High Temperature Crystallization of Poly(Ethylene Terephthalate)

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Annealing poly(ethylene terephthalate) (PET) at high temperature results in a crystalline phase stable to 10°C higher than the temperature previously regarded as the equilibrium melting point. Melting temperatures as high as 289°C can be attained, which is equivalent to the equilibrium melting point determined herein for PET. The high melting point and tendency to superheat suggest that the crystals possess a substantial extended chain structure, notwithstanding the magnitude of the infrared fold band.

INTRODUCTION

The mechanical properties and dimensional stability of semi-crystalline flexible chain polymers are minified by the absence of continuity in the crystalline phase. An obvious approach to circumventing this limitation is to induce crystallization without backfolding, in the manner of rigid rod polymers (1-3). The excess free energy conferred to the crystal phase by backfolding reduces its stability. This suggests that one can suppress the tendency of flexible chain polymers to form folded chain crystals simply by carrying out crystallization at a sufficiently high temperature. The decreasing free energy of crystallization at higher temperatures promotes extended chain crystallization in order to minimize the excess energy associated with the fold surfaces.

The equilibrium melting point is formally defined as the temperature at which perfect crystals formed from fully extended macromolecules are in equilibrium with the liquid state (4-7). In practice the melting temperature of polymer crystals with negligible surface free energy and insignificant defects is referred to as the equilibrium melting point. From extrapolation of melting data obtained at various crystallization temperatures, equilibrium melting points equal to 279°C (8) and 284°C (9) have been deduced for PET. The extrapolation of melting temperatures measured for oligomeric PET yielded a range of values up to 284°C for the equilibrium melting point (10, 11). From a review of the published work a temperature of 280°C, obtained by annealing (10), has been taken to be the equilibrium melting temperature of PET (12, 13).

Melting temperatures higher than 280°C have been achieved with PET. Under elevated pressures, crystal phase stability to temperatures as high as 368°C has been reported, although such crystals melt at 276°C and lower at atmospheric pressure (14, 15). Orientation will elevate the melting point, although with PET melting still transpires well below equilibrium temperatures (16). A melting temperature equal to 310°C was measured after PET had been annealed several months at 290°C (17). The X-ray diffraction pattern was inconsistent with the known unit cell of PET, however, and the mass density exceeded that of the crystal density of PET. Since PET is not stable to prolonged exposure at such temperatures (18, 19), the material exhibiting a 310°C melting temperature was probably no longer poly(ethylene terephthalate).

Crystallization with minimal or no back-folding has been realized in various experiments with polyethylene. High pressure (20, 21), elongational flow fields (22, 23), and gel spinning (24-26) have all been employed to produce crystalline phases with negligible crystal stem reentry.

In PET the formation of extended chain crystals has been accomplished by the application of elevated pressures (14), by high pressure extrusion through converging dies (27-29) and by low temperature drawing of amorphous films (30) and fibers (31). The present study consisted of annealing PET at temperatures beyond the usual melting point. The nature of the resulting crystalline structure is examined.

EXPERIMENTAL

PET purified by micro filtration and having an intrinsic viscosity of 0.59 (Cleartuf 5901 from the Goodyear Tire and Rubber Company) was dried 14 h at 150°C prior to use. Samples were placed in a Teflon coated mold (dimensions were 90 × 13 × 1.5 mm) contained in a heating clamp (Custom Scientific). The clamp assembly was suspended in a vacuum desiccator and samples were isothermally maintained for various durations. The temperature

during this annealing was monitored by a fine thermocouple wire adjacent to the sample.

Differential scanning calorimetry was obtained using a Perkin-Elmer DSC-7 with the data measured during heating at 10 deg min^{-1} unless noted otherwise. Sample size was typically 3 mg. The melting points were taken as the temperature at the peak of the endotherm, as recommended by previous workers (32). Wide angle X-ray scattering measurements were obtained in transmission using a Philips generator and diffractometer system. Fourier transform infrared spectra were obtained with a Perkin-Elmer Model 1800. Samples were cryogenically ground in a Wig-L-Bug (Crescent Mfg. Co.), and the resulting powder dispersed in KBr. An absence of any disruption of the PET crystal morphology as a consequence of the grinding was assured by calorimetry. X-ray diffraction, FTIR, and DSC measurements demonstrated that after prolonged exposure to high temperature the material remained PET. Annealing does effect some loss of volatiles and sublimation of oligmers and terephthalic acid (18, 19). For the longer annealing times crosslinking at the surface of the films was also observed and removed by polishing the specimens before testing.

RESULTS

Calorimetry

When PET is annealed above its normal melting point, although crystallization is slow, a crystalline phase stable to very high temperature is produced. In *Fig. 1* is shown a DSC curve for PET annealed 472.5 h at 270°C. The crystals melt at 286°C, which is higher than the reported equilibrium melting temperature for PET (12, 13). As shown in the figure, after this melting the PET can be recrystallized at more usual temperatures to yield a conventional melting point. The lower melting PET exhibits a much broader endotherm than PET crystallized at
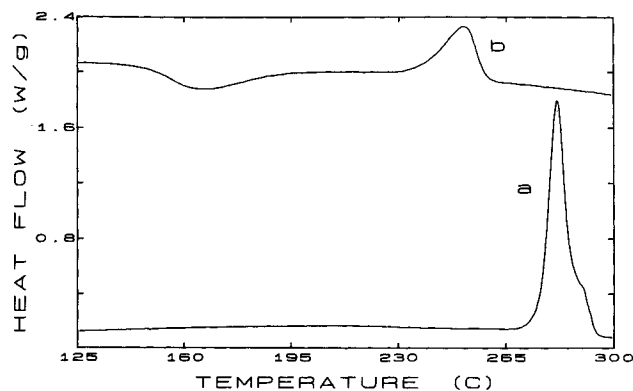
high temperatures. A summary of results obtained at three annealing temperatures is given in *Table 1*.

At 280°C the level of crystallinity achieved after one week is quite low. The DSC data in *Fig. 2* reveals a primary endotherm at 246°C, resulting from PET crystallization which transpired during slow cooling from the annealing temperature. In addition to this there is a very weak transition (2 J/g) at 280°C. When PET is maintained at 280°C for a more extended period of time, the magnitude of the high temperature endotherm increases significantly (32 J/g), with a concomitant reduction in the quantity of crystals melting at lower temperature.

The overall crystallization rate is accelerated by increased undercooling. As seen in *Fig. 2* a comparable time at a 270°C results in a significantly more intense transition (64 J/g) at 282°C than is obtained by crystallizing at 280°C. The lower melting crystal phase is virtually gone. *Figure 3* illustrates that the lower levels of crystallinity attained at higher annealing temperatures reflect a slower rate of crystal nucleation. The reduced undercooling results in a longer induction period; however, eventually crystallization accelerates due to the high chain mobility, thus facilitating crystal growth.

Table 1. Calorimetry Results for PET Annealed at High Temperature.

Time (h)	Annealing Temperature (°C)	Melting Temperature (°C)		Fusion Heat
		Onset	Peak	ΔH_f (J/g)
24.0	260	272	275	71
144.1	260	272	275	75
399.0	260	274	277	82
22.6	270	245	256	37
53.1	270	274	278	64
159.0	270	282	286	67
208.8	270	283	287	74
472.5	270	279	286	81
807.5	270	283	289	83
24.5	280	247	256[a]	51[a]
162.3	280	277	279[b]	<2[b]
256.7	280	280	285[b]	23[b]

[a]this corresponds to melting of crystals formed during cooling to RT
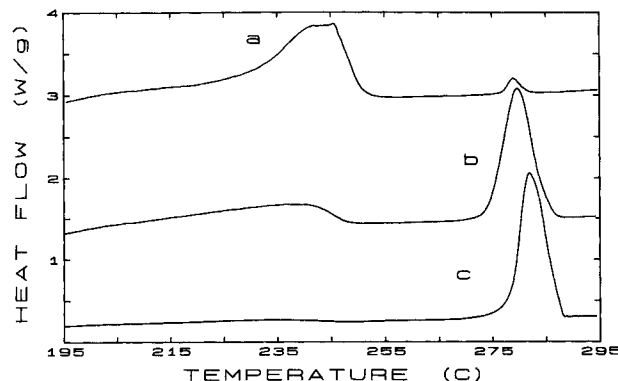[b]a second endotherm was also present about 35°C lower in temperature.

Fig. 1. (a) Differential scanning calorimetry at 10°C/min on PET crystallized 472.5 h at 270°C. Initially an 81 J/g melting endotherm at 286°C was observed. (b) Upon reheating after the sample had been quenched at 200 °C/min to RT, crystallization and melting transitions can be seen. The melting point on the second scan occurs at 251°C.

Fig. 2. DSC measurements on PET annealed (a) 162.3 h at 280°C, (b) 256. 8 h at 280°C, and (c) 208.8 h at 270°C. The heating rate was 10°C/min.

Melting points directly measured for the annealed PET are higher than the reputed equilibrium melting temperature of the polymer (12, 13); nevertheless, the melting points measured herein do not necessarily correspond to equilibrium values. Although equilibrium implies melting of crystals formed from fully extended chains, an extended chain crystal structure can melt below the equilibrium temperature due to crystal imperfections (33). In PET transesterification provides a chemical mechanism for the facile elimination of defects (34, 35). It can be seen in *Table 1* that for shorter annealing times (short relative to the time scale for elimination of defects and any lamellar thickening), the melting point is an increasing function of the crystallization temperature. Extrapolation of these data to a temperature at which equivalence to the crystallization temperature is obtained provides an estimate of the equilibrium melting temperature (4–7). Although just three data are used, only a short extrapolation is required, yielding 288°C as the equilibrium melting point of PET (*Fig. 4*). This is equal to melting temperatures actually measured

for samples annealed for longer times (*Table 1*). These results are consistent with extended chain crystal formation at the crystallization temperatures employed herein.

The activation energy for melting is lowered when sites for amorphous phase nucleation are present (36). Corners and edges are known to provide such sites, and thus facilitate the crystal to amorphous transition. Amorphous phase nucleation is more difficult for an extended chain crystal structure, given the absence of crystal stem backfolding, and thus rates of melting should be slower (36, 37). Furthermore, it has been speculated that melting of extended chain crystals may also be retarded due to suppression in the entropy gain accompanying melting, since less configurational freedom is acquired due to the more constrained morphology of highly crystallized extended chains (38, 39). Since superheating occurs when heat is provided to a crystal faster than it can melt, the retarded melting of extended chain crystals should lead to a proclivity for superheating.

Extended chain crystals of polyethylene (32, 36, 40) and polypropylene (41) are known to exhibit such sensitivity to superheating. In PET the existence of extended chain crystals has been inferred from the observation of extraordinary superheating in crystals formed at elevated pressures (14) and during extrusion through a converging die (27).

In *Fig. 5* is displayed the dependence on heating rate of the melting temperature for PET crystallized at 140°C and at 270°C. The former material evinces no strong sensitivity to heating rate. In fact, initially there is a modest decrease in the melting point, probably indicating crystal thickening at the slowest scan rates. The high temperature crystallized PET, on the other hand, melts at progressively higher temperatures as the calorimetric scan rate is increased. The melting point rises almost 18°C over the range of heating rates from 5°C min^{-1} to 80°C min^{-1}. This is significantly more superheating than was reported for PET crystallized under elevated pressures. The superheating observed therein was
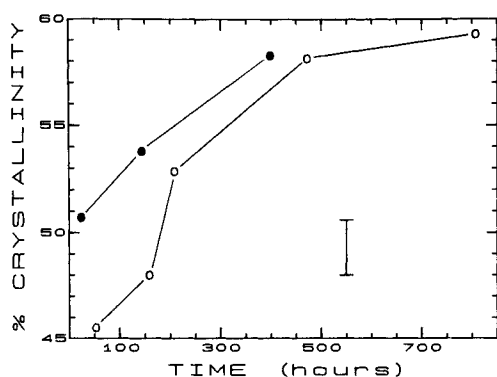

Fig. 3. The level of crystallinity (using 140 J/g as the perfect heat of fusion (10, 12)) obtained in PET after annealing for the indicated times at 260°C (●●●) and 270°C (○○○) respectively. The extents of crystallization determined from the densities were higher, over 74% for the longer annealing times.
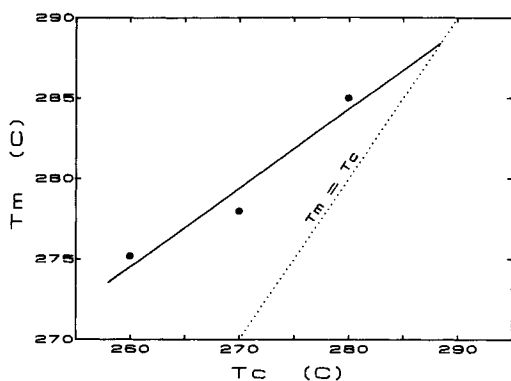

Fig. 4. Melting temperatures measured for PET crystallized for short times at various temperatures. The extrapolation yields an equilibrium melting point equal to 288°C.
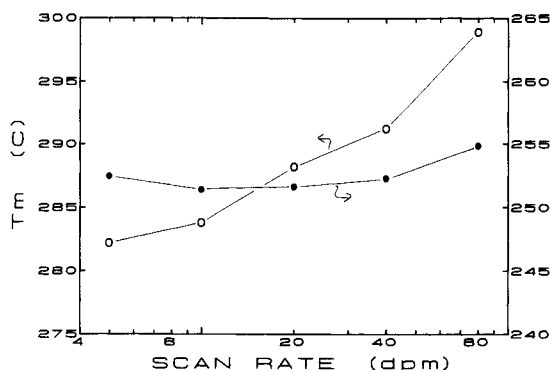

Fig. 5. The dependence on heating rate of the melting point for PET crystallized at 140°C (●●●) and at 270°C (○○○). The crystalline phase of the latter material is significantly more susceptible to superheating, an indication of the presence of extended chain crystals.

taken as evidence for the existence of extended chain crystal. From the results in *Fig. 5* it is evident that a similar argument can be made here.

Infrared Spectra

It is known that annealing at temperatures up through 200°C increases the incidence of crystal stem re-entry in PET spherulites (42, 43). At high temperatures, however, the free energy of crystallization becomes a strongly decreasing function of temperature (7). As the melting point is approached, reduced undercooling will result in a longer fold length. The expectation is that the very high crystallization temperature of the present experiments will severely suppress backfolding.

In PET the re-entry into the crystal is accomplished by a succession of gauche rotamers. This conformation gives rise to a unique vibrational transition, whereby the extent of backfolding can be inferred from the intensity of the "fold band" at 988 cm^{-1} in the absorption spectrum of PET (44). The absorption at 973 cm^{-1}, due to the trans conformation of the ethylene chain units, can be used to normalize the degree of backfolding for the level of crystallinity.

In *Fig. 6* is displayed the FTIR spectrum obtained from PET annealed 807.5 hours at 270°C. The ratio of the absorption at 988 cm^{-1} to that at 973 cm^{-1}, calculated as per previous workers (15, 45), is 0.155 +/− 0.005. For PET crystallization carried out under pressure, this ratio was found to vary from 0.184 to 0.155 over a 1 kbar range of pressures (15). Crystallization without backfolding was reportedly obtained at the higher pressures (14), although the value of 0.155 for the normalized fold band intensity has indicated to others an absence of significant extended chain crystallization (15).

Since the fold band intensity obtained by annealing at high temperature is equivalent to that resulting from high pressure crystallization of PET, the degree of extended chain character in the respective crystalline phases is presumably comparable. The

evidence adduced for pressure induced extended chain crystallization was the high melting point (276°C) and sensitivity to superheating (14). Both effects are manifested to a greater degree in PET annealed at high temperature. Since the equilibrium melting temperature obtained by extrapolation of the melting points of samples with low levels of crystallinity, 288°C, is essentially equivalent to the highest melting points actually measured, the arguments for significant extended chain character herein are persuasive. The measurable fold band infrared intensity may reflect folded chain overgrowth on the extended chain crystals. This might be expected to lead to melting endotherms with extended low temperature tails, although such is not observed in *Figs. 1* and *2*.

X-ray Diffraction

Representative wide angle X-ray diffraction measurements are displayed in *Fig. 7* for PET crystallized at 140°C and at 270°C. The sharpness of the reflections obtained by the high temperature annealing indicate the presence of a well developed crystalline phase. The breadth of an X-ray reflection is governed by crystal dimensions and imperfections. When only a single reflection order is present in a diffraction pattern, separation of the combined influence of size and distortion is not generally possible. In PET it has been claimed that the crystallite size contribution is dominant (46). A lower limit on the crystallite dimension can be obtained by applying the Scherrer equation (47)

$$D = \lambda/\beta \cos(\Theta) \qquad (1)$$

to the peak widths, where β is the full width at half intensity, D represents the average size of the crystallites perpendicular to the planes associated with the Bragg angle Θ, and $\lambda = 1.54$ Å.

More extended annealing at high temperature elevated the PET melting point (*Table 1*), presumably a consequence of further increases in crystal perfection and size. Any change in X-ray line width associ-
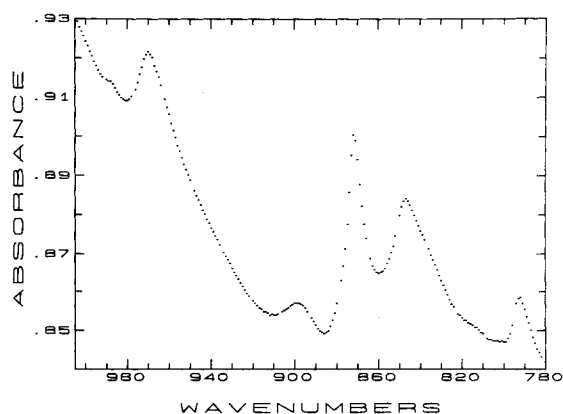

Fig. 6. FTIR spectrum of PET crystallized 187.5 h at 270°C. This material exhibits of melting temperature of 289°C. The fold band is the weak shoulder on the high frequency side of the trans band at 973 cm^{-1}.
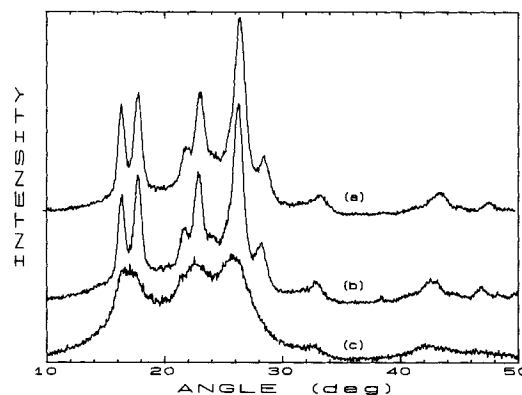

Fig. 7. WAXS results for PET crystallized (a) 472.5 h at 270°C, which exhibited at melting point equal to 286°C, (b) 53 h at 270°C, which melted at 278°C, and (c) at 140°C, resulting in a melting temperature of 256°C.

ated with these alterations of the crystal structure, however, were negligible (*Fig. 7*). Even brief annealing times at 270°C produce lateral crystal dimensions exceeding those previously achieved in PET using a variety of processing conditions (48–52), including high speed spinning (53) (*Table* 2).

Wide angle X-ray measurements have been reported for a low molecular weight PET (I.V. = 0.08 dl/g, corresponding to $M_w = 3000$) (54). Crystallization without backfolding is known to predominate in polyethylene at low molecular weight (i.e., less than about 160 main chain bonds) (55, 56). A PET chain with $M_w = 3000$ has less than 100 "virtual bonds" along the backbone (the coplanar phenyl ring and carbonyl groups conferring no flexibility (57)). Extended chain crystallization is certainly plausible in PET of such low molecular weight. The crystalline phase exhibited especially sharp X-ray reflections (54). The crystallite dimensions, deduced from the peak widths, are comparable to those obtained by high temperature annealing (see *Table 2*).

Although no line widths were reported, exceptionally sharp wide-angle X-ray reflections, similar to those seen in *Fig. 7*, were obtained in PET crystallized under high pressure (14). The authors believed this material to be comprised of extended chain crystals.

The annealing of PET at high temperature produces crystallites with dimensions transverse to the chain axis of a size only achieved previously in PET by processes that resulted in extended chain crystallization. Although no small angle scattering data are available, it might be expected that the long period would provide direct information concerning the extended chain character of the crystalline phase. Since the angle dependence of X-ray scattering is governed by average dimensions, however, the long period can be expected to approach macromolecular proportions only in the complete absence of crystal stem backfolding.

SUMMARY

The high melting temperature, and its equivalence to the equilibrium melting point, suggest that the crystalline phase obtained by high temperature annealing of PET is comprised of extended chain crystals. This inference is consistent with the strong tendency for superheating. Realization in any practical sense of the expected benefits of an extended chain crystal structure (e. g., modulus, strength, and dimensional stability) requires development of a process that is orders of magnitude faster than that

associated with quiescent crystallization at low undercoolings. Nevertheless, the concept embodied in high temperature annealing can perhaps be exploited through the use of nucleating agents and orientation in order to accelerate the development of a crystalline morphology with minimal backfolding.

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Table 2. Crystal Dimensions for PET Determined From WAXS.

Sample	X-Ray Reflection			Reference
	010	110	100	
Annealed at 270°C	160	140	130	this work
Annealed at 250°C	96	62	60	(51)
High speed spun and annealed	100	76	—	(53)
Oligomeric	208	115	107	(54)

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