Study of Polypropylene Annealed at a Temperature near Its Melting Point

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Synopsis

Dynamic mechanical properties as determined by a torsion pendulum were used to study the effect on the crystalline structure of polypropylene of annealing at a temperature very near to its melting point. Crystallinity values as determined by both x-ray techniques and density measurements were reported for the specimens used in this study. Differential thermal analysis was used to show the differences in melting behavior of annealed and unannealed polypropylene. It was found that, although crystallinity may increase slightly, the major effect of annealing polypropylene is an increase in the size and/or perfection of the resulting crystallites. A damping peak not normally found for polypropylene was present at −50°C. in the damping curves for those specimens annealed in silicone oil without protective wrappings. This peak was found to be due to the freezing of the absorbed silicone oil, present in the specimen as small droplets.

INTRODUCTION

The crystallization of polypropylene, together with crystallite size, lamellae thickness, spherulitic growth, and structure–property relationships, has been the subject of many studies and reviews.[1-15] In these studies x-ray measurements, infrared and nuclear magnetic resonance spectroscopy, differential thermal analysis, density measurements, hydrocarbon solubility, dilatometry, kinetic studies, optical studies, and dynamic mechanical properties have been used to elucidate the crystalline structure of polypropylene.

In a previous paper,[16] it was shown that under special circumstances an oriented polypropylene specimen could be heated at a temperature very close to its melting point without the occurrence of any retraction of the specimen. It was suggested that the increase in the size of the crystallites was responsible for the changes in retraction behavior.

It was the purpose of this study to investigate the changes in the crystalline structure of polypropylene as shown by the effects on the dynamic mechanical properties brought about by annealing polypropylene at a temperature near its melting point.

ÉXPERIMENTAL

Specimen Preparation

Hercules Pro-fax 6511E polypropylene was compression-molded into thin sheets about 15 mil thick, with the use of a molding temperature of 400°F. and a platen pressure of 400 psi. All specimens used in this study were cut from these sheets.

With the exception of the control specimen CA, all specimens were annealed in a constant temperature bath (±0.2°C.) according to one of several different time–temperature schedules. The annealing schedule for each specimen is discussed in the next section. Two different bath media were used in this study: Dow Corning Silicone Fluid 710 and Wood's metal. Except where specified otherwise, all specimens were wrapped and sealed in aluminum foil to eliminate the possibility of contamination by the bath liquid. The wrapped specimens were held in a special fixture which prevented any distortion of the specimens. For one experiment, a glass cell, which could be evacuated and filled with nitrogen, was used to hold the specimen during the annealing process.

Density Measurements

The densities reported in this paper were measured by using a density gradient tube of diethylene glycol and isopropanol at 23°C., as described by Tung and Taylor.[17]

Apparatus for the Dynamic Mechanical Measurements

The apparatus used to obtain the dynamic mechanical characterizations was a torsion pendulum, previously described.[18]

RESULTS AND DISCUSSION

The main portion of this study is concerned with the changes in the dynamic mechanical properties of polypropylene after it had been annealed at a temperature near its melting point. In order to form a basis for a comparison of the experimental results, the dynamic mechanical properties were determined for an unannealed specimen, CA. The modulus and damping curves for specimen CA are given in Figure 1.

The damping curve shows the maximum associated with molecular mobility in the disordered or "amorphous" regions at +1°C. and that associated with molecular mobility in the ordered or crystalline regions at +73°C. The first mentioned maximum is related to the glass transition; the latter has been called the "crystal disordering transition."[19] The low, broad secondary transition in the −100 to −50°C. region is presumed to be associated with the hindered mobility of short chain segments in the disordered regions.

The density determined for specimen CA was 0.9043 g./cc.; the relative crystallinity determined by x-ray techniques was 60%. Although the
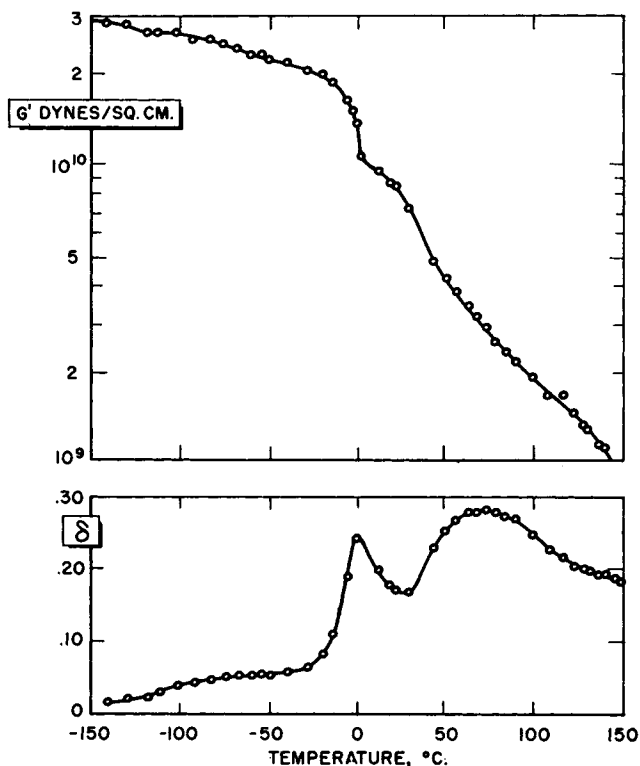
Fig. 1. Dynamic modulus and damping curves for an unannealed polypropylene specimen, CA, showing experimental points.

per cent crystallinity based on x-ray measurements agrees within 0.5% with the value based on density measurements[20] for the unannealed specimen, the values obtained for strongly annealed specimens show significant disagreement.   The discrepancies in the crystallinity values based on density measurements could be due, at least partially, to the formation of voids[21] concomitant with the growth of larger and more nearly perfect crystallites; the discrepancies in values based on x-ray measurements are due to increases in crystallite orientation.   Crystallinity values based on density measurements may also be in error due to the presence of material having near-range order resulting from an intermediate degree of chain packing which could affect the density value without affecting the crystalline maxima in the x-ray diffraction pattern.[2]

The first two specimens were annealed, without protective wrappers, in a silicone oil bath which had been preheated to a temperature of 150°C., heated to 168°C. at a constant rate over a period of 40 min., and held for 1 hr. at 168°C.   At the end of this period, the heaters were turned off, and one of the specimens, SA, was removed from the bath and allowed to cool to room temperature under ambient conditions; the other, SB, remained in the bath until the bath liquid cooled to room temperature.
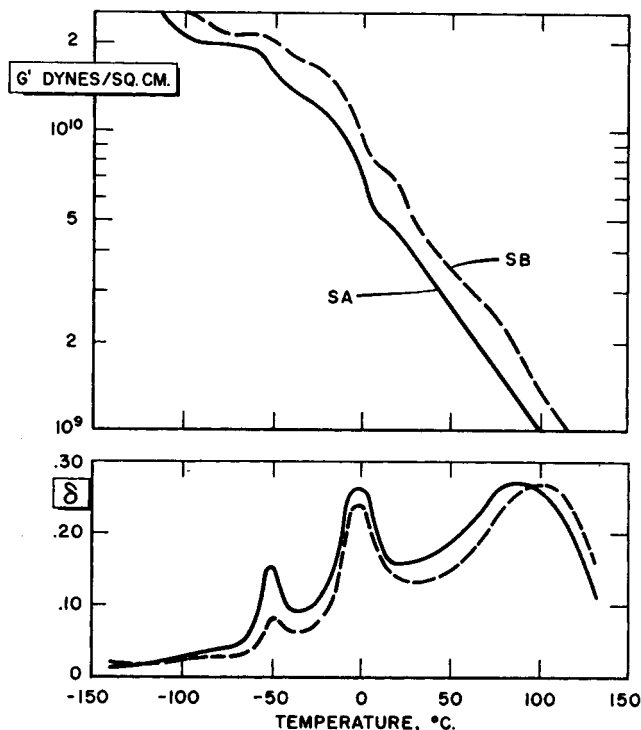
Fig. 2. Dynamic modulus and damping curves for polypropylene specimens annealed in a silicone oil bath heated from 150 to 168°C. in 40 min.: (SA) 1 hr. at 168°C. with ambient cooling; (SB) 1 hr. at 168°C. with slow oil cooling.

The densities were determined to be 0.9357 g./cc. for the former specimen and 0.9250 g./cc. for the latter. Using the density–crystallinity curve for polypropylene, one finds that the corresponding crystallinities are 100 and 86%, respectively. Disregarding the fact that the original polymer was known to contain a significant amount of noncrystallizable polymer, thus definitely ruling out the possibility of a specimen being 100% crystalline, one would have expected that, if there were a difference in crystallinity, the more slowly cooled specimen should have been more crystalline than the rapidly cooled specimen. The fact that the reverse was found to be true led to the conclusion that the polypropylene specimen had absorbed significant amounts of the silicone oil. Since the air-cooled specimen apparently contained more silicone oil than the oil-cooled specimen, a further conclusion was reached that the oil was being squeezed out of the polymer as the disordered regions became more ordered. Optical microscopy showed that the silicone oil was present throughout the specimen in the form of small droplets, 5–10 μ in diameter.

The dynamic mechanical curves were obtained for these two specimens and are given in Figure 2. The damping curves for the two specimens show that the crystalline peak for the oil-cooled specimen, SB, occurs at a higher

temperature than that for the air-cooled specimen, SA, indicative of larger and/or more nearly perfectly formed crystallites.   The 15°C. difference in the temperatures of the two peaks cannot be due to the difference in oscillation frequencies (0.34 cycle/sec. for SA and 0.29 cycle/sec. for SB) at the peaks, since the high-temperature peak was obtained at a lower frequency than the low-temperature peak.   Indeed, it is doubtful that the small difference in frequencies could result in a measurable difference in peak temperatures.

The glass transition peaks are located at essentially the same temperature as that found for the control specimen, implying that the silicone oil is not acting as a plasticizer.   The broad, secondary maxima in the −100 to −50°C. regions are both lower than that for the control specimen, with the maximum for the oil-cooled specimen lower than that for the air-cooled specimen.   This information suggests that the height of this peak is governed by the amount of crystallized material in the specimen.

A well-defined fourth peak, not found in the damping curve for the control specimen, is apparent in the damping curves for both specimens SA and SB at a temperature of −50°C.   The question immediately arises as to the origin of this peak.   The obvious answer is that it is due to the heat treatment and/or the absorbed silicone oil.

The fact that the height of the −50°C. peak in the curve for the oil-cooled specimen is lower than that for the air-cooled specimen is another indication that, as the crystallites grow larger and become more nearly perfectly formed, the bath liquid is squeezed out of the polymer.   This result would seem to confirm the information derived from the density measurements and implies that the absorption had taken place in the less ordered regions of the polypropylene.

Specific volume measurements made on the silicone oil by using a dilatometer over a temperature range of −60 to +25°C. showed that there was a break in the specific volume–temperature curve at approximately −40°C. The silicone oil was completely solidified at a temperature in the vicinity of −50°C.   This transition could be responsible for the −50°C. peak.

In order to see whether the −50°C. peak was due to the heat treatment alone, a specimen, SC, was annealed, by using the same schedule as that for specimen SB, in a specially constructed glass cell containing a nitrogen atmosphere.   The results were similar to those shown in Figure 2, except that there was no indication of a peak at −50°C.   This fact ruled out the possibility that the annealing process was solely responsible for the −50°C. peak.

In order to see whether the −50°C. peak was due to the absorbed bath liquid, silicone oil was blended, at the 10% level, into polypropylene in a Meili Mixer at a temperature of 225°C. for a period of 7 min.   The dynamic curves for a specimen, SD, molded from this material and for a specimen, CB, molded from a milled blank are given in Figure 3.

The −50°C. peak, although not completely separated from the glass transition peak at 0°C., is apparent in the damping curve for the blended
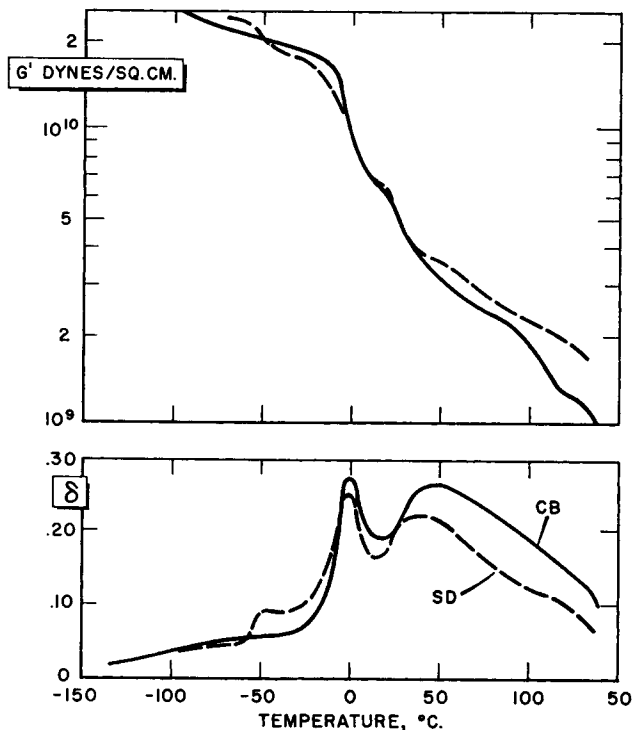
Fig. 3. Dynamic modulus and damping curves for two polypropylene specimens: (CB) a milled blank; (SD) a 90/10 polypropylene–DC710 silicone oil blend.

specimen and is absent in the damping curve for the milled blank. This fact indicates that the absorbed silicone oil is at least partially responsible for the −50°C. peak.

The crystalline peak, located at 73°C. for the control specimen, is found at 46°C. in the damping curve for the milled blank and at 38°C. for the blend. This suggests the possibility that the shearing action and/or thermal history have some effect on the ability of the chains to pack sufficiently well so as to be seen as crystalline material by x-ray techniques. The relative crystallinities of the milled blank and blend were determined to be 55 and 57%, respectively, although the densities were found to be 0.9054 and 0.9234 g./cc., respectively.

Further studies of the effect of silicone oil on the crystallinity of polypropylene will be the subject of a future publication.

Because of the influence that the annealing temperature has on the final crystallite structure which, in turn, has a decided effect on the dynamic mechanical properties, five specimens, cut from the same molded sheet of polypropylene, were annealed at five different temperatures as follows. All five specimens were individually wrapped and sealed in aluminum foil and immersed in a Wood's metal bath which had been preheated to a temperature of 150°C. After 20 min. at 150°C., one specimen, WA, was re-
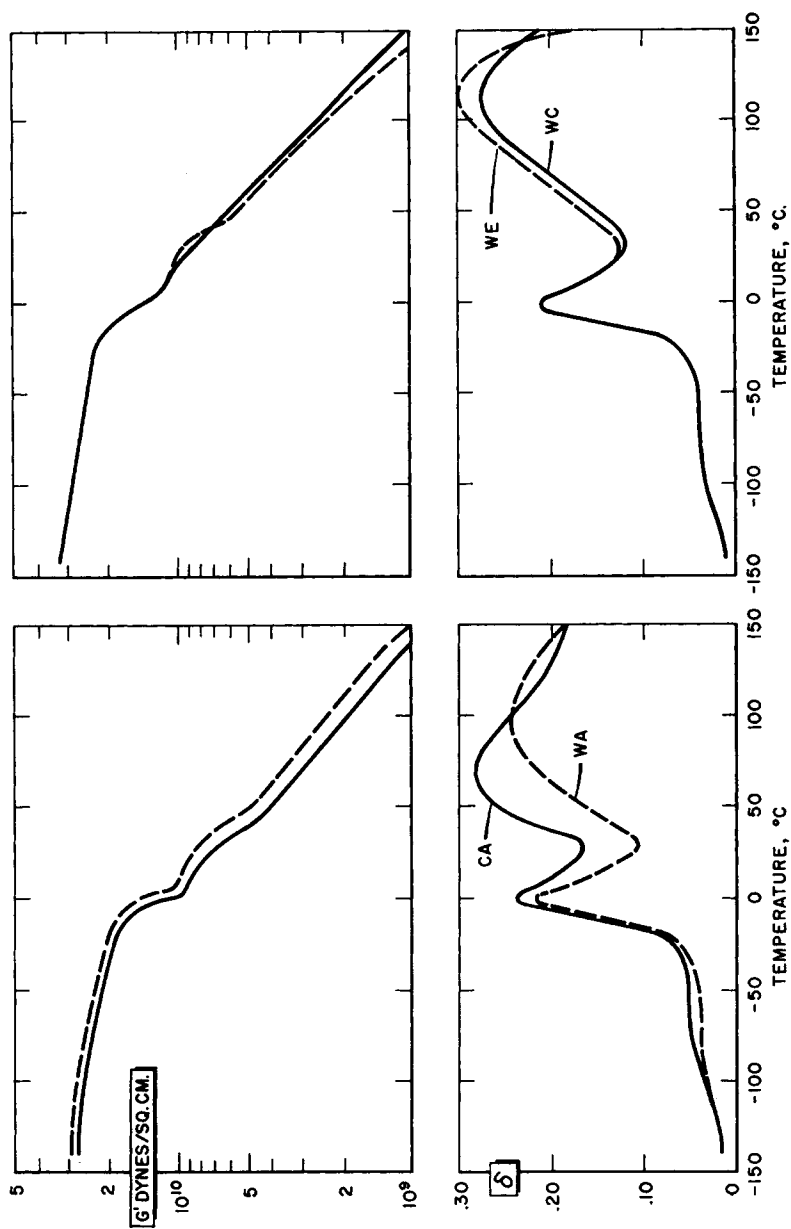
Fig. 4. Dynamic modulus and damping curves for four polypropylene specimens: (CA) unannealed specimen; (WA) annealed in a Wood's metal bath at 150°C.; (WC) annealed in a Wood's metal bath at 160°C.; (WE) annealed in a Wood's metal bath at 168°C.

moved. The temperature was then raised to 155°C. over a period of 20 min.; after 20 min. at 155°C., one specimen, WB, was removed. The temperature was then raised to 160°C. over a period of 20 min.; after 20 min. at 160°C., one specimen, WC, was removed. The temperature was then raised to 165°C. over a period of 20 min.; after 20 min. at 165°C., one specimen, WD, was removed. The temperature was then raised to 168°C. over a period of 20 min.; after 20 min. at 168°C., the last specimen, WE, was removed. All specimens were allowed to cool to room temperature under ambient conditions after removal from the bath.

The dynamic curves for specimens WA, WC, and WE are given in Figures 4a and 4b, together with the curves for the control specimen, CA, for comparison. The dynamic curves for specimens WB and WD follow the trend set by WA, WC, and WE, but are omitted from Figure 4 for the sake of clarity. The secondary transition in the region −100 to −50°C. decreases in height after the first annealing step and remains constant for the following annealing steps. The glass transition peak decreases in height and shifts to slightly lower temperatures, probably due to the very large shift of the crystalline peak. After annealing at 150°C., the crystalline peak decreases in height, gets broader, and shifts from 73 to 101°C. After each of the successively more severe annealing steps, the crystalline peak increases in height and shifts to higher temperatures.

The relative crystallinities determined by x-ray techniques for the control specimen CA and for the series WA, WB, WC, WD, and WE are 60, 56, 62, 65, 54, and 55% respectively; the densities determined by the density gradient method are 0.9043, 0.9110, 0.9128, 0.9145, 0.9094, and 0.9100 g./cc., respectively. The first three specimens in the W series are ranked the same by both x-ray and density measurements, although the crystallinity values determined by x-ray techniques are consistently lower than those determined by density measurements. The crystallinity values reported here do not reflect a very large increase in crystalline content, nor do the changes in modulus values associated with the crystalline peaks in the damping curves suggest any large increase in crystallinity. The crystalline maxima in the x-ray diffraction patterns for WA, WB, and WC become sharper and higher as the annealing temperature is increased, indicating that the change taking place is involved with the growth of larger and/or more nearly perfectly formed crystallites. The x-ray crystallinity values for specimens WD and WE are out of line, due to the effects of a significant amount of crystallite orientation, noticeable in the diffraction patterns, as a result of annealing at a temperature so very near the melting temperature of polypropylene.

The density values for WD and WE are also out of line, possibly due to the presence of large voids resulting from the considerable amount of chain movement that must have occurred during the growth process of large crystallites. The ever present possibility of significant amounts of material having near-range order, which affects the density measurements but not

the x-ray measurements, would also account for all of the density-determined crystallinity values being too high.

The trend concerned with increased heights and temperatures for the crystalline peaks in the damping curves for WA, WB, and WC is continued for specimens WD and WE, again suggesting that the crystallites continue to increase in size and/or perfection with an increase in annealing temperature, even though the total crystalline content does not change appreciably. This conclusion is in agreement with that arrived at by Farrow.[5]

Differential Thermal Analysis

Differential thermal analysis experiments were carried out by Donald and co-workers,[22] employing a method previously described, on a sample of polypropylene which had been annealed by the same schedule as for specimen SB (maximum temperature 168°C.). The resulting curve is given in Figure 5.
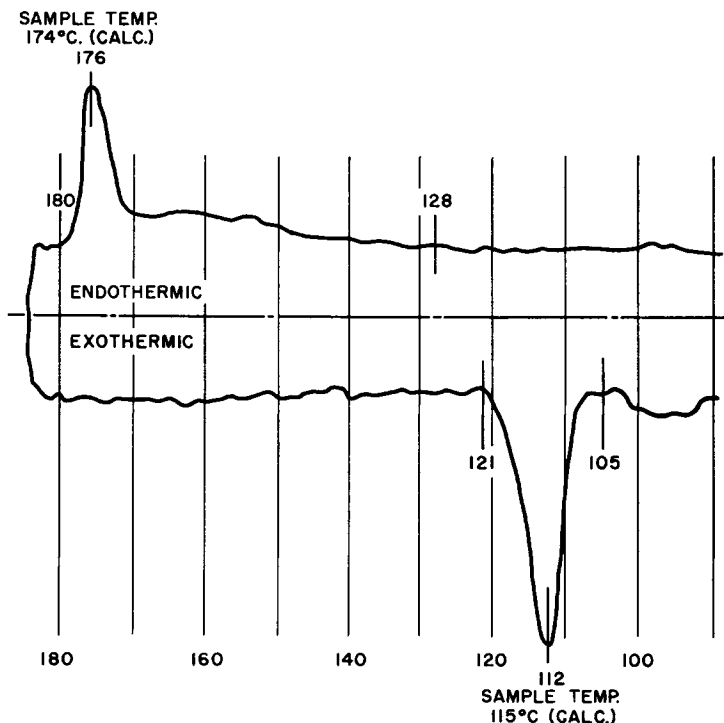
Fig. 5. DTA curve for annealed polypropylene specimen SB.

The heating portion of the DTA curve for the annealed polypropylene sample exhibits a narrow melting peak at 174°C. In the cooling portion of the curve, the normal, spontaneous crystallization peak occurs at 115°C. The same sample was then used for a second DTA run; the heating curve, given in Figure 6, shows a broad melting peak at a considerably lower
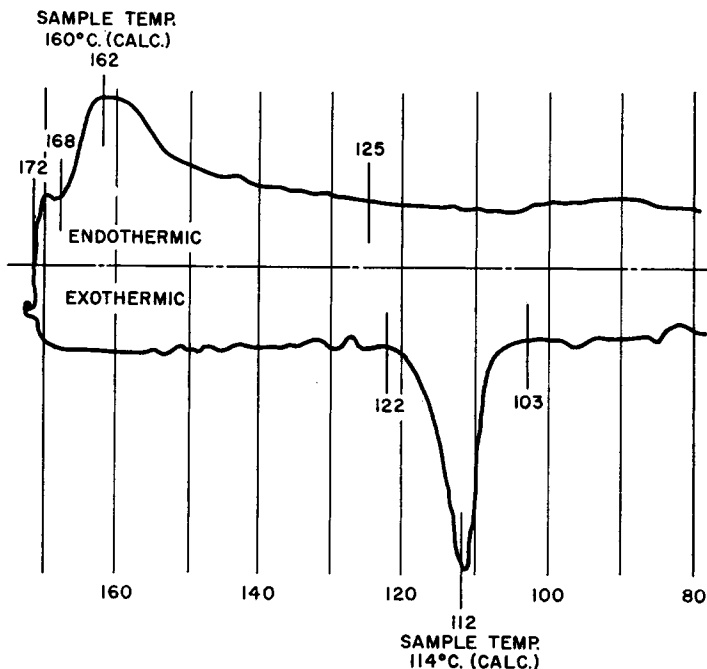
Fig. 6. DTA curve for repeated run of annealed polypropylene specimen SB.

temperature (162°C.), typical of many polypropylenes which have not been annealed at temperatures near their melting points.

An analysis of the two curves shows that the crystallinity of the original heat-treated sample is only slightly higher than that of the rerun sample and that about 50% of the crystallized material of the original heat-treated sample has a higher melting point than that of the rerun sample.

These data provide an additional indication that a careful heat treatment of polypropylene just below its melting point results in a better organization of the crystallizable portion into larger and/or more nearly perfect crystallites having a higher and more narrow melting range. However, after melting a polypropylene sample so treated, it behaves in a fashion typical of a nonheat-treated sample.

Mechanical Properties

The mechanical properties were determined for three specimens to see what effects were brought about by the small, measured change in crystallinity and the large, apparent change in crystallite size and/or perfection. The specimens used in this particular study were the blank specimen, CA, and two specimens heat treated in a Wood's metal bath. The first of the two latter specimens, WF, was heated from 150 to 168°C. in 1 hr.; the second specimen, WG, received the same heat treatment as WF, plus 1 hr. at 168°C. The properties are listed in Table I.

TABLE I
Mechanical Properties

Specimen	Density, g./cc.	Relative crystallinity by x-ray, %	ASTM properties, 73°F.					
			Tensile strength, psi	Elongation, %	Modulus, psi	Notched Izod strength, ft. lb./in.	Creep at 2000 psi, % (at 100 hr.)
CA	0.9043	60	5100	10	1.6×10^5	0.73	3.9
WF	.9172	60	5700	8.5	2.1×10^5	0.56	2.4
WG	.9171	62	5600	6	2.6×10^5	0.52	2.4

TABLE II
Summary of Data

Specimen	Annealing schedule	Bath medium	Density, g./cc.	Crystallinity by density, %	Relative crystallinity by x-ray, %
CA	—	—	0.9043	60	60
SA	150–168°C. in 40 min., 168°C. for 60 min.; air-cooled	Silicone oil	0.9357[a]	—	—
SB	150–168°C. in 40 min., 168°C. for 60 min.; oil-cooled	Silicone oil	0.9250[a]	—	—
SC	Same schedule as for SB	Nitrogen	—	—	—
SD	10% silicone oil blended with polypropylene at 225°C. for 7 min.	—	0.9234[a]	—	57
CB	Polypropylene blank milled at 225°C. for 7 min.	—	0.9054	61	55
WA	150°C. for 20 min.; air-cooled	Wood's metal	0.9110	68	56
WB	WA schedule, plus 150–155°C. in 20 min., 155°C. for 20 min.; air-cooled	Wood's metal	0.9128	70	62
WC	WB schedule, plus 155–160°C. in 20 min., 160°C. for 20 min.; air-cooled	Wood's metal	0.9145	72	65
WD	WC schedule, plus 160–165°C. in 20 min., 165°C. for 20 min.; air-cooled	Wood's metal	0.9094	65	54
WE	WD schedule, plus 165–168°C. in 20 min., 168°C. for 20 min.; air-cooled	Wood's metal	0.9100	66	55
WF	150–168°C. in 60 min.	Wood's metal	0.9172	76	60
WG	150–168°C. in 60 min., 168°C. for 60 min.	Wood's metal	0.9171	75	62

[a] High density values due to presence of absorbed silicone oil.

Here again we see a significant increase in density accompanied by little or no increase in crystallinity, implying again that the annealing process results principally in an increase in the size and perfection of crystallites rather than in an overall increase in crystallinity. The data given in Table I show that large changes in the amount of crystallinity in polypropylene are not necessary to produce large changes in mechanical properties.

A summary of the annealing schedules, densities, and crystallinities for all specimens is presented in Table II.

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Résumé

On a utilisé les propriétés mécaniques dynamiques déterminées par un pendule de torsion pour étudier l'influence sur la structure cristalline du polypropylène du recuit à une température très proche de son point de fusion. On donne les valeurs de la cristallinité déterminées par l'examen aux rayons-X et par des mesures de densité pour les échantillons utilisés dans cette étude. On a utilisé l'analyse thermique différentielle

pour montrer les différences dans le comportement à la fusion du polypropylène recuit et non-recuit.   On a trouvé que, bien que la cristallinité puisse augmenter légèrement, l'effet majeur du propylène non-recuit est une augmentation dans la taille et/ou de la perfection des cristallites qui en résultent.   Un pic d'amortissement que l'on ne trouve pas normalement pour le polypropylène existe à −50°C dans les courbes d'amortissement pour les échantillons recuits dans l'huile de silicone sans enroulements protecteurs. On a trouvé que ce pic est dû à la congélation de l'huile de silicone adsorbée, présenté dans l'échantillon sous forme de petites gouttelettes.

Zusammenfassung

Mit Hilfe eines Torsionspendels bestimmte dynamisch-mechanische Eigenschaften wurden zur Untersuchung des Einflusses einer Temperung bei einer Temperatur in der Nähe des Schmelzpunktes auf die kristalline Struktur von Polypropylen verwendet. Durch Röntgenverfahren und Dichtemessungen wurden für die in der vorliegenden Untersuchung verwendeten Proben Kristallinitätswerte bestimmt.   Der Unterschied im Schmelzverhalten von getempertem und nicht getempertem Polypropylen wurde durch Differentialthermoanalyse festgestellt.   Es zeigte sich, dass zwar die Kristallinität schwach zunehmen kann, dass jedoch der Haupteffekt einer Temperung von Polypropylen in einer Erhöhung der Grösse und/oder der Perfektion der gebildeten Kristallite besteht.   Ein bei Polypropylen normalerweise nicht vorhandenes Dämpfungsmaximum trat bei den in Siliconöl ohne Schutzumhüllung getemperten Proben in der Dämpfungskurve bei −50°C auf.   Dieses Maximum wurde durch Gefrieren des absorpbierten, in der Probe als kleine Tröpfchen verteilten Siliconöls verursacht.