–D (*Figure 6*). *Figure 6a* (sample A) shows the typical X-ray diffraction pattern of the normal α form crystal, while a pattern with an additional small peak at 16.1° is shown in *Figure 6c* (sample C). A reflection at 16.1° has been related in the literature[4,7] with the β form crystal; this indicates that sample C contains not only α form but also β form crystals. From the small relative intensity of the peak at 16.1°, however, it can be concluded that only a small portion of β form exists in sample C.

The formation of β form crystals has been reported by several workers[3,4,15]. For example, the use of pigments has been reported by Duswalt and Cox[15] to result in preferential nucleation of β form crystals. Keith *et al.*[3] and Turner-Jones *et al.*[4] found that the β form crystal formation is favoured by rapid cooling of the melt. Cooling rate and quenching temperature have been known as crucial factors in producing β form crystals[3,4,15]. A quenching temperature of 100–125°C

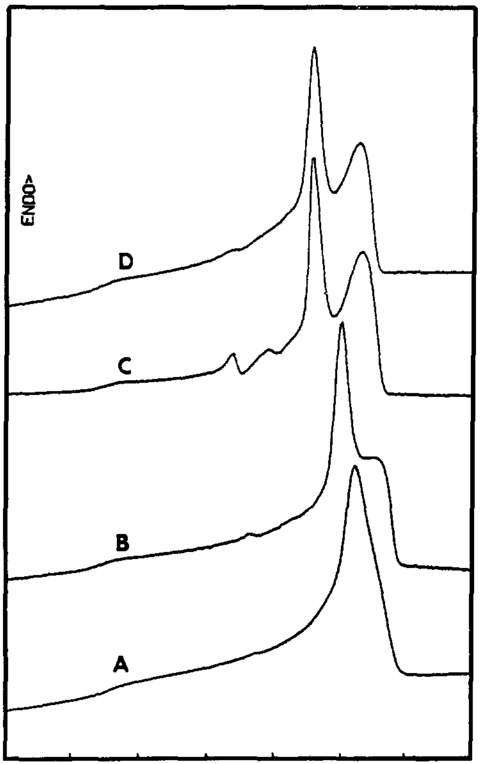

Figure 5 D.s.c. thermograms of samples isothermally crystallized at 120°C and heated at a rate of 5°C min^{-1}. Curves A, B, C and D correspond to the respective samples

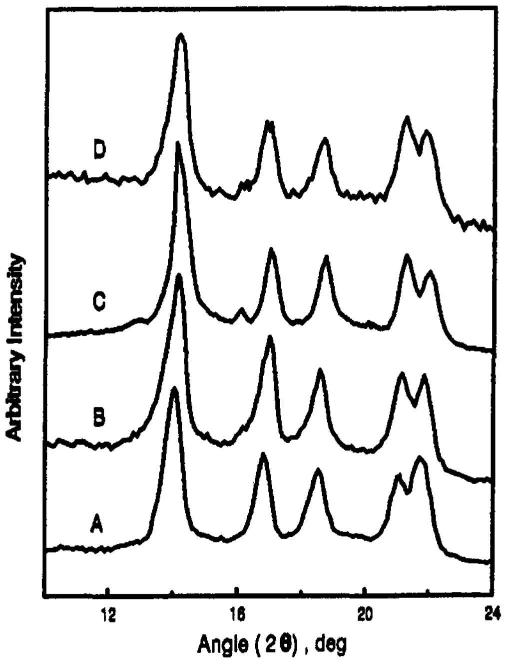

Figure 6 X-ray diffraction patterns of samples A–D that were isothermally crystallized at 120°C for 30 min

was found to produce the β form crystal. The transformation of β form crystals into the α form at temperatures above the melting point of the former, has been established by several workers[2,4,16] who have conducted extensive studies on the unit cell of β-PP. These workers concluded that the transformation from the β form to the α form must occur through a melt recrystallization process since the two unit cells are so different. The melting temperature of the β form was observed around 145–150°C[4,15]. Thus, the small endotherm peak between T_1 and T_2 of the d.s.c. thermogram of sample C in *Figure 5* probably shows such a recrystallization process.

To investigate the presence of β form crystals in samples B and D, X-ray diffraction patterns were also taken and the results are shown in *Figures 6B* and *D*. Though the presence of a peak at 16.1° is not prominent as in *Figure 6C*, a trend for peak formation is indicated by the mild shoulder appearance at this position. The possibility of the existence of β form crystals in these samples is further supported by the existence of a very small melting peak T_1 in *Figure 5*. Thus, from the combined evidence of the d.s.c. and the limited X-ray studies, it appears that the low endotherm peak T_1 of the isothermally crystallized CR-PP samples can be attributed to the melting of β form crystals.

The half-time of crystallization ($t_{1/2}$) at 120°C is plotted against molecular weight in *Figure 7*. The curve appears to show a maximum corresponding to sample C which has the lowest crystallization rate. Recently, the presence of a maximum in $t_{1/2}$ *versus* MFI plots of CR-PP has been reported[18] and it is attributed to the opposing crystallization rates between chains becoming increasingly shorter and chains containing an increasing number of polar end groups as a result of the peroxide initiated degradation process. Hence, it is possible that a reduced crystallization rate for sample C may favour the formation of crystal forms other than α. In fact, Turner-Jones *et al.*[4] speculated that the retardation of α form nucleation and/or growth rate could be partially responsible for the development of the β form.

The presence of γ form crystal in low molecular weight fractionated PP was reported by Addink and Beintema[7], its amount decreasing with increasing cooling rate. The presence of γ form crystals (usually associated with a diffraction peak at 20.1°), is not clearly observed in the CR-PP samples of this study crystallized at 120°C for 30 min. Under different crystallization conditions, however, it may be possible that samples such as C and D could contain γ form crystals formed from very low molecular weight chains produced by random chain scission during degradation.

Melting behaviour of non-isothermally crystallized PP

Figure 8 shows the melting behaviour of unreacted and reacted PP samples which are crystallized at various cooling rates. *Figure 8a* shows only one melting peak or a broad shoulder depending on the cooling rate, whereas *Figures 8b–d* show double endotherm peaks at fast cooling rates. As shown in *Table 2*, the locations of peaks T_2 and T_3 decrease with increasing cooling rate. This indicates that smaller size or less perfect crystals are formed under fast cooling conditions, since less time is available for crystallization during cooling. The effect of cooling rate on the location of peak T_3 during heating, i.e. the degree of recrystallization or reorganization, becomes more significant for the lower molecular weight samples. This observation agrees with the results obtained for the isothermally crystallized samples shown in *Figure 2*. As before, heat of fusion of all samples is approximately the same, regardless of the cooling rates or the molecular weight of the samples. This indicates that both unreacted and CR-PPs are very susceptible to crystallization.

CONCLUSIONS

Combined evidence from d.s.c. and limited X-ray studies indicate the existence of the β form crystals in CR-PP samples isothermally crystallized at 120°C but not in commercial unmodified PP. The formation of β form crystal is probably related to rapid cooling from the melt to the crystallization temperature. From the X-ray diffraction patterns, it is suggested that only a small portion of β form crystals exists in isothermally crystallized CR-PP. The presence of γ form crystals,

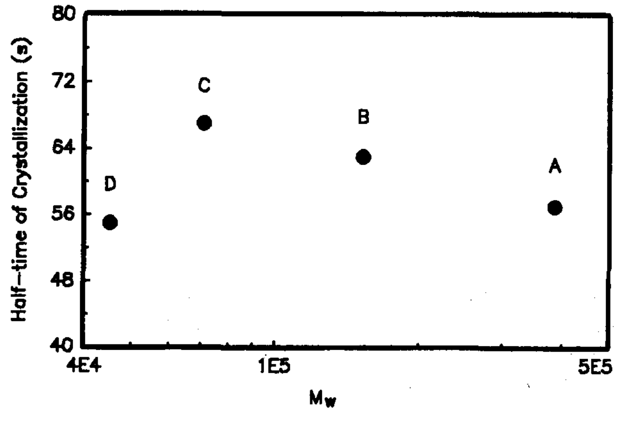

Figure 7 Effects of molecular weight on the half-time of crystallization of unreacted PP and CR-PP samples

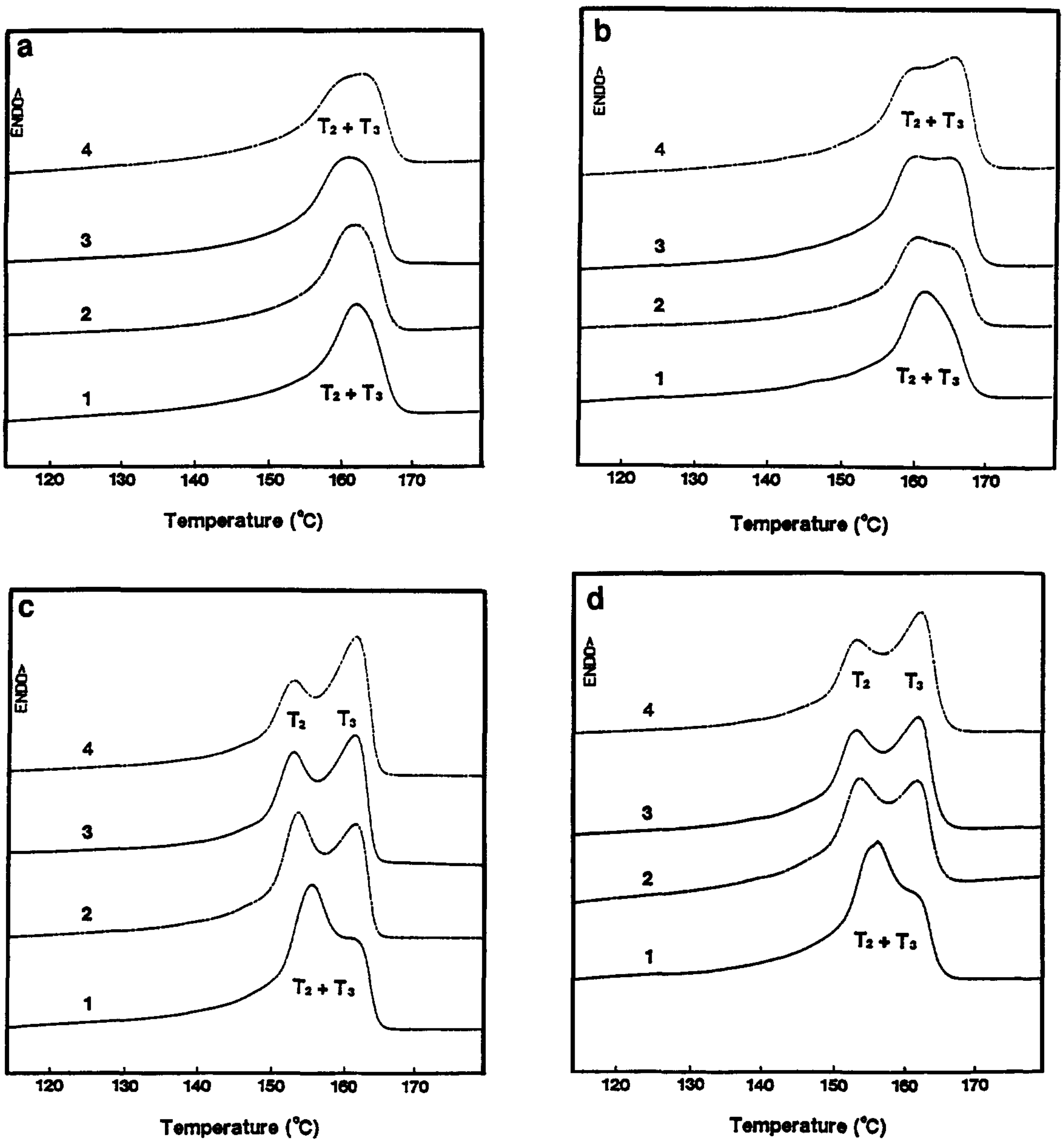

Figure 8 Effect of cooling rate on the melting behaviour of the non-isothermally crystallized samples: (a) sample A (unreacted PP); (b) sample B (CR-PP); (c) sample C (CR-PP); (d) sample D (CR-PP). Curves 1, 2, 3 and 4 correspond to cooling rates of 10, 20, 30 and 60°C min^{-1}, respectively

Table 2 Effect of cooling rate on the melting peaks T_2 and T_3 for non-isothermally crystallized samples

Cooling rate (°C min^{-1})	Peak temperature (°C)							
	Sample A		Sample B		Sample C		Sample D	
	T_2	T_3	T_2	T_3	T_2	T_3	T_2	T_3
10	161.9	–	161.1	S	155.3	S	156.0	S
20	161.8	–	160.1	S	153.5	161.5	153.4	161.6
30	161.3	–	159.5	164.2	153.0	161.5	153.0	161.7
60	S	163.0	S	164.8	153.0	161.6	153.1	162.1

The presence of a shoulder is indicated by S

although quite possible in low molecular weight samples such as C and D, was not clearly observed in this study. It was also shown that, in general, recrystallization or reorganization during melting of crystals originally formed during isothermal crystallization becomes significant with decreasing molecular weight and heating rate.

Under the non-isothermal crystallization conditions, smaller size or less perfect crystals were formed at increasing cooling rates. At the same time β or γ form crystals were not observed. As expected, the melting temperature of normal α form crystals decreases with molecular weight under both isothermal and non-isothermal crystallization conditions.

Though not currently feasible, it may be quite possible that the unique melting behaviour of both isothermally and non-isothermally crystallized CR-PP could be further exploited in attempts to monitor the PP peroxide controlled degradation process through on-line measurements.

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