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THERMAL ANALYSES OF POLYMERS

XIV. MULTIPLE MELTING PHENOMENA IN POLY(ETHYLENE TEREPHTHALATE)*

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ABSTRACT

The observation of multiple melting phenomena in poly(ethylene terephthalate) (PET) by DSC or DTA has been confirmed to arise from recrystallization by the changes in birefringence occurring in the thermal regime of the polymer. Isothermal birefringence changes illustrate the melting of crystallites around 230–248 °C, with the formation of more perfect and higher melting crystallites at temperatures of annealing above 248 °C. The formation of diethylene glycol residues in the PET during solid state polymerization may be a cause of the higher melting endotherm occurring at lower temperatures when annealed under vacuum.

INTRODUCTION

A number of reports have described the occurrence of multiple melting phenomena of certain semi-crystalline and isotactic polymers. These melting phenomena have been observed for the most part by differential thermal analysis or differential scanning calorimetry techniques, and can, in certain cases, be generated by the thermal history imparted to the polymer sample. Bell and coworkers[1,2] have shown that polyamides, polyethylene, polypropylene, poly(ethylene terephthalate) and isotactic polystyrene can show multiple melting phenomena, according to the thermal regime and history of the samples.

Mitsuishi and Ikeda[3] have shown that annealing for two hours at 238 °C caused an increase in the temperature of the endotherm accompanying fusion of poly(ethylene terephthalate) (PET), whereas annealing at 120 °C showed no change in the fusion endotherm near 260 °C. Values of n from the Avrami equation for annealing at 120 and 238 °C were 0.96 and 3.12, respectively, and they postulated fibrillar growth near 120 °C and spherulitic growth at 238 °C.

Wakelyn and Young[4] examined the crystallization of PET with X-ray and DSC techniques to show the variations that accompany crystallization in a sealed

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ampule versus that in a continuously pumped vacuum atmosphere. Those experiments carried out in a sealed ampule showed no increase in number average molecular weight with time of annealing, whereas the crystallinity (by DSC) increased substantially during that time. Pumping under a vacuum while crystallizing at 200 °C produced an increase in the number average molecular weight of two to three times the original molecular weight, with an accompanying smaller increase in crystallinity than that for the sample in the sealed ampule.

Bell and Murayama[5] have shown double melting behavior for both PET and Nylon 66 by both DTA and dynamic mechanical analyses. Their annealing conditions for the formation of Form I were to hold the amorphous sample of PET for 30 minutes at 110 °C, whereas the formation of Form II was carried out by holding the sample at 220 °C for 24 hours in a sealed vessel. The data of Wakelyn and Young[4] have shown that annealing in a sealed ampule produces a multiple peak fusion phenomenon, whereas a sample of PET which has been pumped under vacuum at 220 °C for 24 hours shows only a single fusion endotherm and a higher molecular weight.

Ikeda[6] postulated that the melting endotherm of Form I is a structure which is not initially present in the sample, but formed through annealing or recrystallization during the programmed heating of the DTA measurement. Form II endotherm was then considered a folded chain crystal structure initially present in the sample.

Nealy et al.[7] have concluded from DSC measurements that the Form I endotherm was due to a folded chain crystal structure and that possibly annealing occurred during the isothermal crystallization process for the formation of Form II crystals.

Roberts[8] has recently shown that annealing bulk crystallized PET resulted in the same type of rearrangements as those for single polymer crystals. At very rapid heating rates via DSC measurements, the melting behavior of PET was the opposite of that reported by Bell and Dumbleton[2]. After heating the annealed sample at a heating rate of 16 °C min^{-1} to 248 °C, Roberts found that holding the sample isothermally at 248 °C for only 5 minutes increased the peak area of the high melting crystalline form. His work indicated that the low melting crystalline form is converted to the high melting crystalline form, depending upon the rate of heating of the sample.

Holdsworth and Turner-Jones[9] have confirmed the results of Roberts[8] by DSC, and illustrated further that both density and crystallinity (X-ray) increased with annealing times at high temperatures. They concluded that only the use of DSC for determining morphological changes was dangerous. Bell and Sweet[10] have recently demonstrated that recrystallization in the DSC can occur for PET and Nylon 66.

For the most part, all of the information gathered on the multiple melting phenomena in polymers has been observed by either DTA or DSC. Since polymer crystals exhibit birefringent behavior during growth and fusion and since the technique of thermal depolarization analysis (TDA) has been used by some authors for the study of crystallinity and molecular ordering effects in polymers and other materials[11–13], much of the data reported herein is a manifestation of changes in birefringence as a function of temperature or time to illustrate the isothermal recrystallization of PET. TDA measurements have shown excellent correlation with fusion and recrystallization behavior by DTA, DSC and dilatometric techniques[15]. This report contains data illustrating the recrystallization of PET isothermally, which had only been demonstrated dynamically, as well as an explanation of the generation of a lower melting peak as the sample is thermally annealed under vacuum.

EXPERIMENTAL

1. Materials

Amorphous PET was prepared by casting a film on a cold drum immediately after extrusion. The PET of 3.5 and 8.5% diethylene glycol content were prepared by conventional melt polymerization techniques. PET (I) was prepared by annealing at 110°C for 30 minutes. PET (II) was prepared by heating at 224°C under a vacuum for 24 hours.

2. Methods

A. Density measurements

These measurements were carried out on a density gradient column using calcium nitrate solution as the suspending medium (see Table 1). Inherent viscosity measurements were determined in tetrachlorophenol (see Table 1). DTA and DSC measurements were carried out at a heating rate of 10°C min^{-1}.

TABLE 1

DENSITIES AND INHERENT VISCOSITIES OF MORPHOLOGICAL FORMS OF POLY(ETHYLENE TEREPHTHALATE)

Sample	*Density*	*Inh. viscosity*
Amorphous	1.3389	0.59
Form I	1.3432	0.59
Form II	1.4026	Insol.
3.5% DEG	1.3771	0.60
8.5% DEG	1.3899	0.31

B. Thermal depolarization analyses

Thermal depolarization analyses were carried out in the same manner as described previously[13–15]. Heating rates of 5°C min^{-1} were standard, and an interference filter with a maximum of 530 nm was used to approach monochromatic irradiation.

C. Isothermal TDA measurements

These were made with the use of the timebase X–Y recorder on the TDA instrument.

D. DTA measurements

DTA measurements were carried out on a DuPont 900 at a heating rate of 10°C min^{-1}.

RESULTS AND DISCUSSION

Recrystallization and fusion

Bell and Murayama[5] have reported that PET (I) crystals have a melting point of approximately 243 °C, whereas PET (II) has a melting range from 224 to 238 °C, depending upon the time of annealing at 220 °C. Temperatures of 256 °C were determined by differential scanning calorimetry for PET independent of its thermal history.

In Fig. 1 are shown the TDA responses for amorphous, PET (I) and PET (II). The extinction of polarized light in forming the isotropic liquid is the temperature of fusion. The temperature interval between the peak in the TDA scan and the point at which zero light level is attained is a consequence of both the heating rate and the rate at which the crystallites melt. The peak maxima for the amorphous, I and II PET materials are 268, 267, and 262 °C, respectively, whereas the isotropic fusion points, that is, the temperature at which no further depolarization occurs, are 273, 272, and 264 °C, respectively. Note also that as one converts from the amorphous to the

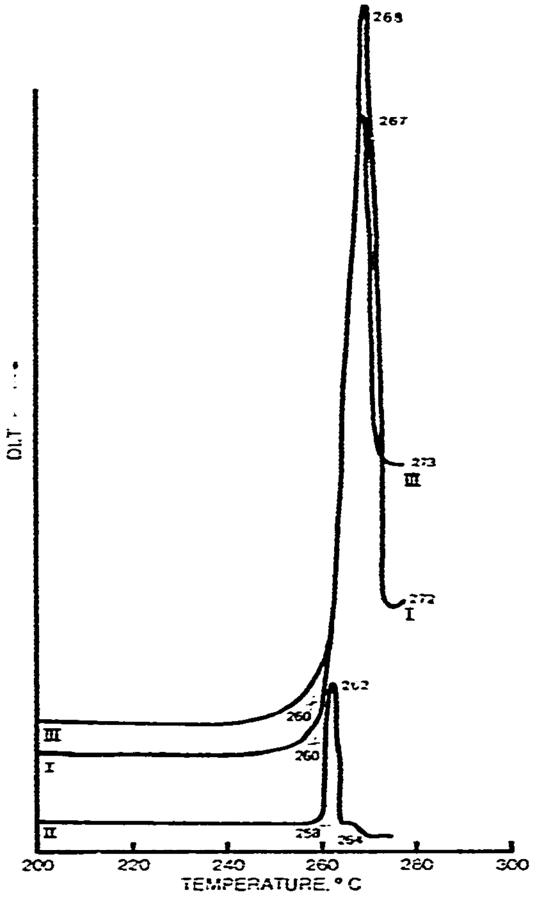


Fig. 1. TDA fusion response for amorphous (III), form I and form II PET.

crystalline PET, a knee forms on the trailing edge of the peak, increasing in magnitude with the crystallization time and temperature.

The peak response during the melting of PET results from spherulite growth, causing an increase in birefringence. The beginning of this recrystallization occurs at the DTA melt temperature. The fact that crystallizing PET under vacuum near 220°C causes the melting to occur at a lower temperature than crystallizing PET during the normal rate of heating is unexpected, but the reason for this will be treated later in this text. However, the onset of fusion (onset of increase in depolarized light transmission (DTA)) for PET in any case is the same as observed by DTA.

Isothermal TDA

Annealed poly(ethylene terephthalate)

In an attempt to follow the crystallization kinetics for annealed PET (110°C), an isothermal TDA run at 110°C illustrated that fusion occurred for the first 30–35 minutes, as shown by a decrease in birefringence in Fig. 2. After 30 minutes at 110°C, the light level begins to increase, showing the nucleation of the polymer.

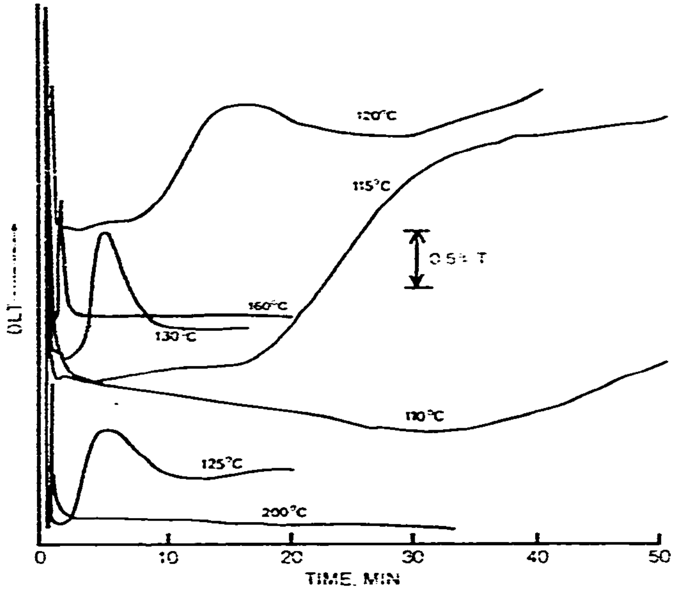


Fig. 2. Depolarized light transmission isotherms for amorphous PET.

Curve A would indicate that annealing at 110°C for 30 minutes tends to erase much of the lower melting structure[14]. The molecular order accompanying changes in the temperature range 50–85°C has been reported[14], showing that the level of low melting (110°C) molecular order can be raised as the PET sample is annealed in that temperature range. Isothermal annealing at higher temperatures shows both the primary and secondary crystallization stages. Hence in going from isothermal measurements at

115°C with an induction time of 16 minutes, to 120°C with an induction time of 8 minutes, to isothermal operation at 125°C with an induction time of 1 minute, we see two crystallization phenomena occurring. The induction time, i.e., time until the

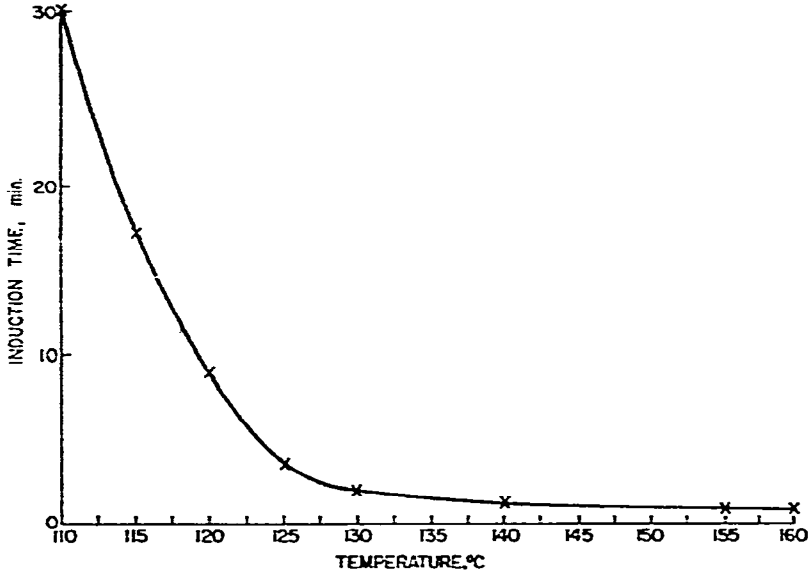


Fig. 3. Induction time for crystallization of PET vs. temperature.

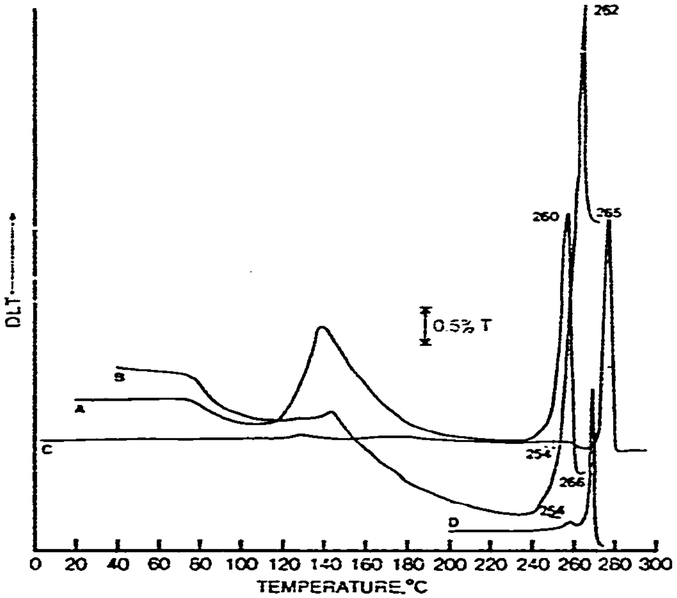


Fig. 4. TDA response after annealing PET for 30 minutes at (A) 110°C; (B) 120°C; (C) 140°C; (D) 200°C.

DLT begins to increase under isothermal conditions, is plotted against temperature in Fig. 3, illustrating the time necessary for crystallization to begin.

After annealing for 50 minutes at 110°C, the sample was transparent when removed from the instrument and quickly cooled. However, on annealing at 115°C for 40 minutes, or at 110°C for more than 90 minutes, the material was translucent when removed from the instrument, and the translucent character of the specimen occurred at the maximum in the time–depolarization curve at each of the indicated isothermal temperatures, up to and including 130°C (Fig. 2).

If, on the other hand, a dynamic scan is made after isothermal annealing, the curves such as those shown in Fig. 4 appear for annealing at 110, 120, 140, and 200°C for 30 minutes each. It is obvious from Fig. 4 that as the temperature of annealing is increased, the maximum fusion point of the annealed PET increases.

Crystallized poly(ethylene terephthalate)

Whereas Roberts[8] has shown the complementary change in area of two melting endotherms for PET from DSC, the recrystallization process which he describes can be easily demonstrated by DLT changes. The change in birefringence with annealing is clearly shown in Fig. 5 for amorphous PET at temperatures of 230, 240, 249, 250,

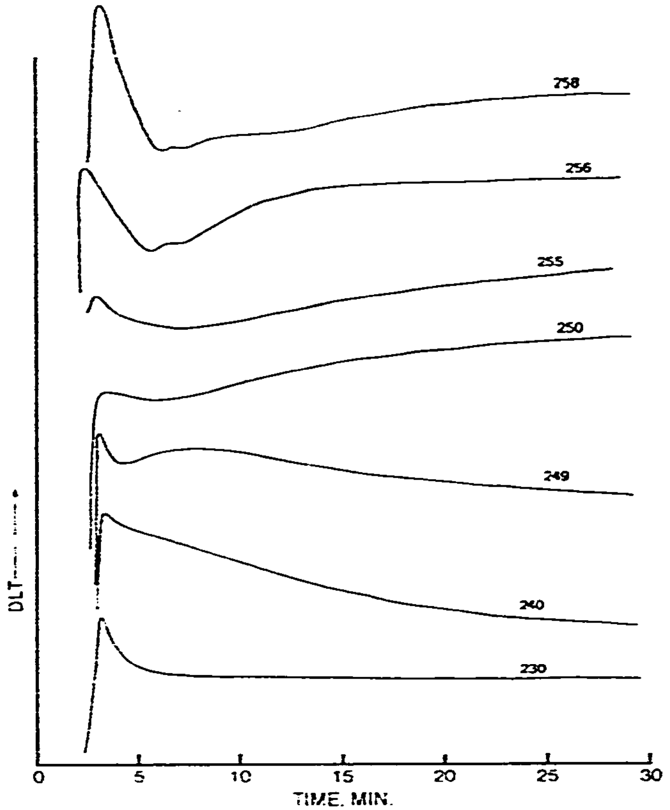
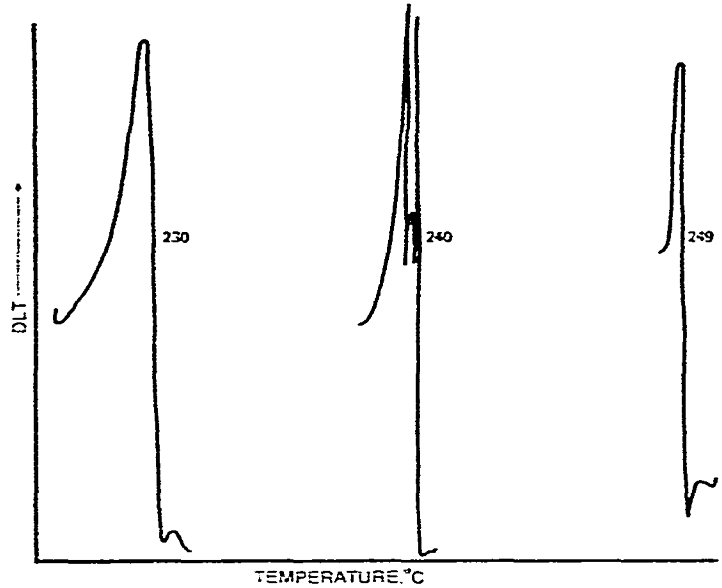
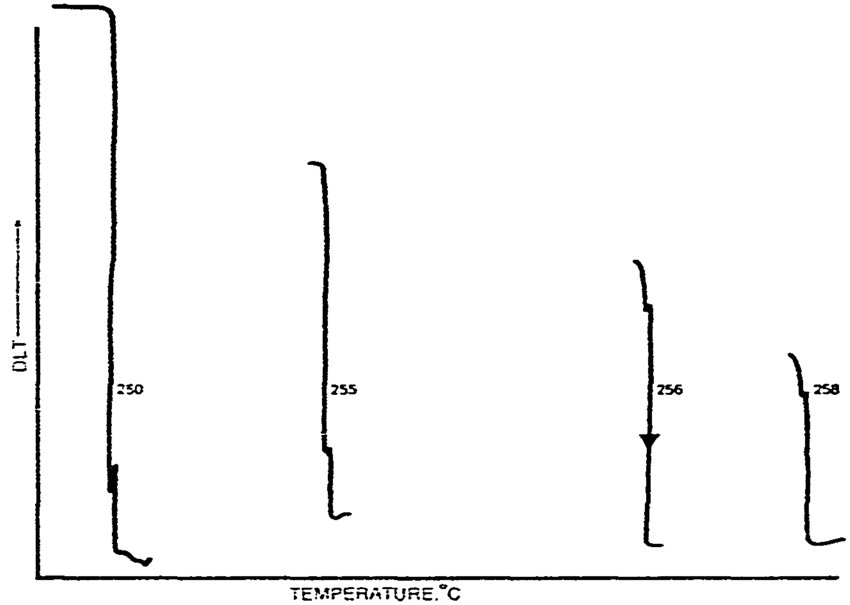


Fig. 5. Depolarized light transmission isotherms at various temperatures.

255, 256, and 258 °C. These measurements were made by rapidly inserting the sample in the TDA at the preset annealing temperature. At temperatures below 250 °C, the birefringence decreases with time after the initial birefringence rise, due to spherulite



(A)



(B)

Fig. 6. TDA for fusion of PET after annealing for 30 minutes at: (A) 230, 240, 249 °C; (B) 250, 255, 256, 258 °C.

formation in the PET. At 230 and 240°C the birefringence decreases with time At 249°C, there is an intermediate increase, followed by a decrease within the first 4 minutes, indicating the formation of a more birefringent structure, followed by fusion or disordering.

At 250°C and up to the fusion temperature of 260°C, the birefringence increases as the sample is annealed after the initial crystallization, and this behavior results from the growth of spherulite size or perfection at temperatures between 250 and 260°C. This decrease in molecular order below 250°C and increase above that temperature illustrates the recrystallization of the PET in this temperature range, proving conclusively that Form I and Form II are not distinct crystalline species but Form II is the recrystallized form of I. As a crystalline material increases in size or in order texture, it has been shown that the birefringence level increases[16]. This is illustrated by the equation:

$$\Delta = \frac{\text{(retardation) (wavelength)}}{\text{thickness}}$$

for as the crystallite size increases, the retardation increases, raising the birefringence.

In Fig. 6 are shown the fusion responses of the amorphous PET samples annealed between 230 and 260°C. Those samples annealed below 250°C show a decrease in birefringence with time and a fusion peak, whereas those samples annealed between 250 and 260°C show an increase in birefringence with time and no peak upon fusion.

These data support published DSC results[8–10] to show clearly the recrystallization occurring during the heating of PET to its melting point. The errors in interpretation that may occur when only one mode of analysis is used have already been pointed out[9], but what may be even more important is the determination of isothermal behavior with time.

Thermal degradation of poly(ethylene terephthalate)

An interesting part of the study of multiple melting phenomena is alluded to in the study of Wakelyn and Young[4], wherein they showed the increase in number average molecular weight as a function of time, when heating PET at 220°C under a continuously evacuated atmosphere. On the other hand, when the PET is heated under the same conditions in a sealed ampule with no continuing vacuum, then no change in the number average molecular weight was registered. They have also shown that the DTA scan from a continuously evacuated sample exhibited only one single high melting endotherm, whereas the DTA scan from the sealed ampule under the same conditions exhibited two melting endotherms. The data in Fig. 7 show that in addition to the increase in Mn, there is a reduction in fusion temperature when PET is crystallized under continuous vacuum.

In order to investigate the effect of environment on the formation of the crystalline phase of PET, it was treated for 24 hours at 224°C in a methyl salicylate bath, in air, in nitrogen, and in vacuum, and the TDA responses are shown in Fig. 8.

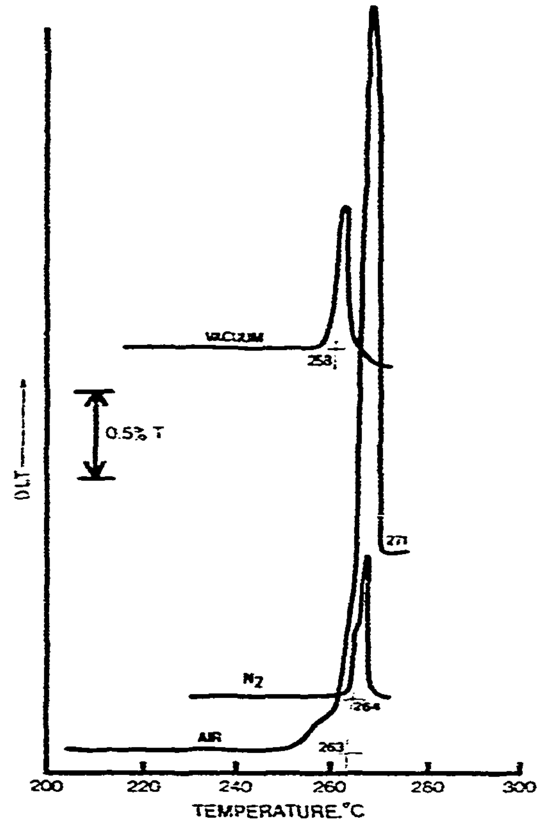


Fig. 7. TDA fusion behavior for PET annealed for 24 hours at 224 °C in air, under nitrogen and under constant evacuation.

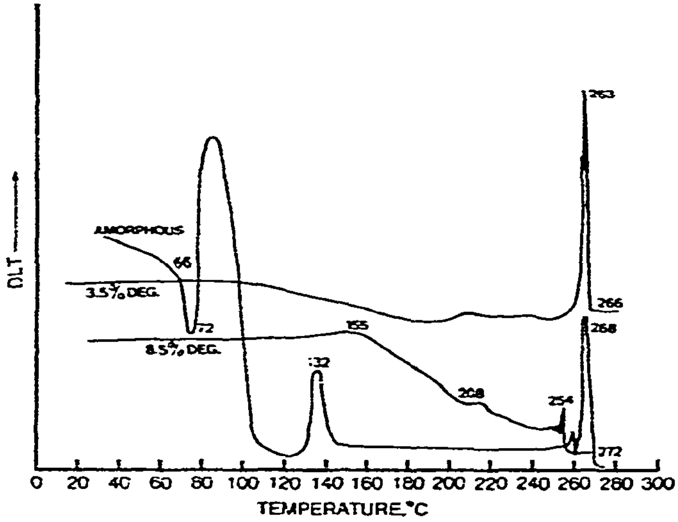


Fig. 8. TDA response for amorphous PET, PET copolymer with 3.5% diethylene glycol, and PET copolymer with 8.5% diethylene glycol.

The melting of the PET which had been crystallized in vacuum was quite sharp, beginning at 258 and peaking at 262 with final fusion at 264°C. Sealing the PET in nitrogen induced a peak with a shoulder which began at 263°C, with the peak maximum at 266°C and final fusion at 270°C. The PET which had been recrystallized in air under the same conditions showed the onset of melting, beginning as low as 252°C, with a peak maximum of 268°C and final fusion to the isotropic state at 271°C. Qualitatively, the broadness of the melting peak as well as its intensity would indicate a distribution of crystallites when PET was annealed in air at 224°C, whereas the PET films which had been crystallized in nitrogen and under vacuum represent a more uniform crystallite distribution. More importantly, however, is the fact that the PET which had been annealed under vacuum conditions fused at a lower temperature than that which had been annealed under nitrogen or in an air environment. The constant evacuation at 224°C under vacuum caused further polymerization to occur, indicated by a higher molecular weight with possible thermal degradation.

It is well known that polyethylene glycolate (DEG) is formed as a side reaction in the production of PET[17] and that the amount of DEG influences the physical properties of the polymer. For example, the melting point of PET is reported to be lowered by 4–5°C for each percent of DEG content[18–20]. By incorporating 3.5% DEG into PET, the fusion point was observed to occur at 265°C, whereas increasing the DEG content to 8.5% lowered the fusion point to 256°C (Fig. 8). In comparing the fusion points of DEG-dosed PET with that of the native polyester, we found a decrease from 270 to 265°C on going from 0 to 3.5 to 8.5% DEG. This change does not exactly follow the suggested lowering of 5°C for each percentage of DEG content, but it poses the probability that the lower melting endotherm is a result of the degradation of the PET, forming DEG during the solid state polymerization as PET is annealed at 224°C in vacuum. This increase in solid state polymerization is supported in the production of an insoluble PET after annealing for 24 hours at 224°C, independent of the environment.

CONCLUSIONS

The measurement of the fusion characteristics of PET which had been annealed at low temperatures (110°C) and at high temperatures (224°C) for varying times, had been reported to show a high melting endotherm for the former and a lower melting endotherm for the latter. In examining the fusion behavior of amorphous PET, which had been annealed at low temperatures, and PET which had been annealed at high temperatures, DTA measurements show very little difference in these fusion phenomena. However, the TDA measurements show that as the severity of the temperature conditions under which the PET is annealed, are increased, the fusion point of the PET creases. After annealing for 30 minutes at 110°C and dynamically scanning the temperature range to 232°C, via depolarization analysis, switching to the isothermal mode shows a continuous melting of crystallites to form the completely opaque and spherulitic PET. The increase in crystallinity or spherulitic growth observed by annealing above 249°C and the decrease in crystallinity observed below that temperature confirm earlier data on recrystallization as PET is heated through a temperature regime. The fusion behavior of these annealed samples also supports this view. Furthermore, these data support the postulate of Roberts that the high melting endotherm is always produced in annealing PET above 130°C.

A decrease in fusion temperature observed by Bell in going from PET (I) to PET (II) can be brought about by the degradation of PET with the formation of diethylene glycol residues within the polymer backbone. These, then, tend to lower the melting point of the PET polymer, and may account for the downward shift in fusion temperature with annealing time. The crystalline melting point of PET–DEG copolyesters has been shown to decrease as the mole % DEG is increased. Apparently at some temperature or time the formation of DEG as a side product diminishes, and the fusion point of the spherulitic PET continues to increase as the crystallites grow. The PET polyester containing 8.5% DEG crystallizes in a similar manner to the native PET, forming an opaque material whose fusion characteristics also became dependent on thermal history.

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