

Effects of Thermal History on Polypropylene Fractions

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Synopsis

The effects of thermal history on the melting behavior of several polypropylene fractions have been studied. The specific fractions investigated include one that has crystallized in the triclinic modification, one that has crystallized in the monoclinic modification, and a third that contained a combination of the two types of crystals. Thermal histories given to these specimens included a series of stepwise annealings at steadily decreasing temperatures, a series of annealings for various times at a given elevated temperature, and a series of stepwise annealings at a set of steadily increasing temperatures. The melting behavior was investigated by means of a differential scanning calorimeter and various DSC peaks are presented. The nature of multiple peaks produced by the different treatments is discussed, and the results are compared with similar data obtained on whole polymer.

INTRODUCTION

In a preceding paper,¹ the specific effects on melting behavior of a wide variety of thermal treatments have been investigated for a particular whole polymer, viz., isotactic polypropylene. It was shown that double, and even multiple, DSC peaks could be produced by appropriate variation of past thermal history.

It is the purpose of the present paper to consider the effect of another material variable, viz., molecular weight. Polypropylene fractions of three different molecular weights have been studied. Some of these fractions have such low molecular weights that the lamellar crystals formed from them should not exhibit chain folding. By variation of thermal history on these samples and comparison of DSC thermograms with those obtained by similar treatment applied to whole polymer, the possible influence of chain folding or of crystal thickness should be revealed. Another interesting feature of the present studies is that x-ray diffraction indicates that one of the low molecular weight fractions has crystallized in a triclinic γ phase rather than the usual monoclinic α phase that is found in whole polymer. Another fraction, however, has crystallized in the α phase, and the third fraction exhibits both phases. Hence, it should be possible to study the influence of past history on the thermal properties of both the γ phase and the α phase of polypropylene, as well as combinations thereof.

Differential thermal analysis studies of some polypropylene fractions (\bar{M}_n from 20×10^3 to 38×10^3) have been reported by Urabe and co-

workers.² For quenched samples of high molecular weight fractions they found only a single endothermic peak with maximum at 166°C. However, upon annealing at temperatures above 130°C, they observed a second small peak at temperatures of 142°C to 147°C, depending upon the particular sample being studied. The authors raised the possibility that this second peak might arise from the presence of another phase (hexagonal β or triclinic γ) despite the fact that their x-ray diffraction data indicated only the presence of the α phase.

For another sample, in which x-rays did indicate the presence of a hexagonal β phase together with the monoclinic α phase, double peaks were again found, with the lower one at 157°C, apparently arising from melting of the β phase, and the higher one near 167°C, arising from melting of the α phase.

There is little doubt, in view of the work of Kardos et al.³ and of Pae⁴ on DTA studies of pressure-crystallized whole polymer, in which the γ phase may also appear, that multiple peaks do arise, depending upon the heating rate, as a result of melting, or conversion, of the γ phase and as a result of melting of the α phase. However, it is known from the work of Gray and Casey⁵ and others⁶ that multiple peaks may also occur in single-phase materials and may arise from the presence of varying internal morphologies produced by variations of past thermal history.

Physical and mechanical properties of some polypropylene fractions have been measured by van Schooten et al.⁷ They recorded the melting point T_m as the temperature at which birefringence disappeared. The fractions studied varied in T_m from about 115°C to about 170°C, and one fraction was completely amorphous. The measured density of this fraction was 0.861, and the most crystalline fraction had a density of about 0.910. As might be expected in view of these large differences in density, the fractions, and mixtures thereof, were observed to have widely different properties. The crystal structure of these fractions was not given, nor is it known whether any thermal transformations or crystal structure transformations occurred prior to the final melting point.

Turner-Jones et al.⁸ have investigated the effects of thermal treatment on whole polymer of polypropylene, obtained in both the α and the β form, and in fractions of polypropylene, obtained in γ form. They did not study the nature of thermal behavior in the vicinity of melting, but did show that the intensity and position of the x-ray diffraction lines of the various samples depended upon prior thermal treatment. For example, they noted that the hexagonal β form reverted to the monoclinic α form on heating above 150°C and that the γ form, which could only be obtained by cooling low molecular weight fractions from the melt, was converted to the α form by mechanical drawing, whether done at room or elevated temperature.

Some studies of polypropylene fractions have also been made by Raspopov et al.⁹ These fractions varied in molecular weight from about 20000 to about 160000. The low molecular weight fractions were reported to be brittle but the yield stress was found to vary little with change of

molecular weight. The effects of prior thermal treatments or the effect of different crystalline forms were not studied.

The results of quenching and of variation of thermal treatment on polypropylene powder has been studied by Nishioka et al.¹⁰ using x-ray and nuclear magnetic resonance techniques. It was noted that annealed films, annealed at temperatures as low as 100°C, had a larger crystallite size than those quenched into a Dry Ice-methanol bath. Another finding was that the x-ray scan of an *n*-heptane extract differed from that of the quenched powder. The authors attributed this difference to heat treatment (the *n*-heptane extract was slowly solidified on cooling from 150°C); in view of more recent information^{3,4,8} it seems likely that the effect observed was the result of production of a new phase (γ rather than α).

In the present study, fractions of polypropylene containing predominantly the α phase or the γ phase, or mixtures thereof, are subject to a wide variety of thermal treatments, including variations of anneal temperature and variations of anneal time. The effects of combinations of separate annealing treatments, such as a series of anneals at steadily increasing temperatures, or a series at steadily decreasing temperatures, will also be reported. As in the preceding paper,¹ it will be shown that multiple DSC peaks can be produced by thermal treatment alone. The presence of these multiple peaks appears to be the result of a discrete bunching of crystallites of varying degrees of perfection.

EXPERIMENTAL

All investigations of melting behavior herein reported were obtained by use of a Perkin-Elmer type differential scanning calorimeter (DSC 1B). Since peak temperatures are considerably affected by rate of heating or cooling,^{11,12} all heating runs have been made at a constant speed (40°C/min). Cooling runs have been made at various speeds ranging from 5°C/min to 40°C/min. All annealing treatments were given under a nitrogen atmosphere while the samples were in the sample pan of the DSC unit. Specimen weights used were kept constant at approximately 20 mg.

The three specific polypropylene fractions studied had number-average molecular weights of 1260, 1880, and 3800. Samples of each of these were subjected to various thermal treatments, as indicated in Tables I-III. Data are also given in the tables concerning subsequent melting behavior of both the treated samples and of the so-called control samples.

X-ray diffraction patterns of powder samples of each fraction were obtained on a Norelco diffractometer with $\text{CuK}\alpha$ radiation and a Geiger counter. The results are shown by the upper curves of Figures 1, 2, and 3. These scans show that the 3800 \bar{M}_n fraction has crystallized in the α phase, the 1260 \bar{M}_n fraction has crystallized predominantly in the γ phase, and the 1880 \bar{M}_n fraction contains both phases.

TABLE I
Annealing Procedures and Peak Temperatures for Sample $\bar{M}_n = 1260$

Sample desig.	Specific thermal treatment			DSC peak temperatures, °C		No. peaks
	Anneal temp, °C	Anneal time, min	Subsequent cooling rate, °C/min	Lower	Upper	
Control	140	3	5(to 60°C)		109.5	1
J	110	10	"			
	100	3	"			
	90	4	"			
	80	5	"	82	121	5
K1	109	0.5	"	99	120	3
K2	109	1	"	99	118.5	3
L1	109	30	"	100	121	3
L2	109	60	"	100	121	3
M	85	15	None			
	90	15	None			
	95	15	None			
	100	15	None			
N	105	15	5(to 60°C)	100.5	117	2
	80	3	None			
	85	3	None			
	90	3	None			
	95	3	None			
	100	3	None			
	105	3	None			
	110	3	5(to 60°C)	100.5	120	3

TABLE II
Annealing Procedures and Peak Temperatures for Sample $\bar{M}_n = 1880$

Sam- ple desig.	Specific thermal treatment			DSC peak temperatures, °C		No peaks
	Anneal temp, °C	Anneal time, min	Subsequent cooling rate, °C/min	Lower	Upper	
Control	160	3	20(to 70°C)		134	1
O	135	10	"			
	125	1.5	"			
	115	5	"			
	105	10	"	118	137.5	3
P	135	30	"			
	125	1.5	"			
	115	5	"			
Q1	105	30	"	113	145	5
	133	2	"	129	143	2
Q2	133	5	"	130	143.5	2
R1	133	30	"	131	144	2
R2	133	60	"	129	144	2
R3	110	3	None			
	115	3	None			
	120	3	None			
	125	3	None			
	130	3	20(to 70°C)	130	141	2

TABLE III
 Annealing Procedures and Peak Temperatures for Sample $\bar{M}_n = 3800$

Sample desig.	Specific thermal treatment			DSC peak temperatures, °C		No. peaks
	Anneal temp, °C	Anneal time, min	Subsequent cooling rate, °C/min	Lower	Upper	
Control	165	3	40(to 80°C)	144.5		1
S	150	10	"			
	140	1	"			
	130	3	"			
	120	5	"	119.5	152.5	4
T	148	20	"			
	138	5	"			
	128	10	"			
	118	20	"	115	162	5
U	144	2	"	149.5	156	2
V	144	10	"	146.5	157	2
W	144	30	"	143	158	2
X	120	5	None			
	125	5	None			
	130	5	None			
	135	5	None			
	140	5	40(to 80°C)	142	153	2

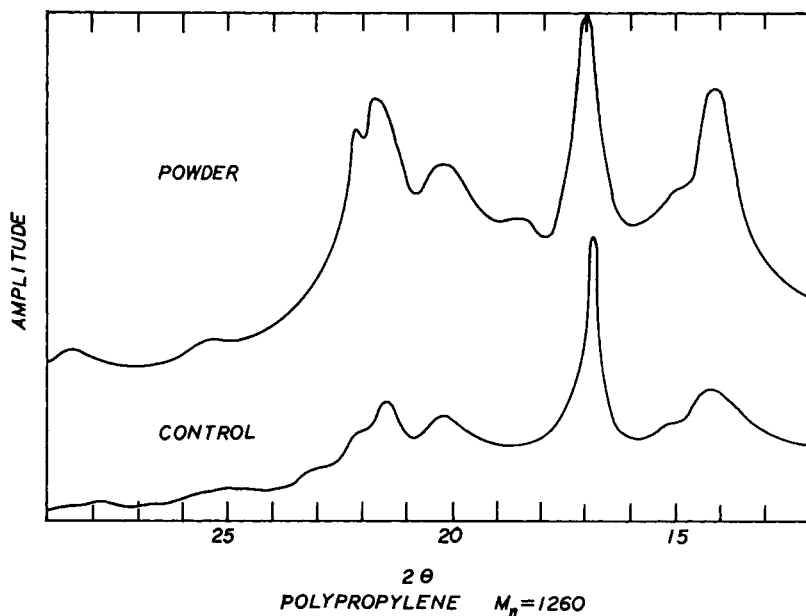


Fig. 1. X-ray diffraction scans for powder and control samples of polypropylene fraction, $\bar{M}_n = 1260$.

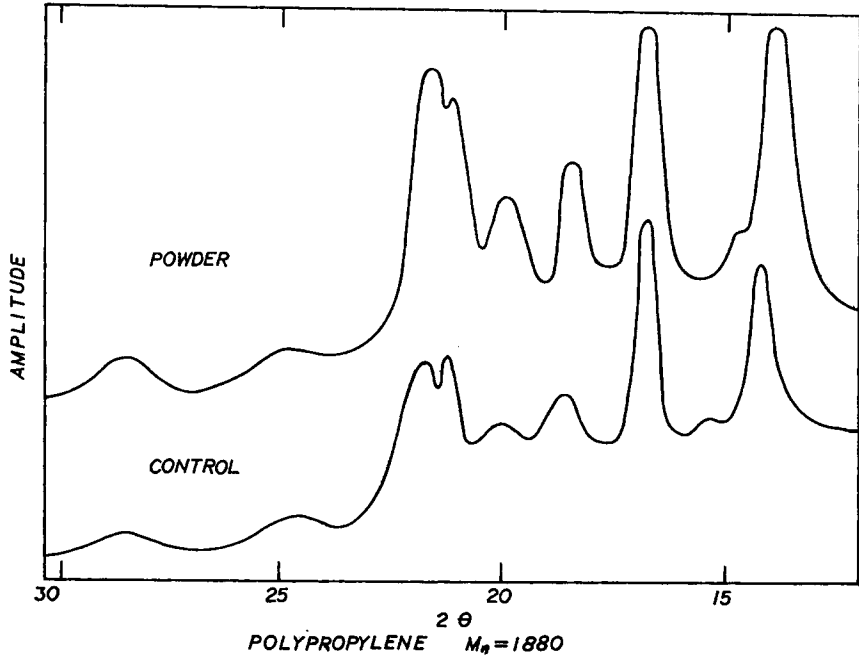


Fig. 2. X-ray diffraction scans for powder and control samples of polypropylene fraction, $\bar{M}_n = 1880$.

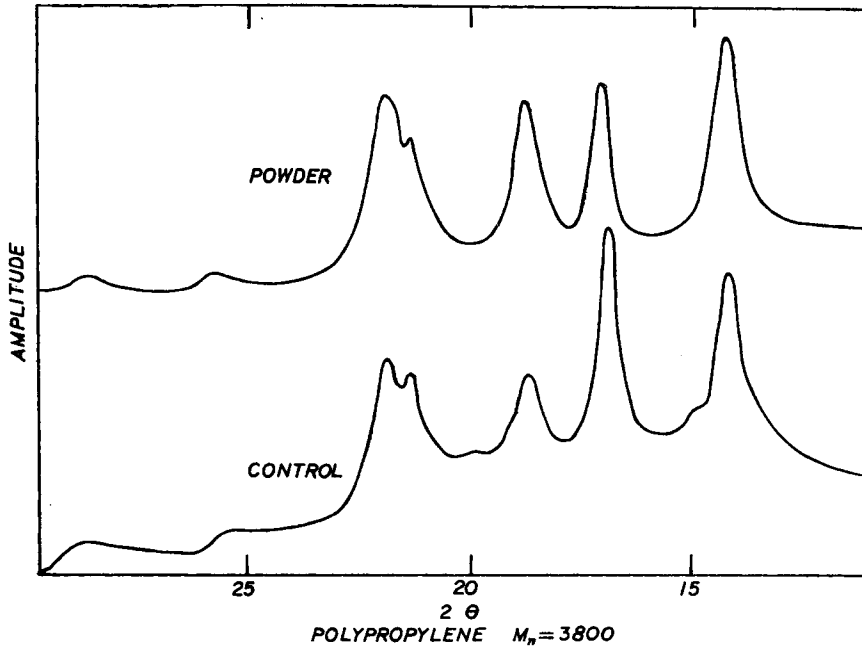


Fig. 3. X-ray diffraction scans for powder and control samples of polypropylene fraction, $\bar{M}_n = 3800$.

The fractioned samples used in this study were obtained from the Shell Oil Co. They were prepared as indicated by van Schooten and Wijga.^{13*}

RESULTS AND DISCUSSION

Molecular Weight Fraction with $\bar{M}_n = 1260$

The DSC endotherm of the powder sample of this fraction is shown by the upper graph of Figure 4. The endotherm is broad, with the main fusion peak occurring at a temperature of 111°C. There is also evidence of a broad shoulder, or premelting peak, near 95°C. The powder sample was then held for 3 min at 140°C and subsequently cooled at 5°C/min to 60°C.

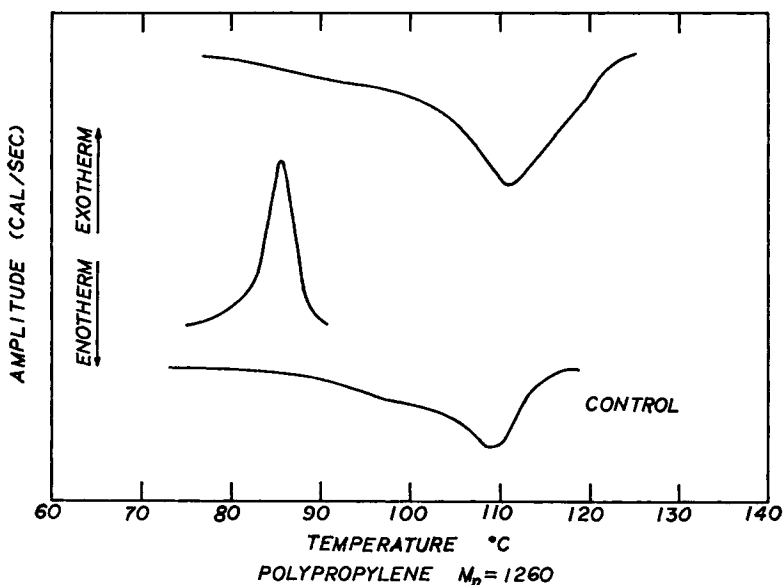


Fig. 4. DSC scans of polypropylene fraction, $\bar{M}_n = 1260$. Initial heating rate 40°C/min, cooling rate 5°C/min, reheating rate 40°C/min.

The crystallization exotherm gives a single sharp peak centered at 85.5°C, as shown in Figure 4. The sample was then held at 60°C for 1 min and the temperature again increased at the rate of 40°C/min. The resulting endotherm, with main fusion peak at 109.5°C, and a shoulder near 97°C, may be taken as the control or standard form with which to compare effects of different thermal histories. The reason this is possible is that further repetitions of the procedure indicated above have essentially no effect on either the cooling or heating thermograms of this control sample for the given rates of heating and cooling.

* The designations of the samples as given in the paper are $\bar{M}_n = 1260$ (B3), $\bar{M}_n = 1880$ (B2), and $\bar{M}_n = 3800$ (C4).

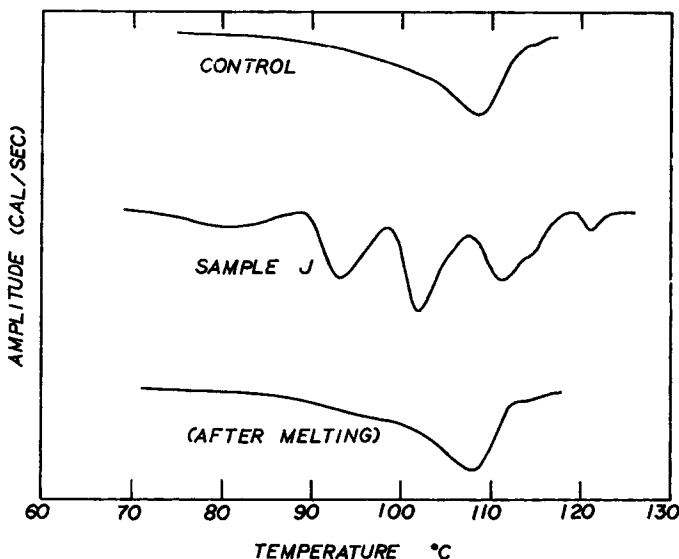


Fig. 5. DSC scans of polypropylene fraction, $\bar{M}_n = 1260$. Sample J after annealing at a series of successively decreasing temperatures as indicated in Table I.

To see whether the treatment given to the control sample had any effect on the crystalline structure of the original powder sample, an additional x-ray diffraction scan was taken on a sample subjected to a similar treatment as that given to the control sample mentioned above. The results are shown by the lower graph of Figure 1, and this scan can be compared with the upper scan to see what effect a 40°C/min heating to 140°C followed by a 5°C/min cooling has done to the sample. From the respective scans, it is clear that the treatment given has caused the crystal structure to convert fully to the γ phase. The small trace of the monoclinic α phase, present in the initial powder sample as indicated by the peak at 18.5°C, has disappeared. In fact, the 5°C cooling rate was selected so as to be able to retain the triclinic γ structure. It was found that at high cooling rates, of the order of 40°C/min as used in the previous study,¹ much of the γ phase of this fraction was converted to the monoclinic α phase.

Another sample, treated as indicated above but then designated J, was subjected to a series of four stepwise annealing treatments at decreasing temperatures varying from 110°C to 80°C in 10° intervals. The sample was held at each of these temperatures for the times indicated in Table I and subsequently cooled to 60°C. After the final 80°C anneal and subsequent cooling, the DSC diagram shown in Figure 5 was recorded. There are five distinct endothermic peaks with one peak occurring slightly above each temperature at which annealing took place and with a fifth high temperature peak occurring at 121°C, or 11–12°C above the highest anneal temperature. The valleys between the peaks are located slightly below the anneal temperatures. A similar phenomenon has been previ-

ously reported for a copolymer sample of ethylene and butene.⁵ However, the sample used in this study has such a low \bar{M}_n that crystals formed from it should not exhibit chain folding. Hence the presence of multiple peaks for this sample cannot be attributed to the existence of lamellar crystals of varying thickness arising as a result of the discrete annealing procedures.

It is clear from the DSC results that the microstructure of the treated sample has been markedly altered, and that some recrystallization has occurred after each anneal. One interpretation of the multiple peaks that occur in this sample is that each successive anneal has resulted in an improved packing of chain molecules in those portions of the heterogeneous polycrystalline sample which would ordinarily have melted in the vicinity of, or a few degrees above, the annealing temperature. As a result of this improved packing, the overall perfection of this material is increased, and its average melting temperature is raised. Successive anneals at steadily lower temperatures behave in like manner except that each anneal essentially affects only the material that would melt in the vicinity of, or a few degrees above, the specific anneal temperature. Except for the presence of the small endothermic peak at 121°C, the overall result after the four successive anneal treatments appears to be a discrete bunching or segregation of crystals of four different average degrees of stability or perfection.

The effect of time for a specific anneal temperature was also investigated. The anneal temperature selected was the approximate peak temperature of the DSC thermogram of the control sample, viz., 109°C. Four samples, K1, K2, L1, and L2 were studied, K1 and K2 being annealed for 30 sec and 2 min, respectively, and L1 and L2 for 30 min and 1 hr, respectively, as indicated in Table I. Some of the DSC scans are shown in Figure 6. They reveal a triple peak with a broad low-temperature peak some 10°C below the peak for the control sample, with a small second peak a few degrees above the anneal temperature, and with a sharp high-temperature peak located at about 11°C above that of the control sample. The results suggest that the material which would have ordinarily melted in the range 109–118°C or so has been improved by the annealing procedure. Evidently the increased thermal mobility associated with the annealing process has resulted in better packing of chains, in larger crystallite sizes, and in increased thermal stability of the recrystallized material. Hence the melting point rises from 109–110°C to above 120°C. This effect, however, cannot be attributed to increased lamellar thickening, as the chain molecules for this molecular weight are too small to exhibit folding. The main peak that is centered near 100°C arises from material that has melted at the anneal temperature and has recrystallized not at the anneal temperature but upon subsequent cooling. The lower temperature value of this peak as compared to the control sample indicates that a greater concentration of vacancies and defects, and hence poorer thermal stability, is present in the melted and recrystallized portion of the sample.

There is an effect of anneal time, as Figure 6 indicates, but this effect appears to stabilize after about 30 min. Hence there is little difference

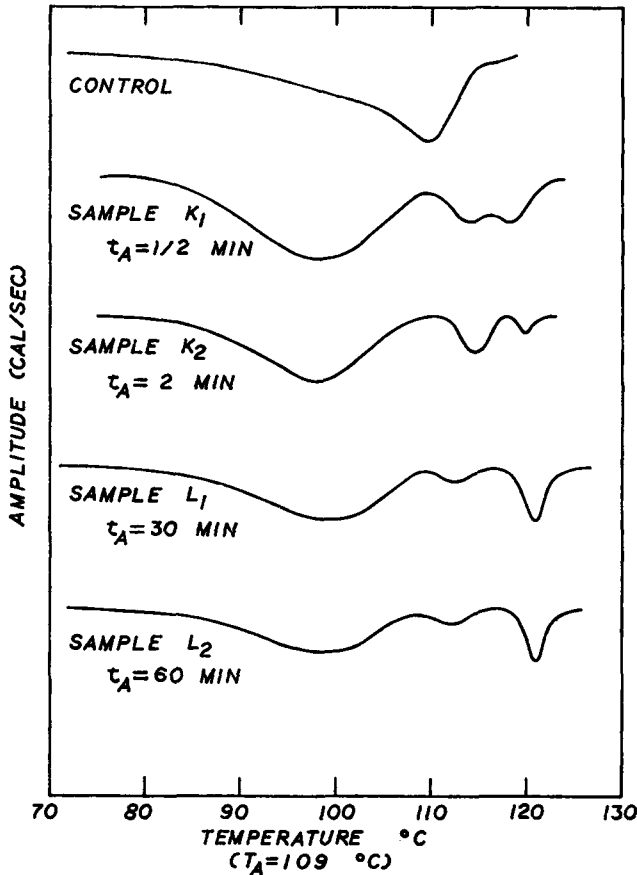


Fig. 6. DSC scans of polypropylene fraction, $\bar{M}_n = 1260$. Samples K₁, K₂, L₁, and L₂ after annealing at 109°C for times indicated.

between the DSC thermograms for the sample L₁ annealed 30 min., and sample L₂, annealed 60 min. For very short times of anneal, of the order of 2 min or so, the high temperature peak is present but is reduced in magnitude, while the intermediate peak is larger. The longer the time of anneal, the greater is the improvement in stability and perfection, especially of that material which was not melted at the anneal temperature.

To investigate the effect of successive anneals at steadily increasing series of temperatures, two additional samples of this fraction were studied. One sample, M, was annealed for 15 min at each of several temperatures, 5°C apart, ranging from 85°C to 105°C; the second sample, N, was annealed for 3 min at successive temperatures 5°C apart ranging from 80°C to 110°C. The annealings were carried out in the DSC instrument and the specimens were not subsequently cooled after each anneal. The results of the DSC runs on these two samples are shown in Figure 7 and in Table I. The principal effect of the successive anneals at steadily higher temperatures

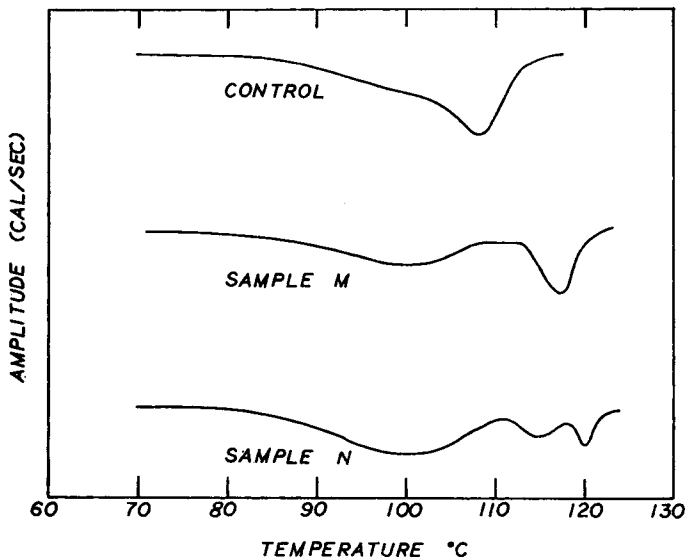


Fig. 7. DSC scans of polypropylene fraction, $\bar{M}_n = 1260$. Samples M and N after annealing at a series of successively increasing temperatures as indicated in Table I.

is to increase the perfection and stability of that portion of the sample that would ordinarily not be melted at the final anneal temperature. Thus with sample M with final anneal temperature at 105°C , the melting temperature is raised from 109°C for the control sample to 117°C . For sample N, with the final anneal temperature of 110°C , two higher melting peaks are present, one centered at 115°C and another at 120°C .

Molecular Weight Fraction with $\bar{M}_n = 1880$

Despite the fact that x-ray diffraction indicates that this sample contains approximately equivalent amounts of both the monoclinic α and the triclinic γ crystalline phases, the DSC melting endotherm of the powder, or of a control sample crystallized from the melt by cooling at $20^\circ\text{C}/\text{min}$, is but a single peak. This would appear to indicate that there is little difference between the melting temperature of the triclinic γ phase and the melting temperature of the monoclinic α phase, provided both phases have been crystallized from the same molecular weight fraction. Although the γ phase has been reported to have melting temperatures ranging from 125°C to 150°C ⁸ and the α phase is generally considered to melt at 165°C or above, this is because the T_m of the α phase is usually determined from whole polymer, while that of the γ phase is generally obtained from crystals grown from low molecular weight fractions.

The x-ray diffraction scans have been taken both on the powder and on a control sample prepared as indicated in Table II. Both scans are exhibited in Figure 2. Although there are some small changes between the two

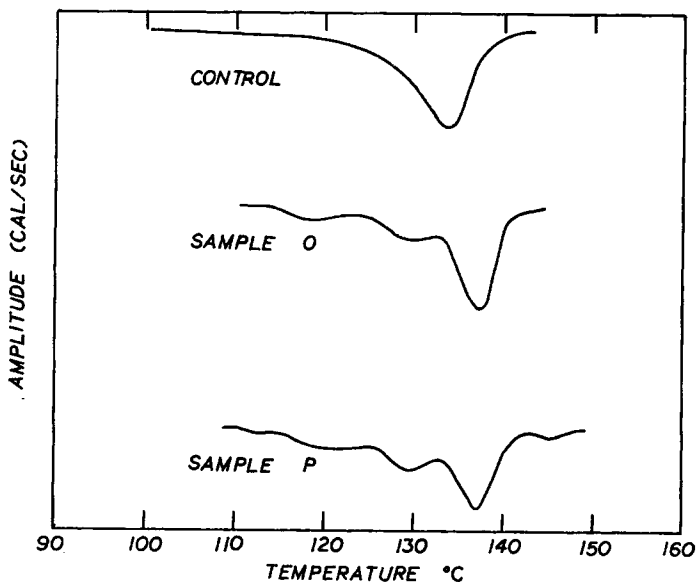


Fig. 8. DSC scans of polypropylene fraction, $\bar{M}_n = 1880$. Samples O and P after annealing at a series of successively decreasing temperatures as indicated in Table II.

scans, the results indicate that both samples contain a mixture of the monoclinic and triclinic phases.

The effect on the sample of a thermal treatment involving a series of anneals at steadily decreasing temperatures is shown in Figure 8 for two samples, designated O and P. Both samples were given four successive anneals at temperatures, respectively, of 135°C, 125°C, 115°C, and 105°C for the times listed in Table II. The only difference in treatment between samples O and P is that P has been annealed three times as long at the highest and lowest temperatures.

The results show that three distinct DSC peaks occur for sample O and these are located about 3°C above the temperature of the first three anneals. Sample P gives five separate peaks, the above three plus a small peak near 112°C and another small peak near 145°C. The separate anneals have apparently resulted in a discrete bunching of crystalline perfections with the average melting point of the discrete bunches usually falling a few degrees above the temperature at which each anneal occurred. However, as was found also for the sample of $\bar{M}_n = 1260$, there is a small high melting DSC peak located about 11°C above that of the control sample. The size of the peak is dependent upon anneal time. For small anneal times it may not even appear. For anneal times of 30 min or more, it is clearly present. It should be noted that a similar phenomenon occurs in whole polymer¹ as well.

Further information concerning the effect of time of anneal for this fraction is given in Figure 9, where DSC scans are shown and compared

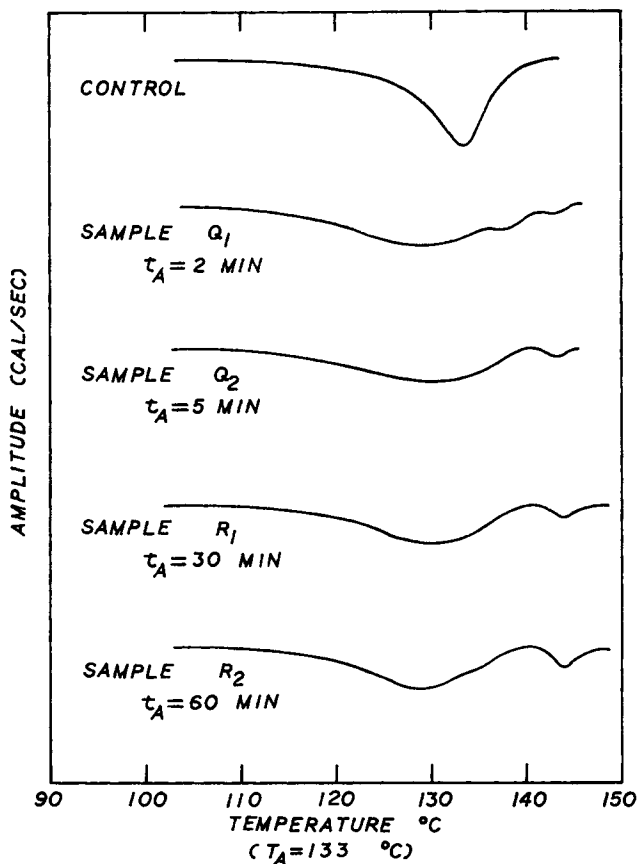


Fig. 9. DSC scans of polypropylene fraction, $\bar{M}_n = 1880$. Samples Q₁, Q₂, R₁, and R₂ after annealing at 133°C for times indicated.

with that of the control sample, and in Table II. Four samples of this fraction were annealed at 133°C. Sample Q₁ and Q₂ were held at this temperature for 2 min and 5 min, respectively, and samples R₁ and R₂ for 30 min and 60 min, respectively. The resulting thermograms indicate that the annealing treatment has resulted in production of a double peak, with the lower-temperature peak falling a few degrees below that of the control sample and the higher-temperature peak lying about 10°C above that of the control sample. The high-temperature peak tends to increase in size with anneal time.

Based on previous studies of whole polymer,¹ the treatment given would be expected to give rise to a double peak. The reason is that that part of the sample which is not melted at the anneal temperature has acquired sufficient thermal mobility to improve its molecular packing and to effectively increase its "crystallite" size, while the melted portion of the sample has recrystallized upon cooling with a somewhat larger concen-

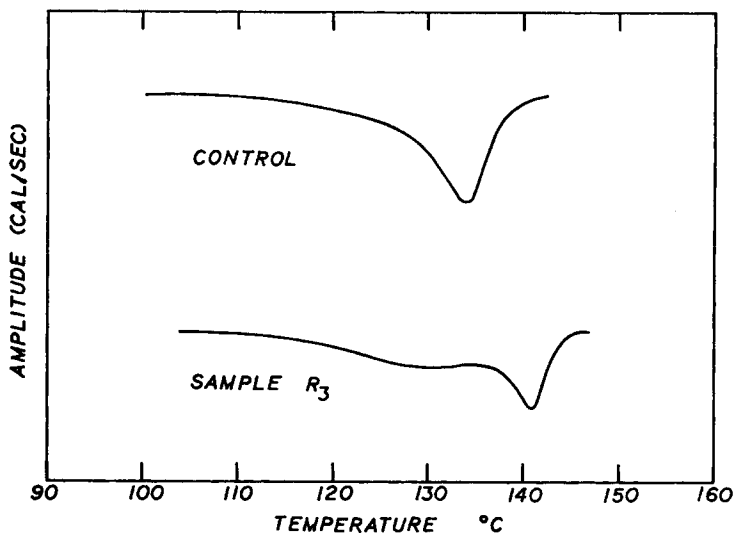


Fig. 10. DSC scan of polypropylene fraction, $\bar{M}_n = 1880$. Sample R3 after annealing at a series of successively increasing temperatures as indicated in Table II.

tration of vacancies and defects. It is this latter effect which accounts for the lower temperature location of the main fusion peak. Thus, though the final melting temperature is higher as a result of the thermal treatment, the overall degree of crystallinity is probably lower as a result of the increased vacancy concentration. Measurement of areas under the thermograms of the annealed and the control samples bears this out, as they appear to be about 10% less for sample Q1 and 17% less for sample R2.

The effect of a series of anneals taken at successively increasing temperatures from 110°C to 130°C in 5°C steps is shown for sample R3 of this fraction in Figure 10 and Table II. As for the previous low molecular weight fraction, this type of treatment also results in a double peak, but the principal effect is to raise the melting temperature from 134°C for the control sample to about 141°C for the treated sample. However, once again, although the final melting temperature is raised, indicating that recrystallization has resulted in production of some better crystals with greater stability and perfection, measurements of areas indicate that the heat of fusion of the treated sample is actually somewhat reduced as compared to that for the control sample.

Molecular Weight Fraction with $\bar{M}_n = 3800$

As noted earlier, the x-ray diffraction scan of the powder sample shows the fraction to have crystallized entirely in the α phase. For the control sample of this fraction, given the treatment specified in Table III, the x-ray scan (lower graph, Fig. 3) shows that the structure is still predominantly α and that a slight trace of γ is present. The treatment given to the control sample, viz., 3 min at 165°C followed by a 40°C/min cooling,

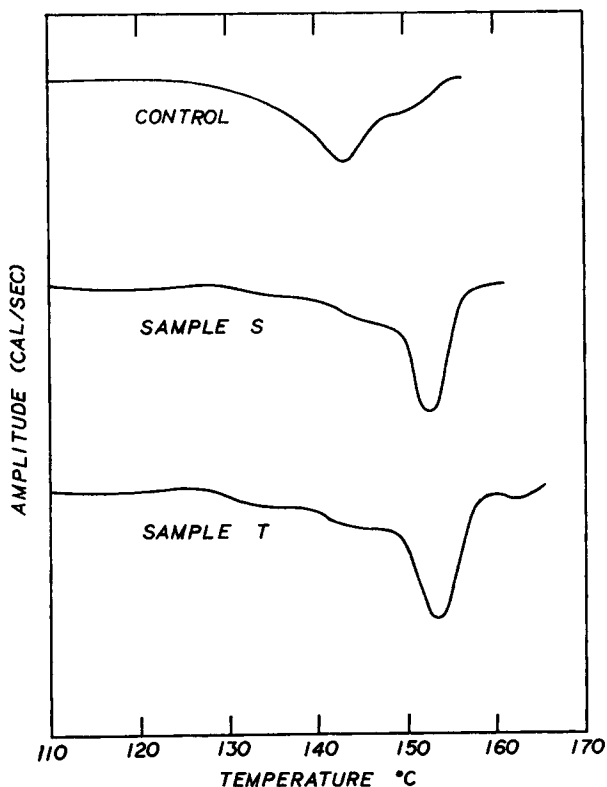


Fig. 11. DSC scans of polypropylene fraction, $\bar{M}_n = 3800$. Samples S and T after annealing at a series of successively decreasing temperatures as indicated in Table III.

also has a rather marked effect on the DSC thermogram. Tests run on the powder give a main melting peak at 151.5°C with a smaller premelting shoulder at 140°C. The control sample, however, after receiving the treatment mentioned, shows the main peak at 144.5°C followed by a smaller post-melting shoulder located at 150°C or so. Because of the fast cooling, it is to be expected that the control sample would have a lower principal melting point and the 7°C shift is in line with previous studies on whole polymer.¹ It is interesting to note that tests carried out on polyethylene fractions also show marked differences between one fraction and another.¹⁴

Figure 11 and Table III show the results obtained after a series of successive anneals at steadily lower temperatures. Two samples were tested: sample S, which was annealed for the times as indicated in Table III and at four temperatures beginning at 150°C and decreasing in 10°C intervals, and sample T, which was given a similar treatment except that the starting anneal temperature was 148°C and the times of anneal were somewhat increased. For sample S, Figure 11 shows that the four anneals have resulted in four separate DSC peaks. For sample T, there are five

peaks, the first four being similar to those of sample S but with a new small high-temperature peak appearing at 162°C, some 14°C above the annealing temperature.

Thus the general results for this fraction are similar to those obtained on the lower molecular weight fraction. The nature of the crystal structure as such does not appear to have a noticeable effect on the thermal behavior

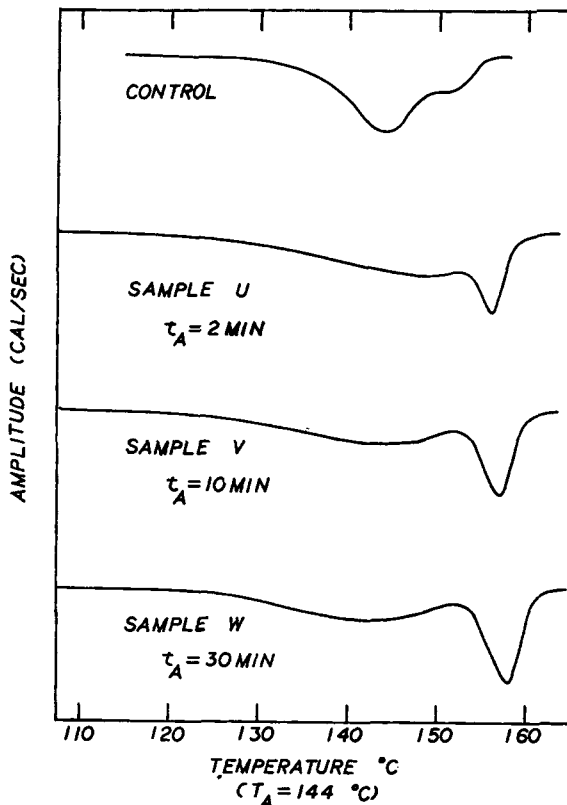


Fig. 12. DSC scans of polypropylene fraction, $\bar{M}_n = 3800$. Samples U, V, and W after annealing at 144°C for times indicated.

as the 3800 \bar{M}_n fraction is predominantly α and the 1260 \bar{M}_n fraction is predominantly γ .

The specific effects of time of anneal for a given anneal temperature, viz., 144°C, are shown in Figure 12 and Table III. DSC scans are shown for three specimens: sample U, annealed for 2 min, sample V, annealed for 10 min, and sample W, annealed for 30 min. In each case there are two peaks, and the difference between these two peaks increases with time of anneal. The higher temperature peak is about 12°C higher than the main peak of the control sample and, in this instance, increases in both relative size and peak temperature as annealing time increases. Thus,

whether the crystal structure is α or γ , long-time anneals at high temperature raise the final melting point by approximately the same amount. For the present sample, annealing at the peak temperature has not apparently introduced significant amounts of vacancies, as areas under the curves for the annealed sample are only 1-2% less than those of the control sample. This may be a result of the fact that the control sample in this case has been crystallized at a fast rate of cooling ($\sim 40^\circ\text{C}/\text{min}$) and hence already contains more disordered regions and less crystallinity than the original powder. Slower rates of cooling would unquestionably lead to higher thermal stability for the control sample and probably a more uniform and symmetrical DSC fusion peak. However, the slower rates were purposely not utilized as, under these conditions, some of the material crystallizes in the triclinic phase.

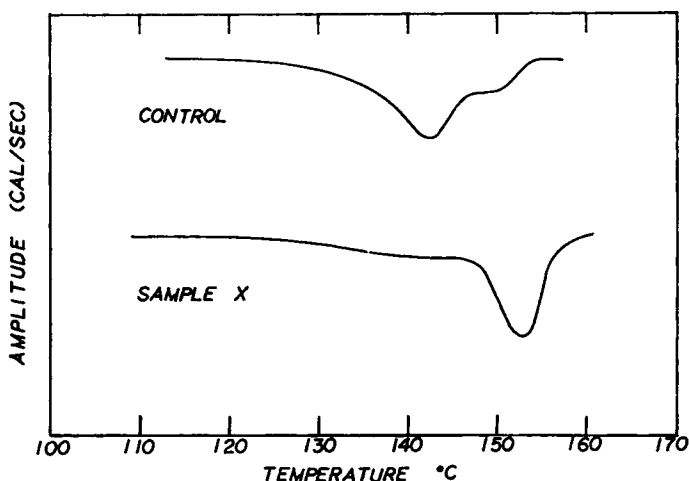


Fig. 13. DSC scan of polypropylene fraction, $\bar{M}_n = 3800$. Sample X after annealing at a series of successively increasing temperatures as indicated in Table III.

The effect of a series of thermal anneals carried out at steadily increasing temperatures, starting at 120°C and proceeding at 5°C intervals to 140°C , was also investigated for a control specimen, X, of $\bar{M}_n = 3800$. The results for sample X are given in Figure 13. The most pronounced change is a shift of the main peak from about 143°C to about 153°C . A somewhat similar shift was found also for sample M, subjected to a comparable five-stage annealing treatment. However, for sample M the area under the thermogram was reduced about 15%, while for sample X it was increased by the treatment by about 1%. It is thought that this difference is not related to the different crystalline form of samples M and X but rather to the fact already mentioned, that X was initially crystallized during a rapid cooling and hence was not in so stable a state as sample M, which was initially crystallized at a cooling rate of only $5^\circ\text{C}/\text{min}$.

CONCLUSIONS

It is usually considered that multiple DTA or DSC endothermic peaks may arise as a result of the presence of different fold periods in lamellar crystals, as a result of the presence of several different crystal modifications, or as the result of a segregation of molecular weights.

The present investigation has shown that even when none of these factors is present multiple DSC peaks can be produced by variation of past thermal history. For a given thermal history, rather similar effects are obtained both for bulk polymer with a wide molecular weight distribution and for low molecular weight fractions with a narrow molecular weight distribution. Rather similar effects have also been noted for one fraction crystallized in the α modification, one crystallized in the γ modification, and one containing a combination of both the monoclinic and triclinic types.

Regardless of whether the sample is a fraction with a molecular weight too small to show folding or a bulk sample of whole polymer, annealing at a high temperature close to the peak DSC temperature will result in production of a double or multiple peak thermogram with the upper peak located some 8–12°C above the original peak temperature, and with the area under the peak increasing with annealing time. Successive annealings at selected decreasing temperatures result in multiple DSC peaks both in whole polymer and in low molecular weight fractions and indicate that a segregation or bunching of crystallites of different degrees of perfection has occurred. This cannot, however, be due simply to the presence of crystals of discrete step heights, as the fractions studied were too small to show folding.

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