Low temperature annealing of isotactic polypropylene by differential scanning calorimetry

W. Ken Busfield and Chris S. Blake
School of Science, Griffith University, Nathan, Queensland, 4111, Australia

Differential scanning calorimetry has shown that secondary crystallization occurs in both smectic and monoclinic polypropylene during annealing processes at temperatures as low as 25°C. This effect has been studied in the range 25–130°C. The extent of secondary crystallization increases with both time and temperature of anneal. The rate is increased by prior annealing at either higher or lower temperature; is slightly reduced in samples cooled more slowly from the melt and is significantly reduced in γ-irradiated samples. Rate curves suggest that secondary crystallization consists of a fast process with a half life of a few hours and a slow process which continues for years. The observations are consistent with the currently accepted structural reorganisation theory for annealing at temperatures closer to the melting point. The occurrence of significant secondary crystallization at room temperature has implications with the ageing effect previously observed for some semi-crystalline polymers.

INTRODUCTION

Molecular motion resulting in increased structural order in semi-crystalline polymers at temperatures between the glass transition and the melting point falls into two categories: primary and secondary crystallization. Primary crystallization is the formation of the first batch of crystals from the melt, amorphous polymer or from solution by cooling or standing. It is a relatively fast process characterized by an Avrami exponent greater than 1, the exact value being dependent on the type of crystals being formed, and by a relatively high exothermicity. Secondary crystallization refers to the changes of structure which follow primary crystallization when the sample is either held at a fixed temperature or scanned in a temperature range within about 40 degrees of the melting point. When carried out isothermally the process, commonly known as annealing, is relatively slow with an Avrami exponent less than 1[1] and, as shown by calorimetry, is slightly exothermic[2]. The latter observation is consistent with the increase in fraction and degree of perfection of the crystalline content which various crystallinity measurements have shown occur during annealing. However when the temperature is being increased in the annealing region, as for example in a d.s.c. scan, the position of the pen indicates that the net thermal change is endothermic. It is now well established that this is due to the occurrence of simultaneous melting and recrystallization (structural reorganization at the fold surfaces resulting in lamellar thickening[3–5]). Under isothermal conditions and presumably at lower scan rates, recrystallization is the dominant process whilst at higher scan rates, melting becomes the dominant process and results in a net endothermic change. During a thermal scan this structural reorganisation is a continuous process which persists until the melting process becomes completely dominant at the melting point when the crystal structure breaks down. The crystal structure of any sample will contain a distribution of degrees of perfection strongly dependent on the previous thermal history. If this includes an isothermal annealing step, there will be a discontinuity in the distribtuion of degrees of perfection. Such effects are conveniently studied by a further d.s.c. heating scan. As the structure reorganises on heating, the discontinuity normally results in an endothermic peak or shoulder in the scan. The size of the peak depends on the time and temperature of anneal and it usually occurs at a temperature a few degrees above the annealing temperature[3]. Investigations of such phenomena in the normal annealing temperature range have been made for several semi-crystalline polymers[3–7]. On the other hand there have been no detailed investigations of the annealing effect in lower temperature ranges; studies of this kind could throw some light on previously observed changes in properties of polymers after standing at room temperature; the ageing effect. For example several investigations of the ageing effect in quenched polypropylene[8,9], where the effect is particularly pronounced, have failed to produce any positive information on the structural changes responsible. Kapur and Rogers suggest that ageing is caused by the occurrence of an ordering process within aggregates of crystallites similar to a secondary crystallization process. They explain the observed property changes in terms of changes in the size and distribution of microvoids and changes in bond flexibility. Both result from the suggested ordering process for which they have no experimental evidence. In this paper we describe a study of annealing in both quenched (smectic) and normal α-monoclinic isotactic polypropylene (PP) from room temperature to 130°C by differential scanning calorimetry (d.s.c.). Detailed studies of annealing in the range 130°C to the melting point have been previously reported[6,7].

EXPERIMENTAL

Polypropylene samples were in non-oriented film form produced by extrusion, as previously described[10]. The α-monoclinic (density 900.6 kg m^{-3}) and smectic (quenched)

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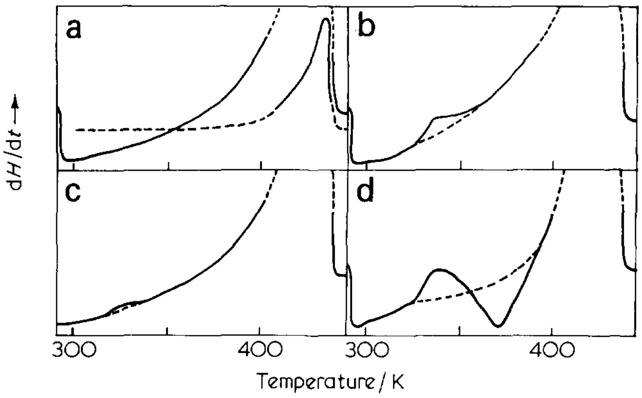

Figure 1 D.s.c. melting scans of polypropylene after (a) cooling from the melt at 80 K min^{-1} (b) storage for 6 years at room temperature in monoclinic form (c) storage for 7 days at room temperature following direct cooling from the melt (d) storage for 6 years at room temperature in smectic form. Heating rate: 10 K min^{-1}, sensitivity is 10–20 times that required to keep the main melting peak on scale. Lower curve in 1(a) is at 0.1 times the sensitivity of the upper curve

(density 890.1 kg m^{-3}) forms were produced by chilling the extrudate at 55° and 9°C respectively. X-ray diffractometer tracings showed that the smectic form contained about 5% of α-monoclinic crystals. The structure of α-monoclinic PP has been well characterized[11]. That of smectic PP is still uncertain, the various possibilities have been reviewed by McAllister *et al.*[12]. We have retained the name originally suggested by Natta[13].

Most of the experiments were carried out with ICI grade GWE 21F (stated M.F.I. = 4.5; $\bar{M}_n = 2.6 \times 10^4$, $\bar{M}_w = 1.4 \times 10^5$ by g.p.c.[14]); for effects of molecular weight some experiments were also carried out with Shell grade HY 61 (stated M.F.I. = 1.5; $\bar{M}_n = 1.5 \times 10^5$, $\bar{M}_w = 6.8 \times 10^5$ by g.p.c.[14]). The non-isotactic content was 2–3% and the antioxidant content 0.2%[10].

Differential scanning calorimetry. The instrument was a Perkin Elmer model 2. Samples were 5 small discs of film of mass 12 to 16 mg. Except for experiments designed to study the effect of scan rate, a scan rate of 10 K min^{-1} was used for all heating thermograms. Except where specified, cooling was carried out as fast as possible; i.e. the cooling rate was set at 360 K min^{-1} but thermal control at this high rate was not maintained. The machine coolant was externally circulated ice-water. Except for long term room temperature anneals, annealing programmes were carried out in the instrument. The temperature scale and heat energy response were calibrated with indium. Peak areas were determined by cutting and weighing traces of the peaks. Peak temperatures were the points of intersection of two straight lines drawn tangential to both sides of the peak.

RESULTS AND DISCUSSION

Room temperature annealing

D.s.c. melting curves for PP samples with differing thermal histories are shown in *Figure 1*. The sensitivities are ten times that which would require the main melting peak to be on scale, see *1a*. The scan shown in *1b* is of a monoclinic sample which had been stored for about 6 years at ambient temperature. It clearly shows a secondary endotherm peaking at 335.5 ± 1.0 K with an area equivalent to 3.15 ± 0.05 J g^{-1} above the extrapolated melting curve shown by the dotted line. This represents 3–4% of the main melting endotherm. After the same sample had been held at 500 K for 7 min and cooled to 295 K at 80 K min^{-1}, a re-scan of the melting range, *Figure 1a*, showed complete removal of the secondary endotherm. Thus its presence was due to changes in crystallinity during storage and not to any permanent chemical change. This was confirmed by storing melt annealed samples (i.e. those in which any crystal memory had been removed by holding at 500 K for 7 min prior to the experiments) for various times at room temperature before re-scanning the melting curve. The scan of a sample stored for 7 days, *Figure 1c*, shows the early stages of growth of the secondary endotherm. The scan in *Figure 1d* is of smectic PP after 6 years' storage at room temperature. Again the secondary endotherm is clearly evident with a peak maximum of 335.5 ± 1.0 K, the same as that for the monoclinic sample. The peak area, equivalent to 3.8 ± ~0.3 J g^{-1}, is significantly greater than that for the monoclinic sample although this value is less certain due to the close proximity of the exotherm produced by the conversion of the smectic PP to monoclinic PP[15].

As will be shown by the experiments described below the secondary endotherms are dependent on the time and temperature at which the sample has been held prior to the melting scan and are almost certainly due to changes in the crystalline structure similar to those associated with conventional annealing at temperatures closer to the melting point[6,7]. However this is the first report of annealing effects observed by d.s.c. in a semi-crystalline polymer 130 degrees below the melting point.

Effect of scan rate and thermal history

The influence of scan rate and previous thermal history on the position and size of the secondary endotherm after a fixed anneal of 30 min at 350 K were studied. The results are summarized in *Table 1*. Both the temperature and area of the secondary endotherm increase with scan rate. Structural reorganization consisting of simultaneous melting and crystallizing occurs continuously throughout the d.s.c. scan. At the discontinuity, observed as the secondary endotherm,

Table 1 Peak temperatures and enthalpy changes associated with the secondary endotherm of monoclinic PP[a] after annealing for 30 min at 350 K as a function of d.s.c. scan rate and previous thermal history

Previous history[b]	Scan rate K min^{-1}	Peak temp. K	ΔH J g^{-1}
1. MR[c]	5	361.0	0.64
2. MR	10	363.0	0.80
3. MR	20	376.5	1.25
4. MR then pre-annealed at 423 K for 60 m	10	364.0	1.90
5. MR then cooled directly to 350 K from melt	10	366.0	0.68
6. MR then cooled at 1.25 K min^{-1} from melt	10	365.5	0.50
7. 6 y at ambient T in monoclinic form	10	363.0	1.95
8. 6 y at ambient T in quenched form	10	365.0	2.69

[a] PP for experiment 8 was in the smectic form

[b] In experiments 1 to 6 the samples were cooled to 295 K (350 K for expt. 5) in the d.s.c. as fast as possible (dialled rate was 320 K min^{-1}) (1.25 K min^{-1} for expt. 6) from the melt immediately prior to the final annealing treatment (30 min at 350 K)

[c] MR = memory removed by 7 min at 500 K in d.s.c.

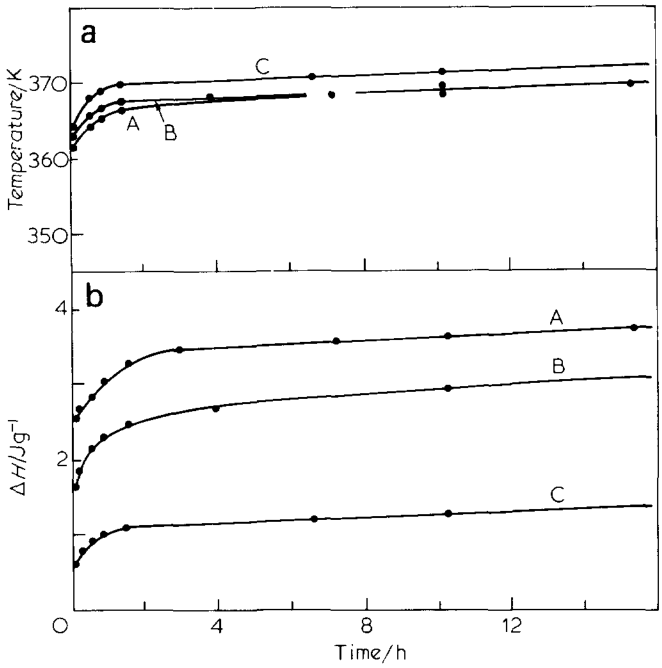

Figure 2 The effect of time on the secondary endotherm peak temperature (a) and size (b) following annealing at 350 K for 6 years old smectic PP(A); 6 years old monoclinic PP(B) and melt-annealed PP(C). Heating rate in d.s.c. scans: 10 K min^{-1}. Melt-annealing procedure: 7 min at 500 K

melting is the dominant process and is thought to be due to a preponderence of crystalline material with a specific degree of perfection corresponding to a melting point of 350 K, i.e. the annealing temperature. At higher scan rates melting becomes even more the dominant process, crystallization is known to be relatively slow[7], such that the peak increases in size. At lower scan rates crystallization has increasing dominance such that the discontinuities in the melting patterm become buried in the overall melting curve. The increase in peak temperature with scan rate is a consequence of the kinetic feature of the experiment i.e. slight super heating. All other experiments in this series were at a constant scan rate of 10 K min^{-1}.

It is interesting to observe that a pre-anneal either at a higher (expt. 4) or a lower (expt. 7 and 8) temperature produces a large increase in peak size, that from a pre-anneal in the smectic form (expt. 8) being the largest increase. The improved facility for reorganisation after a lower temperature anneal indicates that those crystalline regions which have reorganised to a degree of perfection appropriate to the lower annealing temperature have an easier route (lower activative energy) to the degree of perfection appropriate to the higher annealing temperature (350 K) than the crystalline regions produced directly from melt annealed material. The improved facility for reorganisation after a higher temperature anneal is more difficult to understand. One possibility is that the increased secondary peak size is due to a lowering of the overall melting curve in the region between the secondary endotherm and the main melting point. In structural terms this suggests that in the melting/crystallizing competition, crystallization has relatively greater dominance in this temperature range in this sample relative to the sample produced directly from melt annealed PP (expt. 2). If this were the case it would suggest that annealing at higher temperatures, in this case 423 K, causes structural reorganisation of crystalline regions with degrees of perfection appropriate to the temperature range just immediately below 423 K and little change in those appropriate to the lower temperature regions, in particular the region below about 365 K. Recent experiments on heat capacity changes following annealing have confirmed that this is the case. The results will be published in a separate paper. Experiments 2, 5 and 6 show that both a lower rate of cooling and a reduction in the extent of cooling from the melt reduce the rate of formation of the secondary endotherm by a small amount. The lower rate of cooling will result in a lower rate of crystallization and consequently in the formation of more perfect lamellae. During the 350 K anneal the crystallization part of structural reorganization in the inter-lamellar regions will consequently occur to a smaller extent than it does in the corresponding fast cooled samples. The reduced extent of cooling (expt. 5) will reduce the amount of preliminary reorganisation which occurs when the sample is cooled to a lower temperature prior to anneal (expt. 2). Thus again the crystallization part of structural reorganisation in these regions will be retarded. Both these factors therefore result in slightly smaller secondary endotherms, as observed.

Effects of annealing time and temperature on the secondary endotherm

The effect of annealing time on both peak temperature and area following a 350 K anneal for a melt annealed sample, a monoclinic sample after 6 years storage and a smectic sample after 6 years storage at ambient temperature is shown in *Figure 2*. The secondary peak grows at the highest rate in the smectic sample and the lowest rate in the melt-annealed sample. On the other hand the peak temperature increases in the opposite order, that for the melt-annealed sample was always highest. This suggests that in the long-term room-temperature pre-annealed samples, the secondary peak produced by the higher temperature anneal always retains some of the character of (i.e. degree of perfection appropriate to) the lower temperature anneal. The shape of the rate curves in *Figure 2b* indicate that two processes are occurring simultaneously in the formation of the secondary peak. One is rapid and complete within a few hours, the other is very slow and probably continues over a period of years. Further evidence for this latter process is provided by some room temperature annealing experiments. After annealing a melt-annealed sample at room temperature for 120 days the secondary peak at 329 K had an area equivalent to 1.32 J g^{-1} whilst after about 6 years the secondary peak was at 336 K with an area equivalent to 3.15 J g^{-1}. Although experiments were not carried out for such long periods at 350 K the slow growth would presumably be similar. If it is assumed that the rapid growth process is completed after 300 min and that the peak areas at this point represent the maximum amount of crystalline material of that type which can form in that sample, Avrami plots of $\ln \ln [P_{300}/(P_{300} - P_t)]$ vs $\ln t$ can be constructed where P_t is the peak area at time t. These are shown in *Figure 3*. Only that for the melt annealed sample gives a linear plot with a slope of 0.58. Avrami exponents less than unity are typical for secondary crystallizations[1]. The curvature on the Avrami plots for the room temperature aged smectic and monoclinic samples indicates again that secondary crystallization of pre-annealed material is greatly facilitated in the early stages of the process.

There is insufficient information to distinguish between the structural changes responsible for the fast and slow secondary crystallizations suggested by the rate curves. However, if there are two types of structural change occurring in two different structural regions during annealing they will have

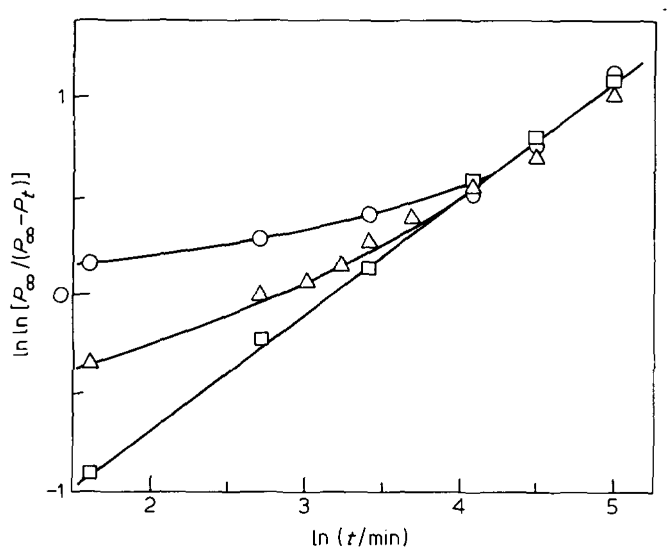

Figure 3 Avrami plot of the secondary crystallization at 350 K of 6 years old smectic PP (○); 6 years old monoclinic PP (△); melt annealed PP (□)

important implications in the explanation of the ageing phenomena observed in smectic polypropylene. Kapur and Rogers observed a marked decrease in diffusion coefficient and an increase in solubility of certain gases in smectic PP over the first 30 h of film age after which both properties remained constant at least up to 100 h. Certain mechanical properties on the other hand, e.g. initial modulus and drawing stress, showed a linear change with ln *t* over at least 100 h. Their detailed explanation was based on changes in both size and distribution of microvoids in the structure being mainly responsible for the changing gas diffusion and gas solubility properties whilst changes in bond flexibility in the interlamellar regions, which will be related in a subtle way to the microvoid structure, are mainly responsible for the changing mechanical properties. Both the structural changes are a consequence of secondary crystallization which as our experiments show can be monitored by d.s.c. scans at high sensitivity. It is interesting that the rate curves for secondary crystallization have similar shapes to those observed for some property changes. A set of parallel experiments on the same sample would be well worthwhile.

Increasing the annealing temperature for a constant annealing time of 1 h causes a steady increase in both the secondary endotherm peak temperature and area, see *Figure 4a*. The peak temperature is always about 15 K higher than the annealing temperature. The increased area indicates that crystallization during the annealing period becomes of increasing importance in the reorganisation process with increased temperature. Samples of smectic PP, which exhibit the highest rate of secondary crystallization, were subjected to 17 h anneals at a series of increasing temperatures. The results in *Figure 4c* show that above an anneal temperature of 360 K the peak areas were approximately constant with an enthalpy value of 3.97 J g^{-1}. This suggests that there is an upper limit to the amount of material which can undergo secondary crystallization; however, it is not known whether annealing times of longer than 17 h above 360 K would further increase this amount.

It should be noted that in annealing experiments with smectic PP, the crystalline form is slowly converted to monoclinic during the annealing process. For example our experiments have shown that after 17 h the conversion of smectic PP to monoclinic PP is 90% at 360 K; 37% at 340 K and negligible below about 320 K. Thus in all annealing experiments relating to smectic PP the crystal form refers to that present initially.

Effect of molecular weight on secondary crystallization

The effects of annealing time at 350 K on the position and size of the secondary endotherm peak formed in melt-annealed samples of differing molecular weight are compared in *Table 2*. The higher molecular wt sample clearly produces a slightly larger endotherm with a lower peak temperature but the difference in both effects is small.

Effect of γ irradiation on secondary crystallization

It is well-known that cross-linking produced by γ-irradiation inhibits structural reorganisation during heating

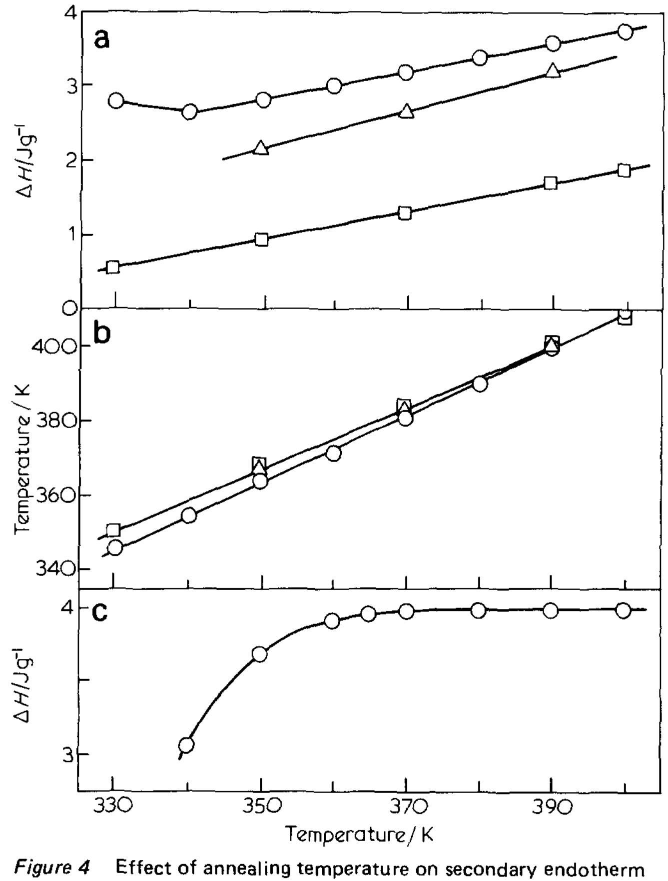

Figure 4 Effect of annealing temperature on secondary endotherm peak area ((a) and (c)) and peak temperature (b) for 6 years old smectic PP (○); 6 years old monoclinic PP (△) and melt annealed PP (□) after annealing for 1 hour (a and b) and 17 hours (c). Heating rate in d.s.c. scans: 10 K min^{-1}

Table 2 Effect of polymer molecular weight on secondary endotherm peak area and temperature after anneal at 350 K for melt-annealed samples

Time of anneal (min)	Peak area/J g^{-1}		Peak temp./K	
	A	B	A	B
30	0.76	0.96	366.5	365.0
60	0.92	1.15	368.5	366.0
90	1.00	1.28	369.0	367.0
300	1.17	1.37	370.5	369.0
1040	1.26	1.43	371.5	371.0

Polymer molecular weights: sample A, $\bar{M}_n = 2.6 \times 10^4$, $\bar{M}_w = 1.4 \times 10^5$; sample B, $\bar{M}_n = 1.5 \times 10^5$, $\bar{M}_w = 6.8 \times 10^5$

in polyethylene[4,16] and presumably in other semi-crystalline polymers which are cross-linked by the action of γ-irradiation. This results in a lowering of the apparent melting point from that which is normally observed when reorganisation occurs in the heating process of any melting point determination, towards that which might be called the true melting point of the crystalline material present at room temperature. The implication is that all secondary crystallization including the annealing process will be suppressed in a γ-irradiated sample. The secondary endotherms of some γ-irradiated samples of monoclinic (*Figure 5*) and smectic (*Figure 6*) PP after 6 years' storage at room temperature are compared with those of unirradiated samples. The melting peaks at one tenth the sensitivity are also shown. A comparison of the peak areas, see *Table 3*, indicates the severe retardation of secondary crystallization during storage with increasing dose in the original sample. The peak temperature on the other hand is little affected. This adds further evidence that during isothermal annealing even at room temperature, structural reorganisation occurs during which a concentration of crystalline material with a degree of perfection appropriate to a melting point of the annealing temperature is formed. Thus although cross-linking by irradiation, which experiments have suggested[10] predominates in the interlamellar regions, retards the extent of secondary crystallization, it does not affect the degree of perfection the structure attains.

CONCLUSIONS

These experiments have shown that secondary crystallization occurs at temperatures at least as low as 25°C in both smectic

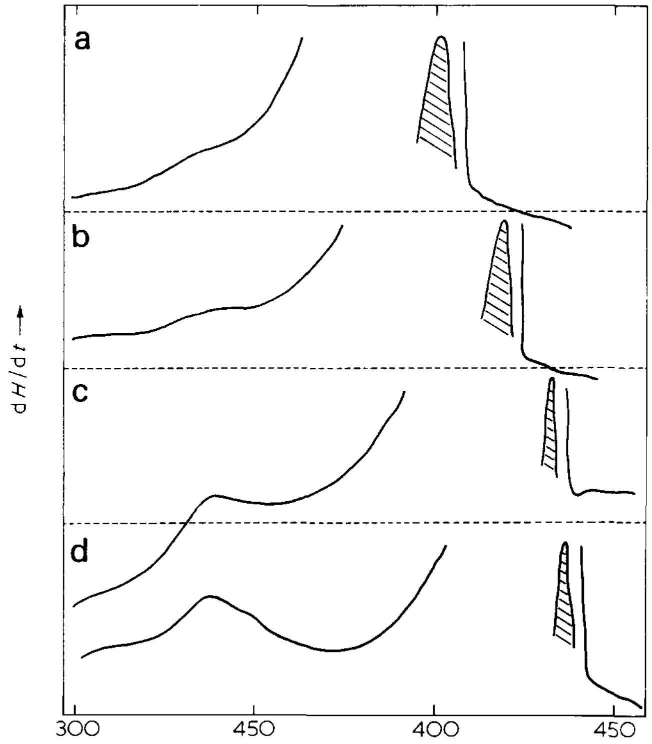

Figure 5 D.s.c. heating scans of 6 year old γ-irradiated monoclinic PP (doses 150 Mrad (a); 50 Mrad (b); 10 Mrad (c); unirradiated (d)). Shaded peaks are the main melting peaks at 0.1 times the sensitivity of the rest of the scan. Heating rate: 10 K min^{-1}

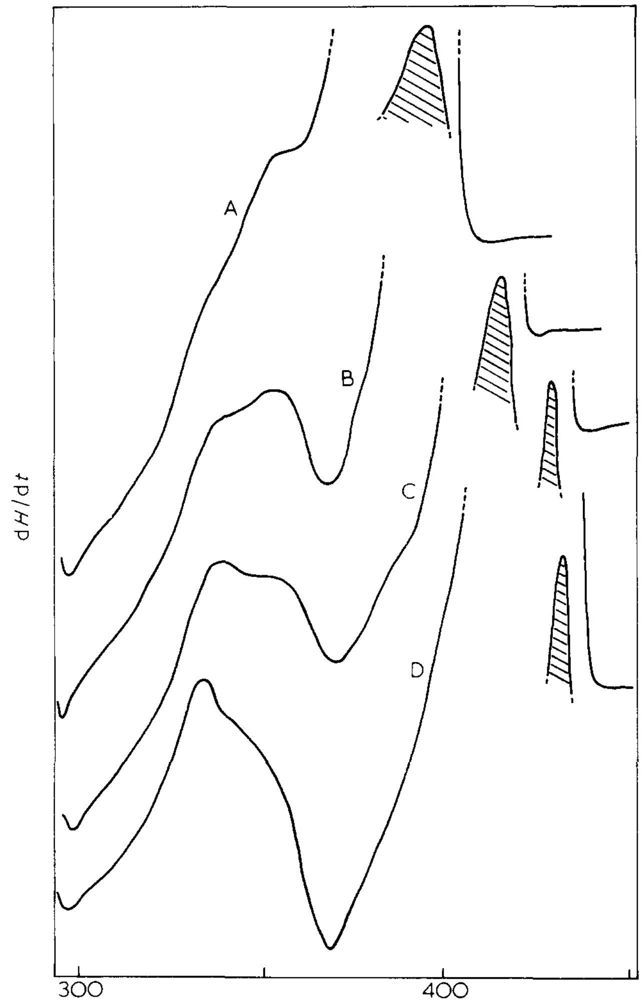

Figure 6 D.s.c. heating scans of 6 years old γ-irradiated smectic PP (doses 150 Mrad(A); 50 Mrad (B); 10 Mrad (C); unirradiated (D). Shaded peaks are the main melting peaks at 0.1 times the sensitivity of the rest of the scan. Heating rate: 10 K min^{-1}

Table 3 Effect of γ-irradiation on secondary endotherm peak area and temperature 6 years after irradiation followed by standing (annealing) at room temperature of monoclinic and smectic polypropylene

	Monoclinic			Smectic		
	Secondary endotherm peak		Main melting peak	Secondary endotherm peak		Main melting peak
Dose/Mrad	Temp/K	Area, J g^{-1}	Temp/K	Temp/K	Area/J g^{-1}	Temp/K
0	338	2.85	437.5	335	3.78	436
10	338	2.48	433.0	335	2.27	431
50	340	0.70	420.5	336	0.93	418
150	334	0.38	402.0	335	0.30	396

(quenched) and monoclinic polypropylene. The extent increases with both the time and temperature of an isothermal annealing programme. The rate is increased by prior annealing at either higher or lower temperature; is slightly reduced in the case of samples cooled more slowly from the melt and is significantly reduced in γ-irradiated samples. In the high molecular weight range, molecular weight has negligible effect on the rate. Rate curves suggest the occurrence of both a fast process with a half life or a few hours and a slow process which continues for years.

These observations suggest that the structural changes causing secondary crystallization are similar to those which occur in higher temperature annealing processes. Thus structural reorganisation consisting of simultaneous melting and crystallization, is a continuous process occurring in the interlamellar regions at temperatures from the melting point down (presumably) to the glass transition. Secondary crystallization at ambient temperature is probably closely related to the ageing effect observed for some polymers, particularly quenched PP, in which mechanical and other properties change significantly with age. Further experiments are required in order to substantiate this relationship.

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