Effects of Thermal History on Isotactic Polypropylene

K. D. PAE and J. A. SAUER, *Rutgers–The State University,*
New Brunswick, New Jersey 08903

Synopsis

The effect of past thermal history on the melting behavior of isotactic polypropylene is investigated in some detail. It is shown that a series of stepwise annealing treatments at steadily increasing temperatures will raise the final melting point and will result in a double endothermic peak if the final anneal temperature is at or close to 160°C. It is also shown that a series of stepwise annealing treatments at steadily decreasing temperature will lead to multiple DSC peaks. The number of such separate peaks is equal to or greater than the number of annealing steps. Even low-temperature anneals (100–130°C) affect the melting endotherm, while high-temperature anneals have a marked effect on both the degree of crystallinity of the sample and the final melting temperature. For a 3-min anneal, the highest degree of crystallinity is produced by an anneal temperature of 155°C. The highest melting temperature ($\sim$182°C) is produced by a 30-min, or longer, anneal at about 160°C. The implications of these results in terms of crystal thickening and perfection are discussed.

INTRODUCTION

Differential thermal analysis (DTA) has proven to be a useful tool for investigation of the relation between polymer texture and microstructure and thermal behavior. It has been of considerable assistance in delineating the nature of the solid–liquid, or melting transition of various polymers and copolymers. For example, Ke[1] has used DTA to determine melting points, degree of crystallinity, and heats and entropies of fusion of several polyethylenes, polypropylene, and copolymers thereof. DTA, or its counterpart, differential scanning calorimetry (DSC) provides a sensitive tool for investigation of the influence of such variables as prior thermal history, and molecular weight, upon melting behavior. There are some data in the literature concerning these factors, but there is also considerable confusion as to their specific effects and as to the nature and significance of multiple DTA or DSC peaks.

The present study is concerned with a rather detailed investigation of prior thermal history on the thermal properties and melting behavior of a particular polymer. The polymer selected for study is isotactic polypropylene (PP) but the results of the investigation are believed to have general significance. Some DTA investigations of polypropylene have been made, and these will be reviewed. However, the important role of prior thermal history on the properties and microstructure of this material is not yet delineated.

For a laboratory sample of polypropylene, Ke[1] has shown that DTA gives a single endothermic peak with an estimated heat of fusion of 15.4 cal/g. Ke[2] also studied block copolymers of ethylene and propylene. Here he found two separate DTA peaks, with the lower temperature maximum near 130°C corresponding to the melting of polyethylene crystals and the higher temperature maximum near 165°C corresponding to the melting of the polypropylene crystallites. Clampitt[3] studied blends of low-density polyethylene and high-density polyethylene and reported the occurrence of multiple endothermic peaks, with the lowest temperature peak ($\sim$115°C) being associated with melting of the branched polyethylene and the highest temperature peak ($\sim$134°C) being associated with melting of the linear polyethylene.

Polypropylene in fiber form has been studied by Schwenker et al.[4] They reported two endothermic peaks, one at 158°C and one at 174°C, for a drawn polypropylene fiber but only a single peak for an undrawn polypropylene specimen. They attributed the first peak to disorientation of the crystallites, and the second to melting of the crystallites.

In 1964 Gray and Casey[5] showed that the presence of multiple peaks in differential thermal analysis endotherms need not reflect the presence of a second ingredient, or copolymer, nor indicate the presence of a phase transformation in the solid state in addition to the solid–liquid transformation. Using an ethylene–butene copolymer of density 0.920, and a Perkin-Elmer type differential scanning calorimeter, they showed that multiple endothermic peaks could arise from prior successive stepwise annealing treatments at specific temperatures. The number of peaks obtained depended upon the number of stepwise annealing treatments given. For their sample, and by annealing at successively lower temperatures each of which was reduced 10°C from the prior annealing temperature, they recorded six distinct peaks in the final endotherm. On reducing the temperature interval between annealing cycles to 5°C, they observed 12 separate endothermic melting peaks. Gray and Casey concluded that these peaks were a consequence of discontinuous crystallite size distributions and that each peak resulted from annealing of that particular material which would ordinarily have melted at, or a few degrees above, the annealing temperature. As a consequence of the annealing procedure, this material is grouped into discontinuous size distributions rather than a continuous size distribution as one would presumably obtain upon ambient cooling.

Annealing of polypropylene (PP) samples at temperatures close to the melting point has been studied by Farrow[6] and by Turley and Keskkula.[7] Farrow[6] annealed various PP samples in evacuated glass tubes for very long times (days) at a temperature of 160°C. From x-ray measurements, he concluded that the initial crystallinity of about 48% increased to about 60% within 8 days and attained a maximum value of about 70% after 70 days. He also noted that the crystallite size increased linearly with annealing time and that the melting point at first increased rapidly from its initial value of about 166°C, and then gradually thereafter, to attain a final value

of about 188°C after 70 days. Turley et al.[7] measured the density and crystallinity of a series of polypropylene (Profax) specimens annealed for 20 min at successively higher temperatures in 5° intervals from 150 to 165°C. They found that both the crystallinity (initially 56%) and the density (initially 0.911) increased with increase of annealing temperature up to 160°C (crystallinity to 65% and density to 0.914) but subsequently decreased again for higher annealing temperatures.

While the literature thus suggests that annealing of polypropylene at elevated temperatures in the vicinity of the melting temperature may result in better packing and a higher degree of crystallinity, it provides little knowledge as to the importance of specific temperatures of anneal, to time at these temperatures, or to the most appropriate temperatures to use to achieve maximum crystallinity. It is also apparent that while multiple DTA or DSC transitions may arise from the presence of a second crystalline phase, as in some samples studied by Kardos et al.[8] and by Pae[9] or from presence of a second component,[2,3] interpretation of multiple peaks in this manner may not be correct. Thermal history of a sample containing but a single phase may also contribute, depending upon specific past history, to the presence of multiple endothermic peaks.

In view of the above, it is in order, for a particular polymer of known phase, to investigate thoroughly the effects of specific temperatures of anneal, times of anneal, and conbinations of annealing treatments involving both decreasing and increasing temperatures. Such is the purpose of the present article. One reason for the selection of PP is that multiple peaks have already been reported for this material[10] and attributed to the presence of a second crystalline phase. While they may arise from this source[9,11] they may also have other origins. In the present study, however, only one phase, viz., the normal α or monoclinic structure, is present; hence any multiple transitions which may be recorded will be a function only of the prior thermal history given to the sample and not to the pressure of a second phase.

The results of prior thermal history on specific fractions of PP and, in particular, on specific fractions that are known from x-ray evidence to possess several different crystalline structures, are reported in a following article.[11]

EXPERIMENTAL

All materials used in the current study were samples of isotactic polypropylene. These samples were taken from regular Profax powder as supplied by the Hercules Powder Company. This material is highly isotactic, being approximately 97% insoluble in n-heptane. The x-ray diffraction patterns taken on this Profax powder show that it has crystallized in the usual (Natta) or α-type monoclinic crystal structure. The average molecular weight is 325000, and the measured average density is 0.91.

All thermal measurements, including annealing treatments, were carried out on a Perkin-Elmer type differential scanning calorimeter (DSC-1). For all test samples, only one heating and cooling rate was used, viz., 40°C/min, and all tests were run under a nitrogen atmosphere. For measurements of the heat of fusion, tin was used as the reference standard. For all experiments, the sample size was kept constant at approximately 30 mg.

It is known[12] that the so-called "melting" temperature as recorded by DTA or DSC during a heating cycle or the so-called "crystallization" temperature obtained by cooling a sample from the melt at a constant rate, is itself a function of the rate of heating or of cooling. In this article we have arbitrarily designated the temperature at the maximum of the endothermic peak as the melting temperature and the temperature at the maximum of the exothermic peak on cooling as the crystallization temperature, the rates indicated above being used.

RESULTS AND DISCUSSION

Control Tests

To assess the effects of various specific annealing treatments, it was considered that all samples should first be brought to a given standardized state. To do this, for each experiment approximately 30 mg of Profax powder was placed in the sample pan of the DSC instrument and then heated to 185°C at the rate of 40°C/min. After being held in the liquid state at this temperature for three minutes, the sample was cooled at the rate of 40°C/min and the crystallization thermogram recorded. After the sample had been cooled to 70–80°C, a heating rerun was made at a steadily increasing temperature, again at the rate of 40°C/min. The melting endotherm obtained in this rerun was taken as the standard for comparing the effects on thermal behavior of different past histories.

The results of this type standardization procedure lead to the melting endotherm* as shown in Figure 1 (lower graph). Marked changes have occurred between the initial run (upper graph) and the rerun, as the figure shows, but additional subsequent runs (not shown) produce no further significant changes in melting behavior. The effect of the initial melting and recrystallization is to lower the peak or apparent melting temperature from about 167°C to about 161°C. At the same time, the area under the melting endotherm increases appreciably from about 9.7 cal/g for the powder to about 17.5 cal/g for the rerun sample. The lower melting point, but the larger area, would appear to indicate that the rerun sample is considerably more crystalline than the powder but, because it has crystallized under rather rapidly varying temperature conditions, it has a broader distribution of smaller crystallite sizes. The exotherm obtained on cooling

* Data shown are not actual records, but diagrammatic sketches thereof. Peak temperatures are estimated from the point of intersection of two straight lines drawn tangent to both sides of the melting endotherms.
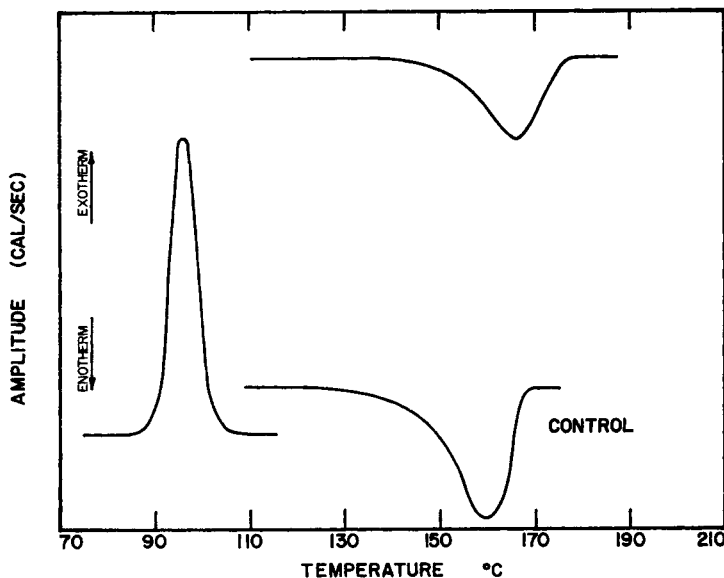
Fig. 1. DSC scans of polypropylene powder. Initial heating rate, cooling rate, and re-heating rate 40°C/min.

(middle graph) gives 96°C as the crystallization temperature and a recorded heat of crystallization of about 18.9 cal/g. The difference between this value and the value obtained for the heat of fusion is probably not significant as errors involved in measurement of the areas are quite large ($\pm 5\%$), largely because of the difficulties involved in drawing in the base lines.

The value obtained for the heat of fusion of the polypropylene rerun control samples, viz., 17.5 cal/g, is comparable to, but somewhat higher, than that obtained by Ke.[1]

A series of different annealing procedures were selected to give the control samples a wide variety of past histories. A complete list of all the heat-treatment procedures used is given in Table I. The actual anneal temperatures may be initially somewhat higher than the values cited because of thermal inertia. The effect of each of these past histories on the DSC melting behavior will now be discussed.

Annealing at Successively Increasing Temperatures

To determine the influence of a series of annealings at successively higher temperatures, a control sample, A, was annealed at 5° intervals from 135 to 160°C. This sample was held at each temperature for the time indicated in Table I. After the designated time at each temperature, sample A was cooled to 75°C and then reheated to the next highest temperature. After the final annealing at 160°C and subsequent cooling, the endotherm shown in Figure 2 was recorded. The melting endotherm of the control specimen is shown for comparison purposes.

TABLE I
Heat Treatment Procedures and Peak Temperatures

Sample designation	Heat treatment given			DSC peak temperatures, °C		
	Temperature, °C	Time, min	Cooling	Lower	Upper	No. peaks
Control	40°C/min to 185	3	Yes		160–162	1
A	135	3	Yes			
	140	5	Yes			
	145	7	Yes			
	150	9	Yes			
	155	11	Yes			
	160	13	Yes	158	173	2
B	120	5	No			
	125	5	No			
	130	5	No			
	135	5	No			
	140	5	No			
	145	5	No			
	150	5	No			
	155	5	Yes		168	1
C	120	5	Yes			
	125	5	Yes			
	130	5	Yes			
	140	5	Yes			
	145	5	Yes			
	150	5	Yes			
	155	5	Yes		169	1
D	145	3	Yes			
	135	3	Yes			
	125	3	Yes	130	160	4
E	160	3	Yes			
	150	5	Yes			
	140	5	Yes			
	130	5	Yes			
	120	5	Yes	125	179.5	6
F1	100	3	Yes		161	1
F2	110	3	Yes		161	1
F3	120	3	Yes		161	1
F4	130	3	Yes		161	1
F5	140	3	Yes		161	1
F6	145	3	Yes		161	1
F7	150	3	Yes		165	1
F8	152.5	3	Yes		169	1
F9	155	3	Yes		172	1
F10	157.5	3	Yes	161	175	2

(continued)

As Figure 2 shows, the annealing treatment has had a marked effect on melting behavior and hence on the microstructure and texture of the polymer sample itself. Whereas the control sample has one single peak with

TABLE I (*continued*)

| Sample designation | Heat treatment given | | | DSC peak temperatures, °C | | |
	Temperature, °C	Time, min	Cooling	Lower	Upper	No. peaks
F11	160	3	Yes	163	177	2
G1	160	0.5	Yes	163.5	175	2
G2	160	1	Yes	163	176.5	2
G3	160	2	Yes	163	177	2
G4	160	3	Yes	164	179	2
G5	160	5	Yes	163.5	179	2
G6	160	8	Yes	163	180	2
G7	160	15	Yes	162.5	181	2
G8	160	30	Yes	160.5	181.5	2
G9	160	60	Yes	160	181.5	2
G10	160	90	Yes	157	181.5	2
G11	160	120	Yes	157	181.5	2
G12	160	3.2 hr	Yes	155.5	182.5	2
G13	160	7 hr	Yes	152.5	183	2
G14	160	12.4 hr	Yes	145.5	182	2
H1	150	3	Yes		165	1
H2	150	6	Yes		165	1
H3	150	15	Yes		165	1
H4	150	30	Yes		165	1
H5	150	60	Yes		166	1
H6	150	120	Yes		166	1
H7	150	180	Yes		166	1
H8	150	12.5 hr	Yes		167	1
I1a	130	30	Yes		163	1
I1b	130	30	Yes		160	1
I2	135	30	Yes		161	1
I3	140	30	Yes		160.5	1
I4	145	30	Yes		162	1
I5	150	30	Yes		167	1
I6	154	30	Yes		172.5	1
I7a	155	30	Yes	148.5	172.5	2
I7b	155	30	Yes	151	173	2
I8a	156	30	Yes	155	174.5	2
I8b	156	30	Yes	157	175	2
I9a	158	30	Yes	157	178	2
I9b	158	30	Yes	159	178	2
I10a	160	30	Yes	160.5	181.5	2
I10b	160	30	Yes	162	181.5	2
I11	161	30	Yes	162	182	2
I12a	162	30	Yes	161		1
I12b	162	30	Yes	162.5		1

maximum near 161°C, annealed sample A shows a double peak with maxima at 158 and 173°C, respectively. Although this behavior somewhat resembles that obtained by Urabe et al.[10] upon annealing of a particular polypropylene sample at 155°C for 3 hr, the multiple peaks, in this case,
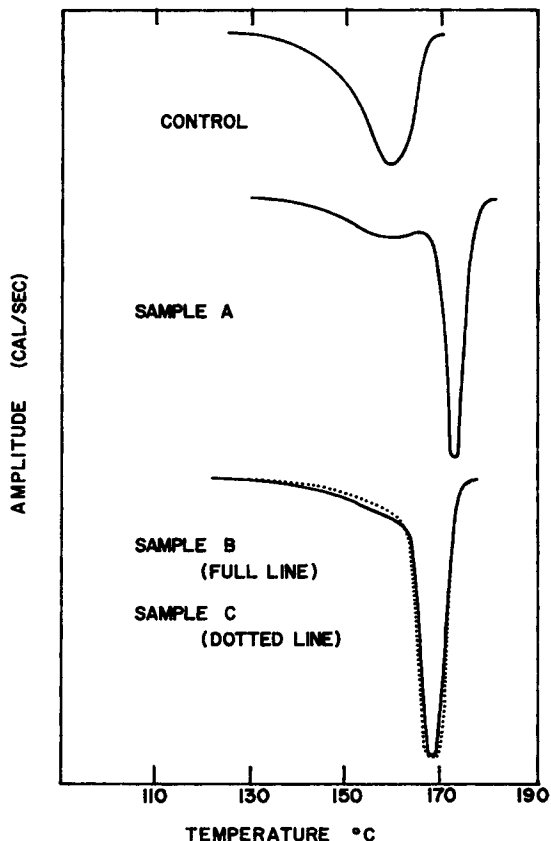
Fig. 2. DSC scans of polypropylene samples A, B, and C after annealing at a series of successively increasing temperatures as indicated in Table I.

are clearly not the result of a second crystalline phase as the annealed powder is entirely in the α or monoclinic form.

Comparison of respective areas shows that the final area after annealing is 13% above that of the control sample. Hence the annealing procedure has resulted in an increase of the overall degree of crystallinity. The significance of the double peak seems to be that the low temperature anneals have improved the perfection or increased the size of the poorer crystals which would have ordinarily melted below 155°C or so, while the higher temperatures, and in particular the final anneal at 160°C, has considerably increased the size and/or perfection of those crystals which would ordinarily have melted near 160°C and above. The sharpness of the upper peak for the annealed sample A indicates that a considerable portion of this sample now consists of uniform, well ordered, highly stable crystals. These are, however, imbedded in a broader distribution of crystals of less stability and perfection, as indicated by the secondary lower temperature peak.

To investigate whether the individual coolings and reheatings after each stepwise annealing procedure are in themselves significant, two additional control samples were selected and given two different annealing programming schedules.

Sample B, as indicated in Table I, was successively annealed for 5 min at a series of increasing temperatures starting at 120°C and proceeding upward to 155°C in 5°C intervals. The sample was not cooled after each annealing procedure but only after the full treatment, as mentioned, had been completed. After this, the melting endotherm, as shown by the full line in Figure 2, was recorded. Again, the melting thermogram of the control specimen is shown (top graph) for comparison purposes.

Sample C was given a similar treatment of five minutes at each of the annealing temperatures mentioned above but, in this case, the sample was cooled down to 75°C and held there for 1 min after each annealing treatment. The final thermogram for this sample is shown by the dotted line of Figure 2.

Inspection of the thermograms shows the effect of the two annealing procedures is almost identical. In both cases the principle melting transition, as Table I shows, is shifted to higher temperatures (approximately 168–169°C) and is narrowed. At the same time an appreciable lower temperature shoulder is present. On comparing these results with those of the previous test, it seems clear that the low-temperature shoulder would result in a separate peak if the annealing temperature had been extended to 160°C instead of 155°C. Another fact that is clear is that samples annealed to 155°C according to the procedure used for samples B and C are considerably more crystalline than the prior sample A, whose final annealing temperature was 160°C. This is revealed from measurements of the areas under the endotherm which are proportional to the heat of fusion of the sample. For annealed sample B, the ratio of the final area (A_f) to the control area (A_i) is about 1.32, while for annealed sample C it is 1.29. Thus the samples having the final anneal at 155°C, B and C, are approximately 15% more crystalline than sample A with final anneal at 160°C. However the final melting temperature, which depends to a considerable degree on whether the remaining crystallites at the final anneal temperature have sufficient solid state mobility to thicken, is higher for the sample A (173°C compared to 168°C).

Annealing at Successively Decreasing Temperatures

Another control sample, D, was subject to an annealing treatment (See Table I) that consisted of exposure to some elevated temperature (145°C) first, followed, by successive annealings at progressively lower temperatures. After each exposure, it was brought down to 80°C and then taken back up to the next lowest temperature. After the final annealing at 125°C and subsequent cooling, a DSC thermogram, as shown in Figure 3 was recorded for this sample.
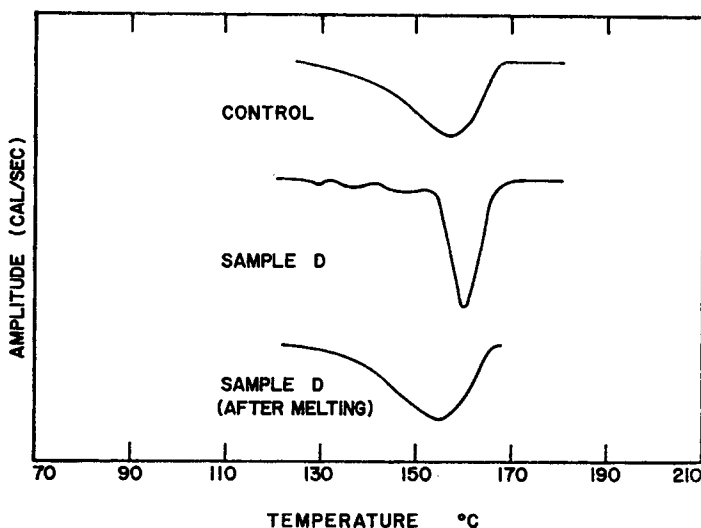
Fig. 3. DSC scans of polypropylene sample D after annealing at a series of successively decreasing temperatures as indicated in Table I.

There are now four separate peaks instead of the one of the control sample. The highest temperature peak at 160°C is about at the same temperature as for the control specimen, but it is considerably sharpened. In addition, there are three secondary peaks, one somewhat above 145°C, one somewhat above 135°C, and one somewhat above 125°C.

The results for this sample are similar to those reported by Gray and Casey[5] for a polyethylene–polybutene copolymer. Each successive annealing appears to be producing a discrete bunching of crystallite sizes and/or perfections and an increased stability, particularly of those crystals which would ordinarily have melted at, or slightly above, the temperature of annealing. As Figure 3 also shows, subsequent recrystallization of the annealed sample, after it has been taken to temperatures above the melting point, effectively wipes out all its past history.

A similar series of progressively decreasing annealing temperatures was given to another control sample, E, except in this case the starting annealing temperature was 160°C and the final annealing temperature 120°C. Sample E was held at each annealing temperature for the times indicated in Table I. After each successive anneal, the specimen was cooled to 70°C. The cooling curve after the first 160°C anneal (Fig. 4) is interesting. The crystallization exotherm now has three humps instead of one. Most of the crystallization upon cooling has apparently taken place near 125°C, as the melted portion of the sample crystallizes epitaxially upon the good crystals which were not melted by the 160°C anneal.

The final melting endotherm of sample E has considerable character. There are now four peaks below the main melting peak and one above. The four peaks below as well as the principal melting peak are again
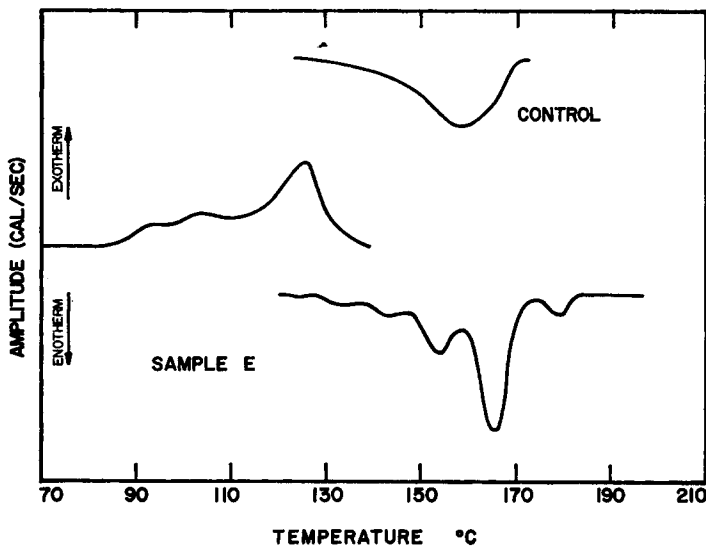
Fig. 4. DSC scans of polypropylene sample E after annealing at a series of successively decreasing temperatures as indicated in Table I.

situated a few degrees above each of the annealing temperatures. Thus, once again, annealing in successive stages has resulted in a bunching of crystallite sizes and/or perfection.

A new feature of these data, which is not found in the study of Gray and Casey,[5] is the presence of a very high melting phase. Hence for sample E, six melting peaks have resulted from only five anneal treatments. The melting peak near 180°C has apparently been produced by the first 160°C anneal and probably indicates a marked thickening of some of the lamellar crystals that are present. For sample D, where the highest anneal temperature was only 145°C, no unusual high melting phase is present.

Effect of Specific Anneal Temperatures

To investigate the nature of the changes being produced in the DSC thermogram by specific annealing treatments, a series of control samples F1 to F11 were selected and each sample given an anneal for three minutes at a specific temperature as indicated in Table I. The first sample, F1, was annealed at 100°C; the second, F2, at 110°C; and so on as indicated in Table I, with the final sample F11 being annealed at 160°C. After each annealing and subsequent cooling to 75°C, the melting endotherm of the particular sample was recorded. The initial control thermogram, together with those obtained for some of the annealed samples are shown in Figure 5 and a listing of all peak temperatures is given in Table I.

The results show that even the low temperature anneals have some effect. They tend to produce a distinct shoulder on the low temperature side of the melting peak. This is perhaps most pronounced for the sample F4,
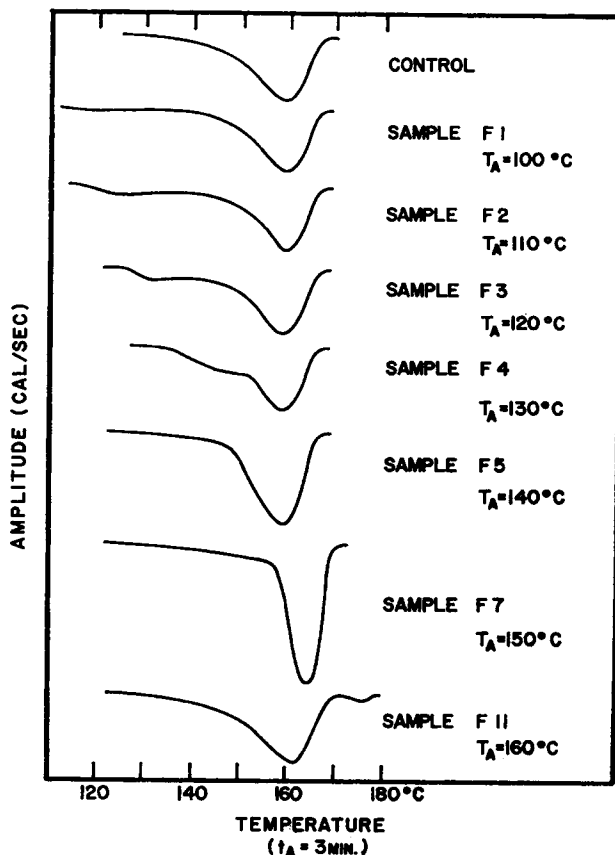
Fig. 5. Selected DSC scans of polypropylene samples after annealing for 3 min at the
temperatures indicated.

annealed at 130°C. At higher temperatures of anneal the main peak
increases in size but no shoulder is present.

For the diagrams shown in Figure 5 the sharpest peak, indicating the
greatest uniformity of internal structure, occurs for the sample F7, annealed
at 150°C. The apparent reason for this behavior is that only a small
amount of the specimen material has melted at 150°C (as inspection of the
thermogram for the control sample shows) and subsequently recrystallized,
while the unmelted remainder of the specimen has acquired sufficient
molecular mobility as a result of the annealing treatment to give consider-
ably improved molecular packing in the solid state. The melting peak of
165°C is about comparable to that of the virgin material, but the degree of
crystalline perfection, as evidenced from the area and shape of the thermo-
gram, is considerably higher.

Upon annealing at 160°C (specimen F11), a considerable amount of the
polymer, perhaps 60–70%, is melted. This material, upon crystallizing
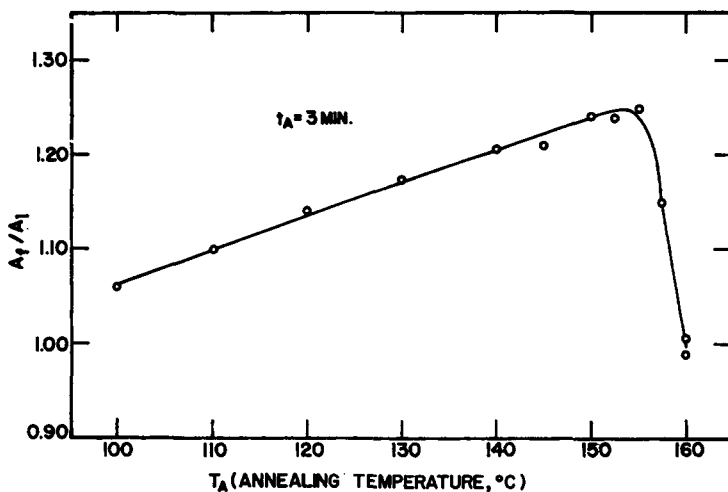under the usual conditions of a 40°C/min cooling, will give a broad, con-

Fig. 6. Ratio of melting peak areas for polypropylene samples FI and FII compared to control sample vs. annealing temperature.

tinuous range of crystallite sizes, and hence the endotherm of the 160°C annealed sample has a more pronounced low-temperature tail in contrast to that of the 150°C annealed sample. However, the material that has not been melted at 160°C has the opportunity and the necessary molecular mobility to improve its packing within the crystal and to increase the fold period of its individual lamellar crystals. The overall result is a broad endotherm with the main peak extending from 130 to 170°C and a small, higher-temperature peak near 178°C that probably arises from thickened lamellar crystals. The size of this peak is dependent upon the total time of anneal, as we shall see.

The effect of each 3-min annealing treatment on the improved packing of molecular chains is demonstrated by Figure 6 where the ratio of the areas under the thermograms for samples F1 to F11 to the area of the control sample is plotted against the annealing temperature. The increase in area, reflecting an overall increase in degree of crystallinity of the sample appears to be approximately linear with increasing temperature up to an anneal temperature of about 155°C. For higher anneal temperatures the area ratio then falls from its maximum value of about 1.25 at 155°C to about 1.00 at an anneal temperature of 160°C. Thus to attain the maximum degree of crystallinity requires annealing at a specific temperature. This temperature must be high enough to give sufficient molecular mobility to allow improved packing but not too high to produce a considerable amount of melting of a major portion of the sample.

Effect of Anneal Time at a Specific Temperature

To investigate the importance of time of anneal, a series of control samples, G1 to G14, were all annealed at the specific temperature (160°C) but
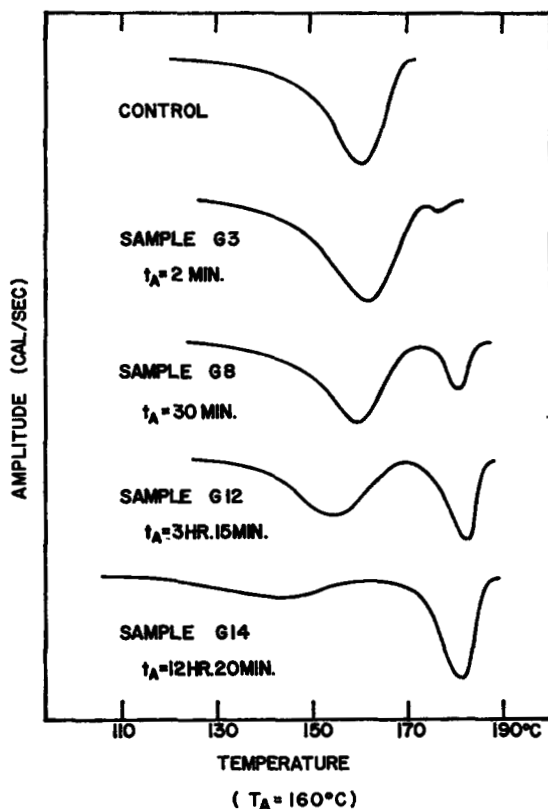
Fig. 7. Selected DSC scans of polypropylene sample G after annealing at 160°C for times indicated.

for varying times ranging from 30 sec (sample G1) to 12 hr and 20 min (sample G14). The resulting melting endotherms for several of these samples are shown in Figure 7.

Inspection of these diagrams shows that all of the annealing treatments have resulted in the production of multiple DSC peaks. For short times of anneal the main melting peak of the control sample is about at the same position, but a second distinct endotherm appears at a higher temperature. For sample G3, annealed for 2 min, this upper peak occurs at 177°C. As the time of annealing is increased, the lower temperature peak decreases in magnitude and shifts to lower temperatures while the higher temperature peak increases in magnitude and shifts to higher temperatures.

The variation of these peak positions with increasing time of anneal at 160°C is shown more clearly by the graphs of Figure 8. It appears that the peak temperature of the high temperature peak initially increases rapidly with anneal time and comes essentially to a final temperature of 182.5°C after about 20 min. On the other hand, the lower temperature peak continues to decrease with increase of anneal time.
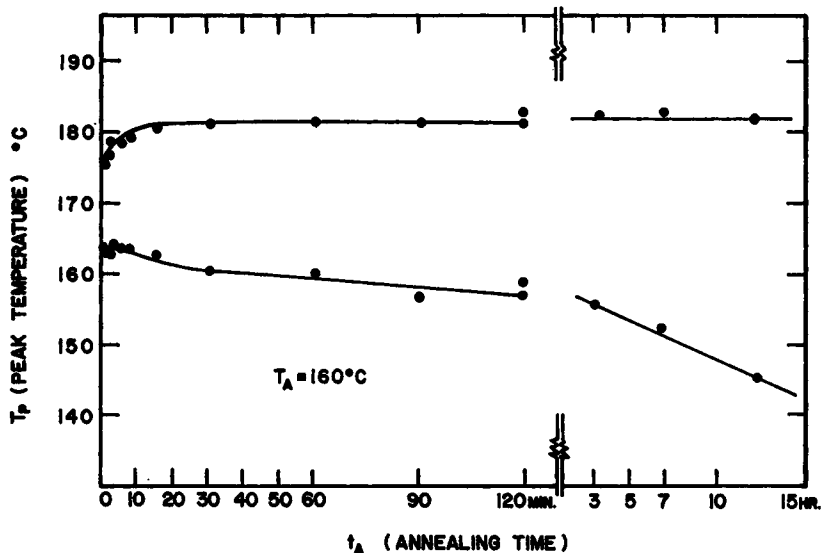
Fig. 8. DSC melting peak temperatures for polypropylene samples G1 through G14 vs. annealing time at 160°C.

A possible interpretation of these data is that with increased time of anneal, a greater amount of the unmelted crystalline material present at 160°C undergoes a refolding process and the crystal lamellae appreciably thicken. The melting point of these partially extended chain crystals appears to be about 182°C with the increased size of the DSC peak signifying that more of the originally folded crystallites have been given the opportunity to thicken and increase their crystallite size. The drop in temperature and in size of the lower temperature peak with increased time of anneal may be the result of increased vacancy concentration and of the decrease in heterogeneous nuclei present as a result of the increase of crystal size due to refolding and thickening.

Another series of sample, H1 to H8, was annealed at a temperature of 150°C for varying times ranging from 3 min for sample H1 to 12.5 hr for sample H8. In all samples, the melting endotherms, not shown, gave only a single peak. Although there was a noticeable increase in the area of this peak with time of anneal, there was almost no change in peak temperature position after the first anneal as Table I shows.

The manner in which the total endotherm area changed for the two series of samples, G and H, annealed at 160°C and 150°C, respectively, for varying times is shown in Figure 9. A great disparity between the two curves exists, and this reflects a significant change in internal structure.

The data of Figure 9 show that the ratio of the final area to the initial area continues to increase with time for the 150°C annealed sample. After 3 hr anneal this ratio is about 1.38, and after 12.5 hr anneal it has risen to 1.78. Hence the degree of crystallinity of all the H samples and in particu-
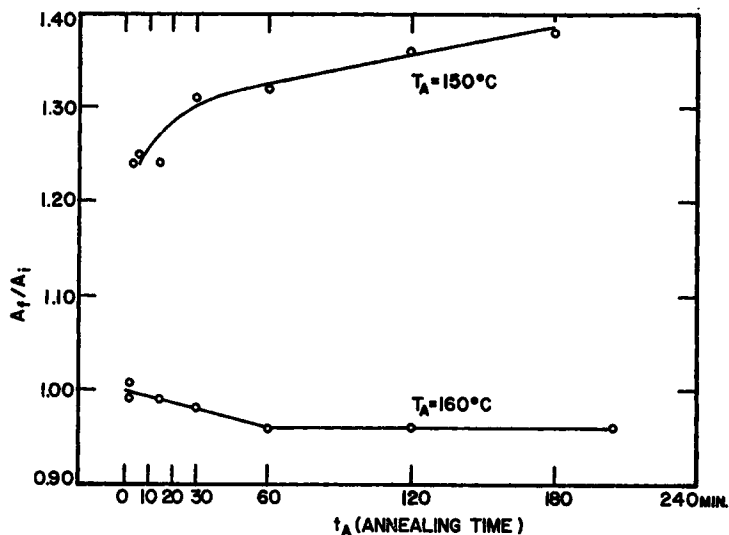
Fig. 9. Ratio of melting peak areas for polypropylene samples G1 through G14 and H1 through H8 compared to control sample vs. annealing time at temperatures indicated.

lar, sample H8, is markedly greater than that of the control samples. However there is no noticeable increase in melting temperature, presumably because lamellar thickening of those crystals which would normally melt in the 160–170°C range has not yet occurred for this temperature of anneal.

For sample G, annealed at 160°C, the data of Figure 9 show that despite the marked increase in final melting point, as already noted in connection with discussions of Figures 7 and 8, the overall degree of crystallinity has actually decreased with increased time of anneal. This may well be the result of voids or vacancies which are introduced during the annealing treatment.

Effect of Anneal Temperatures for Specific Times

It was mentioned in connection with Figure 5 that even 3 min of annealing at temperatures in the vicinity of 130°C and higher had a marked effect on the resulting thermal behavior as detected by DSC. To explore this phenomena more fully, a new series of specimens, I1 to I12, were selected and given a 30-min anneal at specific temperatures varying from 130°C to 162°C as indicated in Table I.

The resulting thermograms of some of these annealed specimens are shown in Figure 10. It will be noted that these endotherms may be a single peak, a peak with a low-temperature shoulder, or a double peak, depending upon the specific annealing temperature. It appears (see Table I) that single peaks are obtained upon annealing at 154°C or below and at 162°C or above and double peaks are obtained upon annealing between 155°C and 161°C. As Figure 11 shows, the temperature location of the single peak is
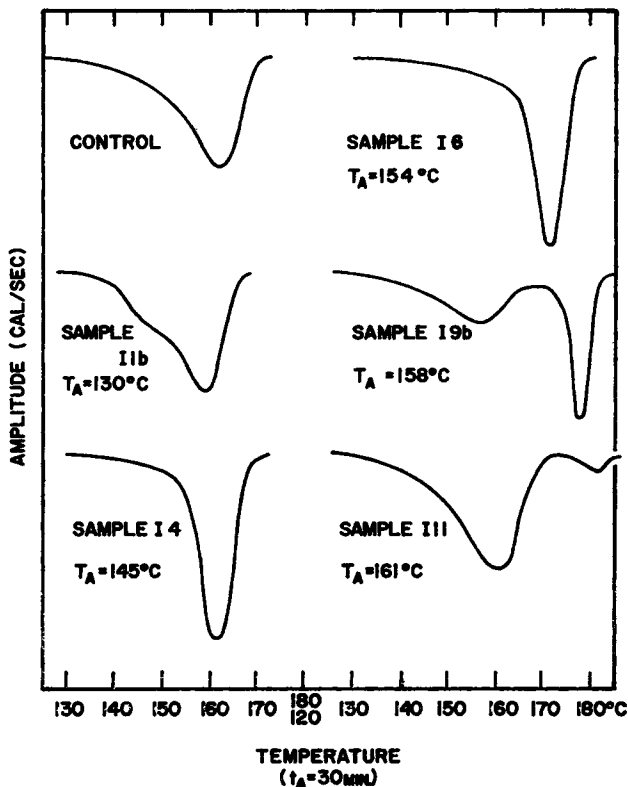
Fig. 10. Selected DSC scans for polypropylene sample I after annealing for 30 min at temperatures indicated.

essentially independent of temperature up to 140°C or so and then rises with further increase of anneal temperature. The lower graph of Figure 11 shows how the temperature location of the lower temperature peak, when multiple peaks are present, varies with anneal temperature.

It is clear from Figures 10 and 11 that marked changes in thermal behavior can be produced by very small changes in anneal temperature.

Note for example, the changes in melting behavior of the samples I6 and I9 annealed at 154°C and 158°C, respectively. Upon annealing at 154°C there is only a single peak which is much sharper than that of the control sample and which is located some 10°C higher. Upon annealing at 158°C rather than 154°C, two things occur. First a considerably larger portion of the sample is now melted at this temperature, and recrystallization of this portion accounts for the low-temperature endotherm located at 159°C. Secondly, there is now sufficient mobility in the solid state not only to result in somewhat better molecular packing relative to the control sample but also to permit considerable chain refolding and crystal thickening. This process apparently gives rise to the higher melting endotherm at 178°C.
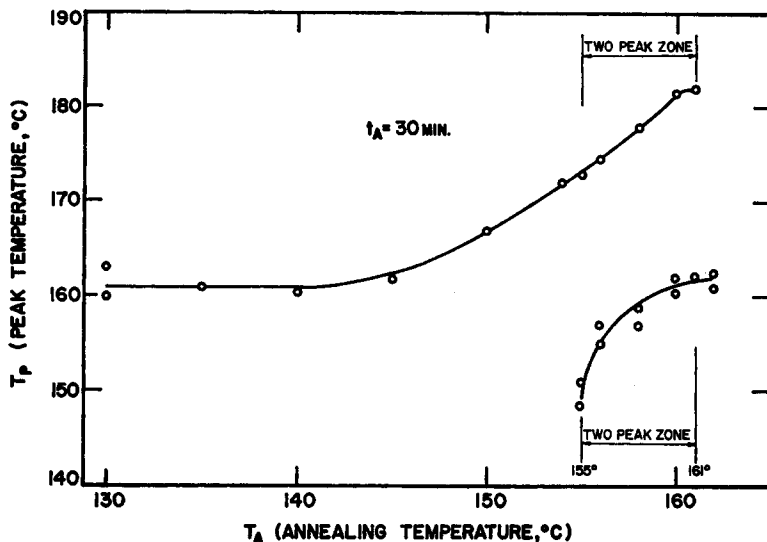
Fig. 11. DSC melting peak temperatures for polypropylene samples I1a through I12b vs. annealing temperature.

However if the anneal temperature is further increased, as for sample I11 (and as noted in connection with discussion of sample F11 annealed for 3 min at 160°C), much more of the original sample is melted, and hence the lower temperature peak is now the larger of the two rather than the smaller as for sample I9. Secondly the upper peak, though still small in magnitude for this time of annealing, is now shifted to 182°C and apparently reflects a further crystal thickening. From our previous discussion of the data of Figure 7, it is to be expected that with increased times at this temperature the area of the upper peak would continue to increase with increase of annealing time as more and more of the crystals participated in the thickening process. If the anneal temperature is increased too high, 162°C or higher, then, because of some degree of overshooting, most of the control sample is melted and the resulting endotherm is similar to that of the control sample.

CONCLUSIONS

From the results of the present study, the following conclusions may be drawn.

(1) DTA melting thermograms of isotactic polypropylene may be affected even by low-temperature (100–130°C) and short-time anneals (2 or 3 min) and are markedly affected by higher-temperature (140–160°C) and longer-time anneals (1/2 to 12 hr).

(2) Multiple DSC peaks can be produced even in a homopolymer with but a single crystalline phase by a variety of prior heat treatments. Double endothermic peaks, for example, can be produced, as Table I shows, by

single annealing treatments of 30 min above 155°C, by 30 sec or more of annealing at 160°C, or by a series of stepwise increasing annealing treatments for varying times extending up to 160°C.

(3) A series of stepwise annealing treatments at successively higher temperatures leads to a double peak if the final anneal temperature is at 160°C but to a single peak if the final anneal temperature is at 155°C or less.

(4) A series of stepwise annealing treatments at successively decreasing temperatures will give rise to a number of DSC peaks which exceed the number of steps in the annealing procedure.

(5) For the heating rates herein investigated the final melting temperature of polypropylene crystallites can be raised to approximately 182°C by appropriate annealing treatment.

(6) For maximum degree of crystallinity, rather than maximum attainable melting temperature, there is a specific anneal temperature, which for an anneal time of 3 min, is about 155°C.

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