Influence of Pressure on Crystallization in Poly(ethylene terephthalate)

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ABSTRACT: The crystallization behavior of poly(ethylene terephthalate) has been studied at pressures up to 2 kbar, with both morphological data and crystallization kinetics data being obtained. A 10-fold increase in nucleation density of spherulites was observed over this pressure range, as well as crystallinity levels of close to 80% for crystallization pressures in excess of 0.5 kbar. No evidence was found to support the formation of extended chain lamellae over this pressure range. Secondary nucleation analyses indicate the presence of a regime II–regime III transition in the vicinity of 165 °C at atmospheric pressure, with all elevated pressure studies being restricted to regime III growth. The fold surface free energy shows a steep and continuous increase with crystallization pressure, attaining values far in excess of those possible for a folded chain surface. It is suggested that the crystal–amorphous interface generated at elevated pressures consists of constricted semirigid chains, possibly comprised of cilia and nonadjacent reentry chains.

Introduction

Polymers are subjected to elevated pressures during many molding operations. These pressures tend to be under 2 kbar but can be much higher in compression molding operations. The applied pressure affects the melting point and glass transition temperature at a rate close to 20 °C/kbar and so exacts a significant influence on the temperatures and rates at which crystallization occurs. Additionally, pressure tends to influence the rates of primary nucleation and linear growth in different ways, leading to fairly complicated synergistic effects. In order to understand the influence of pressure on crystallization it is necessary to investigate the nucleation and growth processes separately.

In the flexible chain polymers, such as polyethylene[1,2] and *cis*-polyisoprene,[3,5] the influences are fairly well understood now. However, the more rigid systems such as poly(ethylene terephthalate) are not well understood at all. In all polymers it is necessary to identify the regime[6,7] under which crystallization is occurring since this affects the evaluation of kinetic data, as well as giving rise to molecular weight fractionation effects. Polyethylene can crystallize in regime I or regime II dependent on molecular weight and supercooling. The pressure dependence of the regime I–regime II transition temperature has been determined.[2] The influence of pressure on crystallization rate has been evaluated for bulk crystallization in both regimes and for the lamellar growth rate in regime II. Its fold surface free energy is independent of pressure over the first 2 kbars.

cis-Polyisoprene has been studied extensively.[3-5] At atmospheric pressure all three regimes of crystal growth have been observed for molecular weight fractions.[8] Phenomenologically, polyethylene and *cis*-polyisoprene are similar with regard to regimes, but the transition temperatures are very different. Unfractionated *cis*-polyisoprene has been investigated thoroughly for pressures up to 4 kbar, and its regime III growth kinetics have been analyzed. The fold surface free energy and structure are sensitive to pressure since the fold is a loop several mers in length. Its primary nucleation is very sensitive to pressures below 1 kbar and produces major changes in spherulite size.[9]

Both polymers show unusual growth at pressure in excess of 3.5 kbar, where hexagonal phases result. In the case of polyethylene, thick chain-extended lamellae result from what amounts to growth at low supercoolings,[1] whereas the *cis*-polyisoprene produces isolated crystals (not spherulites) which are short and only slightly thicker than normal.[10]

Poly(ethylene terephthalate) is a polymer which is believed to have a tight polyethylene-type aliphatic fold;[11] however, longer folds involving skeletal benzene rings cannot be packed into the surface, and so changes in fold surface structure induced by pressure would be major. There is one report in the literature[12] dealing with this polymer where crystallinities close to 80% were reported and extended-chain crystals claimed at pressures in excess of only 1.0 kbar. This paper will report the results of extensive studies of crystallization of poly(ethylene terephthalate) at pressures up to 2 kbar. Major effects on crystallinity, spherulite size, and lamellar growth will be presented.

Experimental Section

The poly(ethylene terephthalate) used was provided by E. I. du Pont de Nemours in the form of pellets and amorphous films (2 and 10 mil). It had a number-average molecular weight of 21 000 and 0.7% diethylene glycol content. All samples were vacuum dried prior to use but without any further treatment such as purification or fractionation.

For the study of morphological and thermal properties after crystallization, punched disks of 50-μm-thick film were used, together with thick molded disks. The specimens were separated by Teflon spacers, melted, and crystallized under the desired conditions in a bomb pressurized with a calibrated hydraulic press. Temperature was controlled to within ∓1 °C. The cell was of external diameter 2.5 in. and internal diameter 0.724 in., the cell body and plugs being constructed of Vascomax 30 CVM maraging steel. Cell design was such that it could withstand pressures of 10 kbar and temperatures of at least 300 °C. Temperature was measured by using a J-type thermocouple inserted into a long vertical hole bored in the center of the cylinder wall so that the thermocouple was in line with the specimens. Heating was accomplished through the use of Thermolyne Fibrax heating tape, its temperature being monitored manually by a VWR 600-W power control. The cell was insulated with high-density ceramic fiber (Cer-wool 2400). It was essential for the PET films and disks to be physically separated from the maraging steel of the bomb because of oxidation/degradation problems. This was done with a Teflon shield. Experimental crystallization procedures utilized the pressure dependence of the melting point reported by Siegmann and Harget.[12]

Crystallization was studied with equipment previously described.[2] Light-scattering studies carried out under pressure

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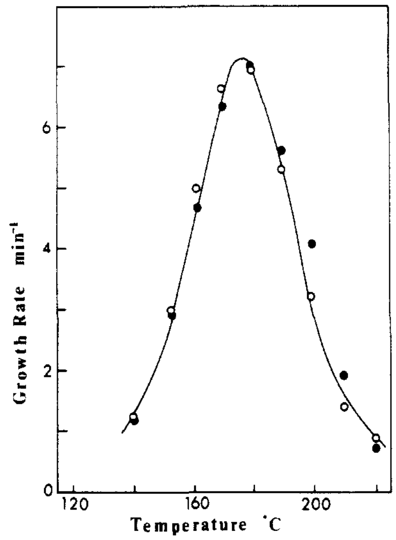

Figure 1. Reciprocal half-time versus crystallization temperature at atmospheric pressure: ○, optical transmission; ●, laser light scattering.

utilized 50-μm unoriented amorphous film. Disks 0.189 in. in diameter were punched from the film to match exactly the confining sapphire crystals. The specimen assembly was confined by using shrink tubing since crystallization was carried out by heating from the glassy state. Spherulite growth rates were estimated from the change in size with time of cloverleaf light-scattering patterns in the conventional manner. A fresh specimen was used for each run because of the impossibility of regenerating an amorphous film on cooling. Bulk crystallization rates were determined by using the change in light transmission intensity at atmospheric pressure only.

Melting curves were determined by using differential scanning calorimetry and processed to yield crystallinities as well as melting points. WAXS studies were carried out on a Diano XRD 8000 instrument with an SPG-2 spectrogoniometer, crystallinities being estimated. Fourier transform infrared spectroscopy was performed on a Nicolet 7199 instrument.

Results

Atmospheric Pressure Crystallization Studies. Bulk crystallization kinetics were obtained by using the intensity of transmitted polarized light as well as the intensity of scattered laser light, as described earlier for polyethylene.[2] A 50-μm-thick unoriented film was used. This film was found to contain 0.3% water, which caused hydrolytic degradation unless removed prior to study. The film was dried in a vacuum oven at 50 °C for 24 h prior to use.

Reciprocal half-time data obtained by using both techniques are shown in Figure 1, where it can be seen that the results of both approaches correlate well. Crystallization curves at temperatures below the maximum crystallization rate temperature of 176 °C were obtained by heating from the glass whereas the data for temperatures above 176 °C were obtained by cooling from the melt. All data were obtained by using the high-pressure hot stage. Specimens were held at 285 °C for 3 min, a condition found by van Antwerpen[13] to be suitable for elimination of thermal history.

Melting points were obtained directly after the crystallization experiment using the optical transmission method. The equilibrium melting point was found to be 278 °C, which is close to the value of 280 °C obtained by Mehta et al.[14]

Linear growth rates were obtained by using laser light scattering and are shown in Figure 2 as a function of crystallization temperature. Also shown are the prior results of van Antwerpen,[13] who used laser light scattering, and of Palys and Phillips,[15] who used transmission electron microscopy of quenched films. All the curves show a growth maximum in the range 176–177 °C. There are, however, major variations in the linear growth rate at the maximum. It is likely that this arises from differences in diethylene glycol content, the specimen being used here having the lowest diethylene glycol content available commercially.

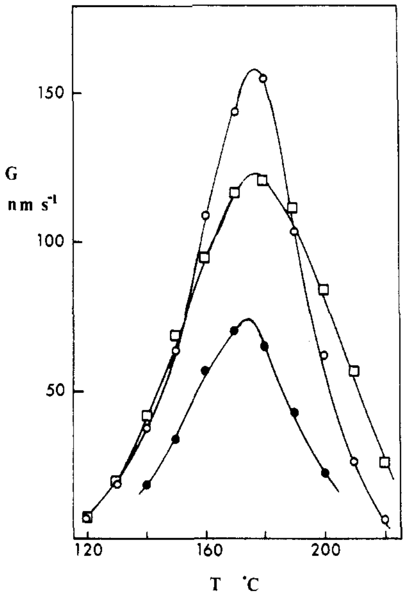

Figure 2. Linear growth rate, G, versus crystallization temperature at atmospheric pressure: ○, this work; ●, Palys and Phillips;[15] □, van Antwerpen.[13]

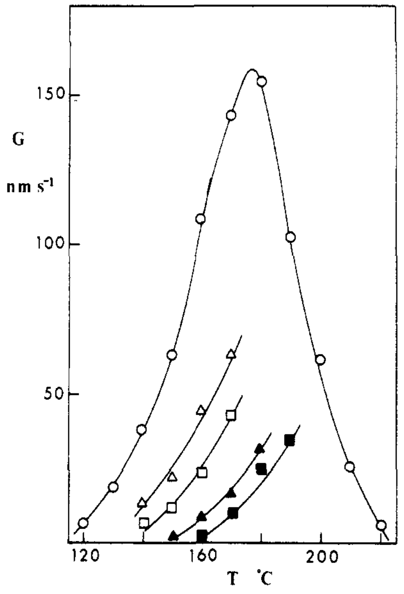

Figure 3. Linear growth rate, G, versus crystallization temperature at different pressures (kbar): ○, 0.001; △, 0.5; □, 1; ▲, 1.5; ■, 2.

High-Pressure Crystallization Studies. Linear growth rate data only were obtained in this experimentation, a different specimen being used in each experiment because of the impossibility of quenching the specimen from the melt to the glassy state in the high-pressure bomb. Specimens were crystallized by warming from the glassy state under pressure. The pressures used ranged from 0.5 to 2.0 kbar at 0.5-kbar intervals. Plots of linear growth rate versus crystallization temperature are shown in Figure 3 along with the atmospheric pressure results. As expected, the curve is translated along the temperature

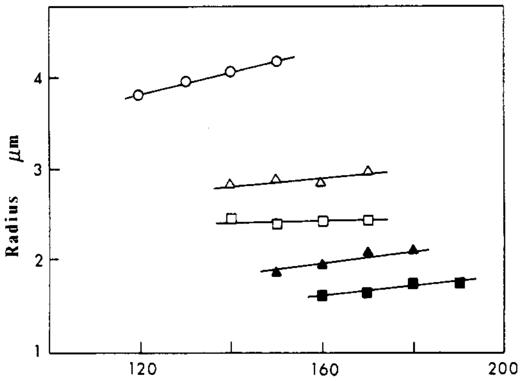

Figure 4. Average spherulite size (R) versus crystallization temperature at several pressures (kbar): ○, 0.001; △, 0.5; □, 1; ▲, 1.5; ■, 2.

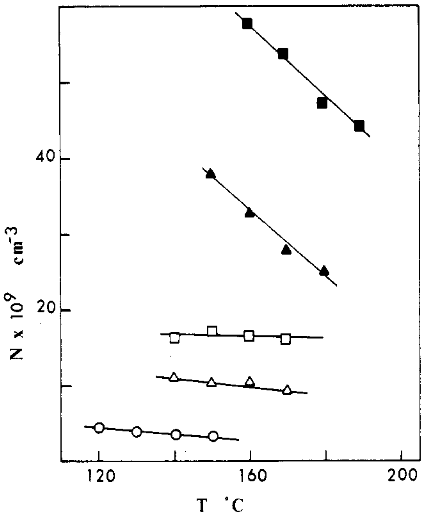

Figure 5. Nucleation density versus crystallization temperature for several pressures (kbar): ○, 0.001; △, 0.5; □, 1; ▲, 1.5; ■, 2.

axis as crystallization pressure is increased. The possible temperature range was limited by the bulk of the cell and the high rate of crystallization as the peak was approached.

The maximum average spherulite size obtained is plotted in Figure 4. Generally, the spherulite size is reduced as pressure is increased. The effect is large and much greater than that observed in earlier studies on polyethylene and *cis*-polyisoprene. At 2 kbar the average spherulite size is about one-third the size obtained in atmospheric pressure crystallization. When converted to nucleation densities, the effect is enhanced because of the inverse dependence of nucleation density on the cube of the spherulite radius (Figure 5). The result is a 10-fold increase in nucleation density over 2 kbar of pressure.

Structural Characterization. Siegmann and Harget[12] have reported that poly(ethylene terephthalate) crystallized from the melt at pressures equal to or greater than 1.0 kbar forms extended-chain crystals. The report was based on differential scanning calorimetry carried out at atmospheric pressure and on scanning electron microscopy of fracture surfaces. Here, differential scanning calorimetry, density determination, wide angle X-ray diffraction, and infrared spectroscopy have been used to investigate the phenomenon in more detail.

Wide-angle X-ray diffraction data are shown in Figure 6, where it can be seen that the crystalline peaks become narrower and sharper as crystallization pressure is increased. These changes reflect an increasing degree of crystallinity with increasing crystallization, in agreement with the observation of Siegmann and Harget.[12] The reflections when indexed are in agreement with those obtained for atmospheric pressure crystallization (i.e., a triclinic unit with a = 4.56 Å, b = 594 Å, c = 1075 Å, α = 98.5°, β = 118°, γ = 112°).[16] Essentially the crystal structure remains unchanged over the pressure range used.

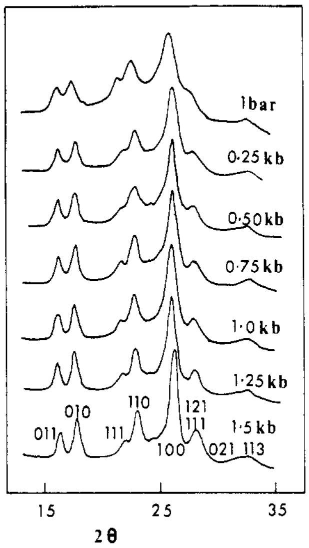

Figure 6. Wide-angle X-ray diffraction patterns of pressure-crystallized samples.

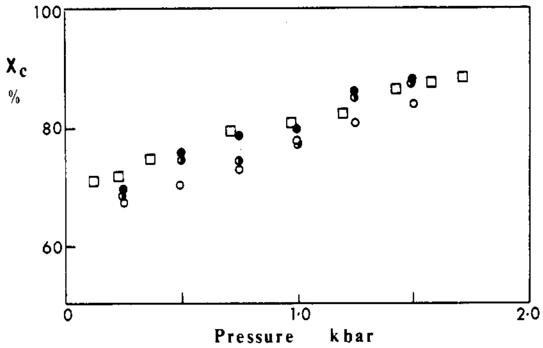

Figure 7. Crystallinity versus crystallization pressure: ○, WAXS; ●, density before annealing; ◑, density after annealing; □, Siegman and Harget[12] density without annealing.

Crystallinities were obtained by using the simple technique of dividing the crystalline intensity by the total diffracted intensity.[17] They are presented in graphic form together with the results obtained by using a n-hexane/chloroform density gradient column (Figure 7). Densities were also determined following several hours of annealing at 90 °C, designed to allow the amorphous phase to relax to normal density. Also presented are the data of Siegmann and Harget[12] obtained by using density determination. The density data prior to annealing give crystallinities that correlate with the results of Siegmann and Harget;[12] however, the more accurate results obtained from the annealed films correlate better with the X-ray data. The differences, however, are fairly small, being on the order of 2%. It is clear that crystallizing at pressures as low as 0.1 kbar results in a level of crystallinity approximately double that obtainable at atmospheric pressure.

DSC melting curves were obtained at a heating rate of 10 °C/min. The melting peak was found to be 261 °C at atmospheric pressure and 264 °C for 0.5 kbar of crystallization pressure. It then decreased almost linearly to 255 °C at 1.25 and 1.5 kbar. Even for a heating rate of 20 °C/min, the 1.25-kbar material gave a melting peak of only 260 °C, whereas Siegmann and Harget[12] reported a melting peak at 276 °C for identical preparation and characteri-

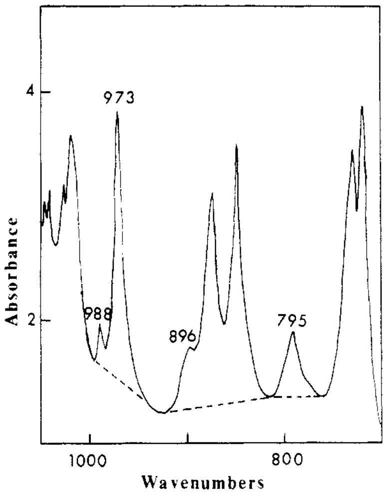

Figure 8. Typical FTIR spectrum showing the base lines used in quantitative analyses.

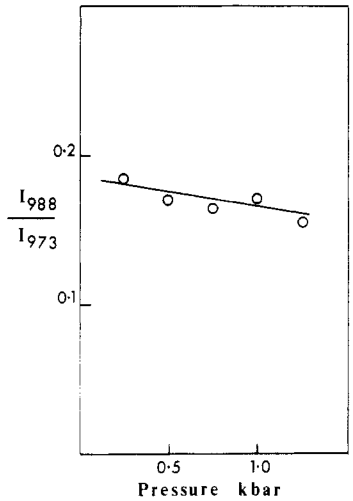

Figure 9. Ratio of I_{988}/I_{973} (folds/crystals) as a function of crystallization pressure.

zation conditions. Since the equilibrium melting point is 278–280 °C, such an observation was regarded as primary evidence for extended-chain crystallization.

Infrared spectroscopy can be used to determine crystallinities for many polymers, but for poly(ethylene terephthalate) a specific band (988 cm^{-1}) has been assigned to folded chains.[11,18] The 973-cm^{-1} band is associated with only the crystalline phase, and the 986-cm^{-1} band arises only from the amorphous phase. Because of differences in thickness between specimens, all intensities have been determined relative to the internal thickness band at 795 cm^{-1}. The simplified method of Koenig and Hannon[19] was used in the calculations. A typical spectrum is shown in Figure 8. If extended chain crystals are present, then the ratio of the folded chain band intensity to that of the crystalline band should decrease. Such a plot is shown in Figure 9, where it can be seen that there is only a minor decrease with crystallization pressure, indicating a minor increase in lamellar thickness over the pressure range thought to give a transition to extended-chain formation. The increased levels of crystallinity are reflected in the infrared data. Relative levels of crystallinity, amorphous content, and fold content are shown in Figure 10.

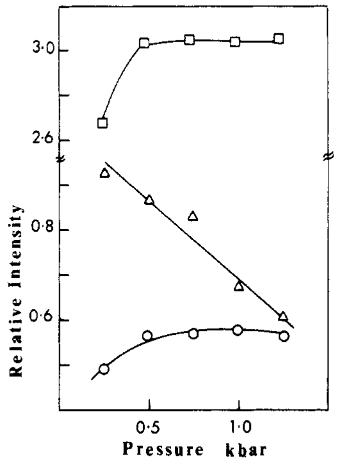

Figure 10. Relative values of amorphous content (△), crystallinity (□), and fold content (○) versus crystallization pressure (all relative to the 795-cm^{-1} band).

Discussion

Structure and Morphology. The data indicate clearly that there is no change of unit cell over a 2-kbar range of crystallization pressure and that the level of crystallinity achievable is considerably enhanced by the use of pressure easily accessible and normally encountered in many forming operations. At the morphological level, the most significant effect is the 10-fold increase in nucleation density that occurs over the first 2 kbar of crystallization pressure. Although there is a slight change in nucleation density with crystallization temperature, it is clear that the crystallization pressure is the controlling variable. The increase in nucleation density is greatest over the first kilobar, as is the increase in crystallinity. It is possible therefore that the two phenomena are related. Quite how this could occur is difficult to explain. In *cis*-polyisoprene an increase in nucleation density with pressure could be seen from electron micrographs[9] to be related to the nucleation of spherulites, occasionally in the form of single lamellae, but more usually as groups of small numbers of parallel oriented lamellae, none of which could be discerned as a heterogeneous nucleus. As such it is likely that these crystals which nucleated close to one another might have had single molecules spanning the region and present as tie-chains. When such an occurrence is found in the growth of crystals, it results in the generation of noncrystallographic branching. Such an event would be expected to increase crystallinity. It seems therefore that pressure might increase the likelihood of larger molecules contributing to both primary nucleation and branching. However, there are likely to be several other possibilities, and the two phenomena may arise from quite different influences. Primary nucleation and branching frequency are two of the least understood areas of polymer crystallization, and little is available theoretically to assist in our understanding.

No evidence was found in our studies to confirm the report of extended-chain crystallization.[12] Differential scanning calorimetry did not record any melting points approaching the equilibrium value. Infrared spectroscopy showed a fold content which was determined by the level of crystallinity. The material used had a M_n of 19000 and a diethylene glycol content of 0.7%, whereas the material used by Siegmann and Harget[12] had M_n equal to 39000. The diethylene glycol content was not given. As mentioned in the Experimental Section, it was found that, in addition to the known effect of moisture, a degradation process occurred that was catalyzed by the metal oxides present in the bomb. In our case, the specimen was encased in poly(tetrafluorethylene) for protection. In the absence of this protection the specimen was found to take on a greenish hue with intensely colored specks. The specimen often resembled a piece of granite. It is suggested that a considerable decrease in molecular weight occurs, in addition to unknown reactions, in the absence of protection against degradation. Low molecular weight material is more easily chain extended. Diethylene glycol moieties are probably rejected from the crystal and would be expected to inhibit chain extension. It therefore seems possible that the chain extension reported by Siegmann and Harget[12] was caused by a close to zero diethylene glycol level or by molecular weight reduction due to degradation.

Crystallization Kinetics. The analysis of lamellar growth kinetics requires a knowledge of the mobility of any polymer in addition to a knowledge of parameters characterizing the crystal. Usually the mobility is described by using some form of the WLF equation involving the glass transition temperature. It was recently demonstrated for fractions of *cis*-polyisoprene that a technique using experimentally determined WLF constants works well even for high supercoolings, where the handling of the mobility is of critical importance. In poly(ethylene terephthalate) the situation is complicated since the glass transition temperature and the WLF coefficients depend on crystallinity. The problem that arises is therefore to decide on appropriate values of the parameters at the growth front. Just ahead of the front the crystallinity is zero, but just behind the front it will be close to or lower than the level of crystallinity normally achieved. Even though a molecule may not be attached to a crystal when it enters into a secondary nucleus, its behavior will be influenced by the close proximity of the crystal. Molecules may be adsorbed on the crystal face prior to attachment. For reasons unknown, but possibly related to the intrinsic chain flexibility, the effect is more severe in the case of poly(ethylene terephthalate) than in other commonly studied polymers. In the absence of any molecular theory of mobility, for poly(ethylene terephthalate) in the vicinity of the growth front we have used parameters characteristic of 25% crystallinity (i.e., the average of the crystallinities ahead of and behind the growth front).

In earlier studies,[15,19] empirical fitting of data to produce a straight line dependence was used. However, since the recognition of the existence of regime transitions such a method is inappropriate. In unfractionated systems, normally only two regimes are encountered,[20] and under such circumstances appropriate manipulation of the mobility exponential produces a straight line plot. The various methods of approach to analysis of PET data and the resulting conclusions will be reviewed in a separate publication.

The general expression used in analysis of linear growth rates is the Hoffman–Lauritzen equation[21]

$$G = G_0 \exp\left(-\frac{U^*}{R(T - T_\infty)}\right) \exp\left(-\frac{K_g}{T(\Delta T)f}\right)$$

where for regimes I and III

$$K_g = -\frac{4b\sigma\sigma_e T_m{}^\circ}{\Delta H_f k}$$

and for regime II

$$K_g = \frac{2b\sigma\sigma_e T_m{}^\circ}{\Delta H_f k}$$

U^* is the activation energy of a WLF type expression, T_∞ the WLF reference temperature, $T_m{}^\circ$ the equilibrium melting point, ΔT the supercooling, σ and σ_e the lateral and fold surface free energies, respectively, ΔH_f the heat of fusion per unit volume, and f a factor to correct the change in ΔH_f with temperature (put equal to $2T/(T_m{}^\circ + T)$).

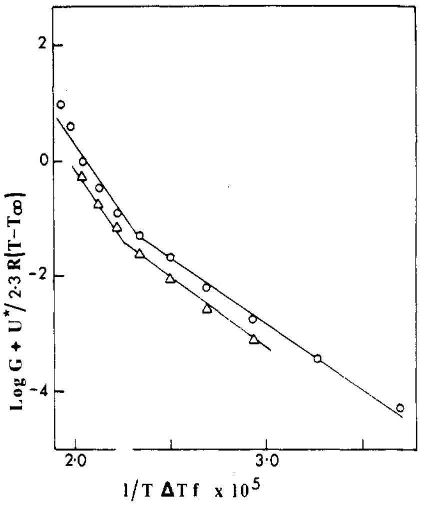

Figure 11. Kinetic analysis of linear growth rates at 1 bar obtained by using the parameters for 25% crystallinity: ○, this work; △, Palys and Phillips.[15]

The plot that is generally made is of log $G + U^*/[R(T - T_\infty)]$ versus $1/[T(\Delta T)f]$; the product $\sigma\sigma_e$ being obtained from the slope K_g. In the analysis used here, U^* and T_g were characteristic of 25% crystallinity (see Table I), T_∞ being taken as T_g - 30 °C. The equilibrium melting point was determined by using light transmission to be 551 K, which is close to the value of 553 K of Mehta et al.[14] There are two likely values of the latent heat of fusion, 1.27 J cm^{-3} from Wlochowicz and Przygoski[22] and 1.8 J cm^{-3} from Mehta et al.[14] The choice results in different values of $\sigma\sigma_e$ but does not affect K_g. Since the value of Mehta et al.[14] was the most recent and used a new estimate of crystal density, it was used in the analyses. A (100) growth face has been assumed[15] and hence a monomolecular layer thickness of 5.53 Å. The kinetic analysis for atmospheric pressures is shown in Figure 11, where the current data are plotted together with the earlier data of Palys and Phillips.[15] Both curves show a regime II–regime III transition having a slope ratio of 2.4. For the data reported here the transition occurs at 167 °C, but at 163 °C for the data of Palys and Phillips.[15] The more extensive regime III data points for this work appear to follow a curve rather than a straight line. On Figure 11 the lines for both sets of data were drawn parallel to one another and are believed to be characteristic of the points closest to the regime transition. If a straight line is drawn through the five points alone, characteristic of regime III, then the transition occurs at 165 °C, but the slope ratio is increased to 3.0. The value of σ used was obtained as 10.5 erg/cm^2 by using the Hoffman–Lauritzen[21] version of the Thomas–Stavely relation.[23] Resulting values of σ_e were 255 (regime II) and 301 erg/cm^2 (regime III) for these data (256 and 301 being obtained from the data of Palys and Phillips.[15]). A straight line fit of the latter data had given a value of 222 erg/cm^2.

When the high-pressure crystallization data are analyzed with the same procedures (parameters used are given in Table I), straight line plots characteristic of the regime III region alone are obtained (Figure 12). Obvious at a glance from the plots is the major increase in the slope that occurs as pressure is increased. When analyzed with the same method as was used for the atmospheric pressure results, a 6-fold increase in the fold surface energy occurs at a fairly steady rate over this first 2 kbar of applied pressure (see Table I). Such a major and continuous increase in σ_e with crystallization pressure has not been seen before in any polymer for which such data are available.

Table I
Analysis of Growth Rate Kinetic Data of PET at Various Pressures in the Semicrystalline System

	input parameters				results		
P, kbar	$T_m°$, K	U^*, cal/mol	T_∞, K	regime assumed	$K_g \times 10^{-5}$, K^2	$\sigma\sigma_e$, erg^2/cm^4	σ_e, erg/cm^2
0.001	551	3050	323	III	12.80	3158	301
0.5	578.2	3230	333	III	44.58	10478	998
1.0	607.4	3400	343	III	59.65	13346	1271
1.5	633.7	3550	353	III	70.17	15048	1433
2.0	659.9	3680	363	III	88.46	18217	1735

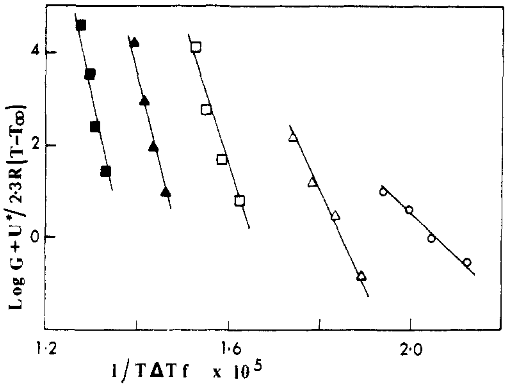

Figure 12. Kinetic analysis of linear growth rates at several pressures (kbar) obtained by using the parameters for 25% crystallinity: ○, 0.001; △, 0.5; □, 1; ▲, 1.5; ■, 2.

General Comments

Since the first studies were carried out on poly(ethylene terephthalate) the results have always been more difficult to understand than those for a much simpler polymer, such as polyethylene. This study has proved to be no exception to the trend in that some aspects of the behavior have been clarified but additional observations have been made that defy any simple explanations.

It has been confirmed that poly(ethylene terephthalate) does indeed achieve very high levels of crystallinity, but the evidence is firmly against the generation of thick extended-chain lamellae. Neither the observed melting points of specimens crystallized at elevated pressures nor the infrared spectroscopic data on fold content provide evidence favoring a chain extension conclusion. Undoubtedly one of the major problems always encountered in comparing different studies on this polymer arises from a variable and usually undefined level of diethylene glycol moieties in the polymer backbone. Clearly this is a problem in trying to compare these studies with those of Siegman and Harget,[12] who did not estimate the diethylene glycol content. The presence of such moieties would tend to be disruptive to the crystal, so they would probably be excluded and reside in the folded surfaces. They would also tend to retard the formation of extended-chain crystals since an additional section ca. 6 Å long is incorporated as a defect in the polymer chain. Our suppliers tell us that the specimens studied here contain the lowest amount of diethylene glycol available commercially, so it seem unlikely that the polymer used by Siegman and Harget[12] had fewer such impurities. Chain degradation might result in an enhanced ability for chain extension as a result of shorter molecules being generated. In our case, specific protective measures had to be taken to prevent a degradation process catalyzed by the metal oxides present on the interior surfaces of the bomb. The need for protective measures was not mentioned by Siegman and Harget;[12] however, the alloy used in their bomb construction was not mentioned, and it may have possessed a different oxide surface. Obviously, it is impossible at this stage to deduce the reasons for the discrepancies; however, it is clear that identical treatments produced different results in the two studies.

One of the most interesting effects observed is the major increase in nucleation density that results from the application of pressure during crystallization. A similar effect had been observed in *cis*-polyisoprene[9] but of much smaller magnitude. Additionally, in that case, a peak resulted at 0.75 kbar when the data were plotted against pressure for a constant crystallization temperature. Such behavior would have been expected for some type of homogeneous nucleation process. Here, no such peak was observed, the nucleation density still increasing at 2 kbar and the increase being 10-fold over 2 kbar of pressurization. Should the nucleation be homogeneous in nature then the behavior can be explained in terms of the pressure dependence of the glass transition and the melting point. Whereas in *cis*-polyisoprene both parameters change at approximately similar rates, in PET the melting point has been claimed to increase at a rate of 50 °C/kbar [12] and the glass transition at a rate close to 20 °C/kbar.[24] The range of temperature over which nucleation is expected to occur should therefore be 60 °C wider at 2 kbar than at atmospheric pressure. Such an effect would translate into a widening of the pressure range over which nucleation would occur at constant temperature. Regardless of the origin of the effect, it is of considerable importance to the processing of objects from this polymer.

The occurence of a regime II–regime III transition in this polymer was not unexpected, since it is now recognized as the common regime transition.[20] The supercooling at which it occurs is quite large, 108 °C, but is presumably a result of the stiffness of the polymer. Studies by van Antwerpen[13] of PET as a function of molecular weight showed that nonspherulitic growth could be detected in light-scatterng studies for a low molecular weight specimen. Presumably this was a result of regime I growth; however, the molecular weight used here was too high for such a regime to be observed. Unfortunately, the crystallization studies under pressure could not be carried out at sufficiently high temperatures for the regime II–regime III transition to be observed at elevated pressures (because of the bulk of the bomb). Data obtained were therefore all typical of regime III growth.

The most difficult observation to understand is the large increase with pressure of the fold surface free energy. Generally three basic modes of pressure dependence can be expected, dependent on the topography of a fold. First, there is an insensitivity to applied pressure, such as that observed for polyethylene,[2] which arises in the case of tight folds in which little change in conformation is possible. Second, there is a step increase with increasing pressure, such as that observed for *cis*-polyisoprene, in which the folds are loose or may be short nonadjacent reentry folds and hence capable of specific conformational rearrangements. In that case a step increase in σ_e occurs since the additional configurational energy generated by a more constricted fold is balanced by a $P\Delta V$ term that arises from the contraction in effective fold volume. Third, there is a steady increase in σ_e that would be expected in the case of long switchboard folds since contraction to more energetic configurations would be averaged over the long fold.

Although the latter possibility seems to apply here in terms of the general scheme, the increase in σ_e with pressure is much larger than would have been anticipated. In the case of PET the infrared data have been interpreted by Koenig and co-workers[11,18] in terms of adjacent reentry folding. The appearance of a specific absorption that was characteristic of neither the crystalline nor amorphous phase led to the assumption of tight adjacent reentry folds believed to be composed of the two ethylene groups together with two ester groups. The studies of this particular infrared band reported here confirm the general phenomenology reported by Koenig's group. The intensity of the band increases with crystallinity, and the ratio of its intensity to that of a crystalline band remains approximately constant. However, the major continuous increase in the fold surface free energy with pressure is not consistent with the infrared data when it is interpreted in terms of adjacent reentry.

Any attempt at altering the length of chain present in a fold would require the incorporation of at least two mers into the fold because of the size and bulk of the benzene rings. Additionally, the size of the fold generated would be so large as to prevent the packing of the folds into the surface unless only a small fraction of them were adjacent reentry. A large increase in fold surface free energy similar to that observed here can only result from the generation of highly constricted chains possibly combined with additional contributions from the polar groups. It should also be borne in mind that the data are typical of regime III crystallization, in which the amount of tie chains, cilia, and switchboarding is maximized. It therefore appears that the surface structure is more akin to the interfacial layer approach of Mandelkern.[25] It appears that the increase in σ_e with pressure is a direct result of the influence of the applied pressure during crystallization on the configurations possible in the stiff chains of this interfacial layer. Although it is clear that the anomalous infrared absorption is associated with crystal formation, but not the crystal itself, it appears that the constricted conformation giving rise to it is not an adjacent reentry fold but a partially extended section of molecule present in a larger section of chain located in the surface. Since poly(ethylene terephthalate) has phenyl groups in the backbone, it should be recognized that it is partially a semirigid or rigid molecule, such as liquid-crystalline polymers, in which folding cannot take place.

Alternative explanations would require that some parameter, such as the heat of fusion, show an unusual dependence on pressure. Since this parameter did not vary on melting at atmospheric pressure of pressure-crystallized samples, any major change seems unlikely. It would be expected to change significantly if, for instance, an intervening phase such as a mesomorph appeared on pressurization. Crystallization through such an intervening state would undoubtedly render our calculations totally inaccurate. However, there is no evidence for such a state being generated. There have always been serious problems in the analysis of X-ray diffraction patterns from PET fibers.[26,27] Some have been interpreted in terms of an additional "phase" being present. This phase could of course be a constricted interfacial layer of intermediate density. PET has always been unique in terms of the large effect of crystallinity on the glass transition temperature, suggesting that at least a part of the amorphous phase is nonrandom.

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