The existence of a stable β form in oriented poly(butylene terephthalate)

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The existence of stable β form crystallites in poly(butylene terephthalate) has been investigated. Wide angle X-ray measurements suggest that such crystallites are only stable provided that they are of comparatively small dimensions and that they are then poorly connected to the bulk polymer. A simple theoretical model is presented to explain the stability of the crystals in terms of the contributions to the free energy from both the crystallites and the surrounding amorphous material.

(Keywords: poly(butylene terephthalate); β-form crystallites; free energy)

INTRODUCTION

Poly(butylene terephthalate) or poly(tetramethylene terephthalate) (4GT) became the subject of much interest in the mid 1970s when three groups of workers[1–3] independently reported that it could exist in two distinct crystalline forms. The α form was found in a relaxed sample, whereas the β form could only be observed when the sample was held under strain. There have been a number of attempts to determine the unit cells for the two crystalline forms[3–6], and there is still some degree of controversy regarding this. However, the general consensus is that in the α form the molecular chain is not fully extended, probably with the glycol residue in a *gauche–trans–gauche* conformation, whereas in the β form the chain is fully extended with the glycol residue in the all *trans* conformation. There has been considerable interest in the mechanism of the α–β transition, and this has been modelled for static and dynamic measurements[7,8].

The research reported in this paper stemmed from some more recent observations by Lu and Spruiell[9], and by Perry *et al.*[10], that it was possible to obtain samples of 4GT which contained the β form in the unstrained state. Lu and Spruiell's results suggested that the proportion of β form was dependent on the processing conditions, increasing with increasing draw ratio and decreasing draw temperature, i.e. increasing with increasing draw stress. In this paper we describe several routes to the production of samples containing stable β crystallites, examine their structure and properties, and propose an explanation for the factors which determine their stability.

EXPERIMENTAL

Sample preparation: fibres

Spinning. Four sets of spun yarns were prepared by melt spinning (*Table 1*) using 4GT polymer provided by Hoechst-Celanese. Samples 1, 2 and 3 were melt spun at 250°C in the Department of Textile Industries at the University of Leeds. A 24 hole spinneret (hole diameter 0.51 mm) was used and yarn taken up directly on a bobbin at the three wind-up speeds indicated in *Table 1*. Sample C was prepared at a higher wind-up speed of 3000 m min^{-1} by Hoechst-Celanese.

Drawing. To facilitate the subsequent X-ray analysis of the drawn fibres, drawing was usually carried out using an Instron tensile testing machine, rather than a draw frame. The fibre samples were therefore wound on a piece of card, creating a bundle of fibres of ~5 cm length and mounted in an Instron prior to being drawn at a cross-head speed of 1 cm min^{-1} at room temperature to a machine draw ratio of 2.

The Instron drawing was undertaken for all four spun yarn samples. Samples 2, 3 and C were also drawn after annealing in a vacuum oven at 155°C for ~21 h with the sample under no tension.

Finally, sample C was drawn on a small draw frame between moving rollers in a silicone bath at 100°C.

Sample preparation: tapes

For comparison with previous research, tapes were spun by melt extrusion through a rectangular slit. The extrudate was immediately quenched into water at ambient temperature and wound up at ~13 m min^{-1}, resulting in isotropic homogeneous tapes with cross-sectional area of the order of 10^{-6} m^2. The tapes were drawn on a small draw frame in silicone oil at 100°C to a draw ratio of 4.

Table 1 Precursor yarns

Sample identification	Number of filaments	Source	Wind-up speed (m min^{-1})
1	25	Leeds	320
2	25	Leeds	800
3	25	Leeds	1120
C	66	Celanese	3000

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* Deceased. The research described in this paper formed the basis of Dr Julian Roebuck's *PhD Thesis*

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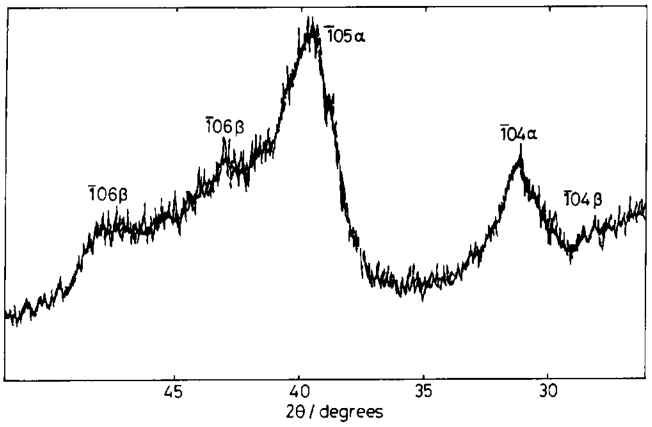

Figure 1 Meridional X-ray diffraction spectrum of the as-spun Celanese fibres (sample C)

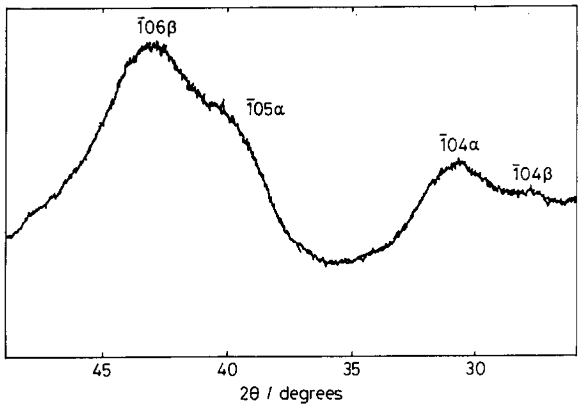

Figure 2 Meridional X-ray diffraction spectrum of sample C after cold drawing

Characterization of spun and drawn fibres

The primary characterization of the fibres was by wide angle X-ray diffraction, but i.r. and Raman spectroscopy and dynamic mechanical measurements were also employed following procedures developed in previous studies[8,11]. In the X-ray analysis, the diffraction peaks of importance were for the α phase the $(\bar{1}04)$ and $(\bar{1}05)$ at 31.4 and 39.4°, respectively, and for the β phase the $(\bar{1}06)$ and $(\bar{1}04)$ at 43 and 28°, respectively.

In the case of the spun yarns, samples 1–3 showed poor or negligible crystallinity and only the α phase was discernible. Sample C did show some β phase but was mainly in the α conformation (*Figure 1*).

These results for the spun yarns were confirmed by i.r. and Raman spectroscopy. Sample C showed i.r. absorption bands at 845 and 963 cm^{-1} corresponding to the β extended form. In the Raman spectrum, sample C showed lines at 965 and 1044 cm^{-1} corresponding to the β form.

After cold drawing the spun yarns in the Instron, sample C showed a substantial proportion of material in the β phase (*Figure 2*). This is confirmed by the i.r. and Raman spectra (*Figures 3* and *4*).

After cold drawing, spun yarns 2 and 3 showed very weak X-ray diffraction 'peaks' at 43°, but sample 1 did not show any discernible crystallinity.

However, sample C, after annealing and cold drawing, showed a substantial proportion of the β phase (*Figure 5*), whereas after annealing only the α phase can be seen (*Figure 6*). Furthermore, sample C showed a significant proportion of the β phase on hot drawing at 100°C on the draw frame.

SAXS measurements

SAXS measurements were carried out using a Franks camera and Ni-filtered CuKα radiation. The system was capable of discerning any long range periodicity up to a limit of ~250 Å.

Table 2 summarizes the results of the SAXS measurements.

Samples which had only the α phase present (samples b and f) showed a clear, but not intense, two bar pattern typical of a lamellar structure with a long period of the order of 100 Å which is rather less than was seen

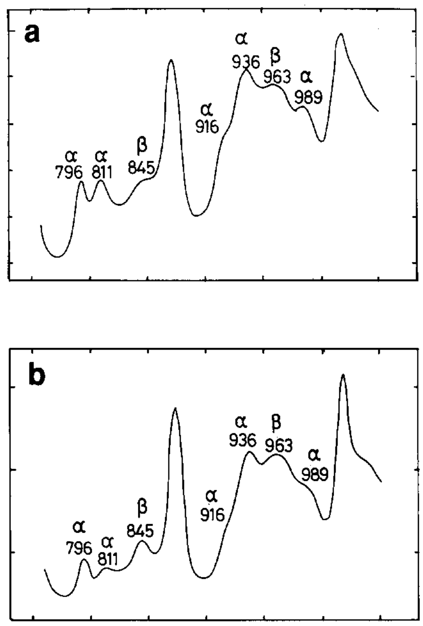

Figure 3 (a) I.r. absorption spectrum of sample C. (b) I.r. absorption spectrum of sample C after cold drawing

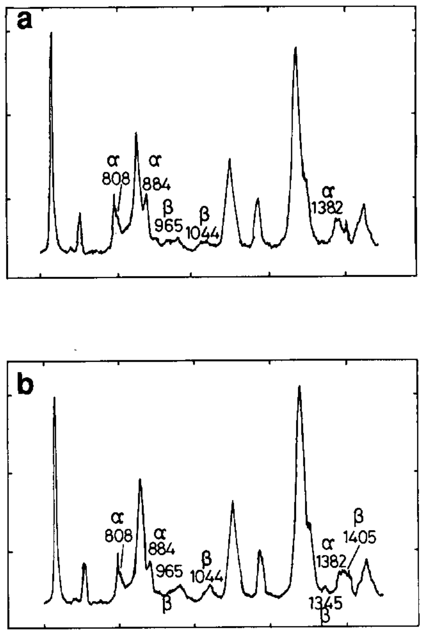

Figure 4 (a) Raman spectrum of sample C. (b) Raman spectrum of sample C after cold drawing

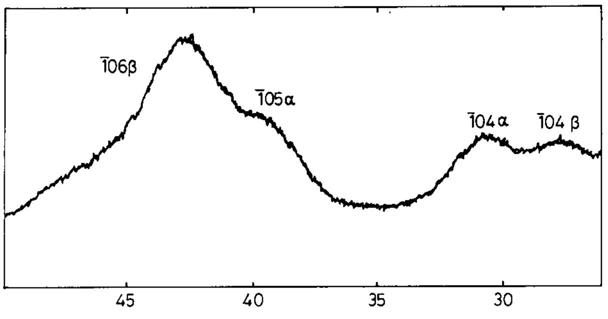

Figure 5 Meridional X-ray diffraction spectrum of sample C after annealing and then drawing

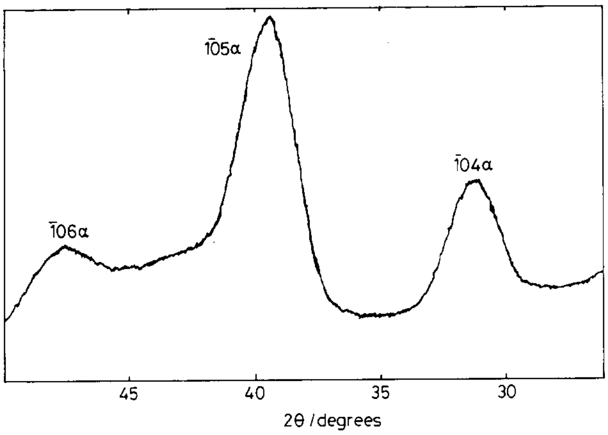

Figure 6 Meridional X-ray diffraction spectrum of sample C after annealing

previously[2] but this is probably because different processing conditions were used. Sample e, which contained some of the crystalline fraction in the β form, showed some evidence of a two bar pattern with a similar periodicity. The key observation, which is relevant to the present study however, is that the diffracted intensity was very low by comparison with the 'α only' samples. This suggests that any lamellar structure present was only weakly developed.

Line breadth and crystal strain measurements

Two X-ray techniques have been used to investigate the structure and morphology of the various tapes and fibres considered. These are line breadth and crystal strain measurements which have been used to powerful effect in studies of other oriented polymers[12–14] and have provided strong evidence in support of proposed morphologies. These measurements were carried out on the C samples mentioned above and on the spun tapes which were produced in this laboratory.

Line breadth measurements. Line breadths were measured using either a scanning diffractometer or a position-sensitive detector together with an extensometer where measurements were required under strain.

Instrumental line breadths were generally substantially smaller than the observed breadths and a simple correction was made for instrumental broadening by assuming Gaussian line shapes and subtracting the instrumental breadth from the observed breadth in quadrature. The Scherer equation was then used to estimate crystallite sizes. Although disorder broadening can be significant in these kind of materials there was no reliable way of assessing its magnitude since higher order reflections were not measurable. The sizes which were derived are therefore effective sizes which may not be correct in an absolute sense but are adequate for the purpose of comparing different samples.

One problem that arose was that the differences between the Bragg angles of the significant equatorial reflections from the α and β forms are comparable with the breadths of the lines themselves. The (010) reflections of the two forms are separated by ~0.5° and the (100) reflections by ~1.0°, which is to be compared with typical line breadths of ~1.5°. There was thus a problem of overlap which made it difficult to measure line widths directly. Computer simulations were carried out in order to estimate accurate breadths for the individual lines[15]. These simulations involved using plausible line shapes and data about the relative intensities derived both from other X-ray measurements and crystallinity estimates. This process enabled reasonably reliable figures to be deduced for the widths of the individual components of the overlapping reflections but it was not possible to do anything other than ascribe the *same* width to each component. There was no problem with the meridional reflections.

Table 3 shows a summary of the crystal sizes deduced using these measurements.

Considering first the meridional measurements it is seen that the length of the β form crystallites in the draw, or c, direction, was always less than the length of the α form crystallites.

The equatorial reflections show a similar pattern in the drawn and annealed tape (sample b). The identical figures which are shown for the other two samples containing β form arise, as mentioned above, from the approximation method which was used to separate the overlapping reflections.

The affect of annealing is generally to increase lateral sizes substantially (e.g. samples a and b) but to increase longitudinal sizes only marginally (samples c and d). Cold drawing, on the other hand, causes significant reduction in lateral sizes but little change in the longitudinal dimensions (samples a and c). Since this is the process which generates the stable extended β crystalline phase, and annealing brings about reversion to the α form, it seems likely that the crystalline dimensions in the sample have considerable relevance to the existence of the stable extended form.

Crystal strain measurements. In these measurements samples were subjected to a programme of mechanical strain during which changes in the Bragg angle of the meridional reflections were followed using a position-sensitive detector as described by Thistlethwaite *et al.*[14].

The result of such measurements is an 'apparent crystalline modulus', the relationship of which to the

Table 2 Long periods measured using SAXS

Sample identification	Sample	Estimated long period (Å)
b	Drawn, annealed tape	98 (±10)
f	Drawn, annealed fibres	90 (±10)
e	Annealed, drawn fibres	(107) (±10)

Table 3 Longitudinal (fibre direction) and lateral crystallite sizes measured using WAXS

Sample identification	Sample	Longitudinal crystallite size (Å) α phase $(\bar{1}04)$	 α phase $(\bar{1}05)$	 β phase $(\bar{1}06)$
a	Drawn tape	40	35	27
b	Drawn, annealed tape	72	70	54[a]
c	As-spun fibres	45	40	–
d	Annealed fibres	42	53	–
e	Annealed, drawn fibres	51	50	31
f	Drawn, annealed fibres	66	66	56[a]

Sample identification	Sample	Lateral crystallite size (Å) α phase (010)	 α phase (100)	 β phase (010)	 β phase (100)
a	Drawn tape[b]	63	45	63	45
b	Drawn, annealed tape	154	120	96	54
c	As-spun fibres[b]	83	54	–	–
d	Annealed fibres	128	88	–	–
e	Annealed, drawn fibres[b]	44	30	44	30

[a] Samples held at ~14% strain

[b] Samples containing both crystalline phases

The uncertainty in each value is ~4 Å

Table 4 Lateral crystallite sizes measured using WAXS

	Modulus (GPa) α form	 β form
Annealed and drawn fibres	5 ± 2	>36
Drawn and annealed tapes (ref. 16)	11 ± 2	19 ± 2
Drawn and annealed tapes (this work)	10 ± 2	19 ± 3
Annealed and drawn fibres held under tension	–	35 ± 3

actual modulus of the crystalline unit provides useful pointers to the morphology of the materials and, in particular, to the extent of mechanical linkage, or connection, of the crystalline fraction with the bulk material. These measurements were not easy since the reflections were broad and, in some cases, of quite low intensity. However a pattern emerged which suggested a morphology which is able to account for the existence of the stable β form at room temperature.

Table 4 shows a summary of the data. The apparent modulus of the α form crystals in the annealed and drawn fibres was measured to be 5 ± 2 GPa which contrasts with a figure of 11 GPa found by Smith[16]. The modulus of the β component was, by comparison, at least twice that seen in tape samples held under tension by Smith and by us in drawn and annealed tapes. This immediately suggests that the α crystals are experiencing a concentration of stress, as we have found to be quite common in other materials[12–14] but that the β crystalline component is partially disconnected from the bulk material and thus experiences a smaller stress than is being applied to the whole sample.

When the present samples were held under strain so that the whole crystalline fraction had converted to the β form a similarly high apparent modulus of 35 ± 3 GPa was measured.

DISCUSSION

General considerations

It has been shown that the crystallites in samples containing the extended form are small compared with those in annealed samples. The crystallite size measurements and the high values for the apparent crystalline moduli also suggest that the stable extended form crystallites are somewhat smaller laterally than those which return to the α conformation. Although these conclusions are based on somewhat indirect evidence, they are consistent with the observation that significant quantities of stable β phase have been reported only in poorly crystallized poly(butylene terephthalate) samples.

These considerations lead us to develop a theoretical model to describe the change in free energy which occurs when a crystallite embedded in an amorphous phase changes its conformation from the α to the β form. It is suggested that the crystallite is formed in the β conformation and to relax to the α form it must compress the surrounding amorphous regions. This will only occur if the reduction in the free energy of the crystallite is greater than the energy associated with the deformation of the adjacent amorphous regions. The free energy change in a crystallite is dependent on the *volume* of the crystallite, whereas the energy associated with the compression of the amorphous regions surrounding the crystallite depends on the volume of the amorphous regions affected which relates to the *surface area* of the crystallite. The total energy change is therefore related to the size and shape of the crystallite which will then be important in determining whether or not it will be stable in the extended conformation.

It is therefore proposed that the stability of the β phase is determined by the equilibrium free energy of the total system. It is assumed that, at room temperature, the activation energy for the β to α crystalline phase transition is $<kT$, where k is Boltzmann's constant and

T is the absolute temperature, and that the concentration of the β phase is therefore not affected by kinetic effects.

For simplicity, we assume that the crystallite is a cylinder of length L in the draw direction, with a circular base of diameter s. Furthermore we will assume that when the crystallite contracts we need only consider the change in axial strain, which is the order of 0.1, and can neglect the increase in lateral strains which are of the order of 0.03 (corresponding to a total observed decrease in volume of ~4%).

The change in free energy for a given crystallite in contracting from the β to the α conformation is given by

$$\Delta F = n(\Delta U - T\Delta S) + \Phi \tag{1}$$

where n is the number of monomer units in the crystallite and Φ the energy required to deform the adjacent amorphous material. The term in parentheses is negative and hence favours the transformation. For a crystallite to be stable in the β conformation $\Delta F > 0$. Hence the transition from a stable extended conformation to the situation where the α conformation is stable will occur at $\Delta F = 0$. The value of Φ is found by integrating the strain energy in volume elements surrounding the crystallite:

$$\Phi = \int 1/2 E_a \varepsilon^2 \, \mathrm{d}V \tag{2}$$

where E_a is the Young's modulus of the amorphous regions and ε is the strain in any element of the amorphous regions of volume $\mathrm{d}V$.

The crystal strain measurements indicate that there is little or no continuity of stress between the crystallites and the amorphous regions in the draw direction. It will therefore be assumed that if a crystallite contracts the amorphous material adjacent to the crystal surfaces in the axial direction will be unaffected. In the lateral direction, however, it will be assumed that there is continuity of strain such that the strain in the amorphous regions has a maximum value equal to the crystal strain at the crystal surface, decaying to zero as the distance to the crystallite increases. In the spirit of St Venant's principle, it will be assumed that the crystal strain ε_c decays exponentially with a characteristic length $w = L/2$, such that

$$\varepsilon_x = \varepsilon_c \exp\left(-\frac{x}{w}\right)$$

The strain energy in a volume element of the amorphous regions a distance x from the surface of a cylindrical crystal will then be given by

$$\mathrm{d}\phi = 1/2 E_a \varepsilon_x^2 2\pi L (s/2 + x) \, \mathrm{d}x \tag{3}$$

and the total energy required to deform the adjacent amorphous regions is

$$\begin{aligned} \phi &= \pi E_a \varepsilon_c^2 L \int_0^w \exp\left(-\frac{2x}{w}\right)(s/2 + x) \, \mathrm{d}x \\ &= \frac{\pi E_a \varepsilon_c^2 L}{4} (sw + w^2) \end{aligned} \tag{4}$$

The number of monomer units in a crystallite is given by

$$n = \frac{\rho_0}{m} L s^2 \tag{5}$$

where ρ_0 is the density of the crystallite and m is the mass of a monomer unit. Combining equations (1), (4) and (5) and putting $w = L/2$ we have

$$\Delta F = \left[\frac{\rho_0}{m}(\Delta U - T\Delta S)\left(\frac{s}{L}\right)^2 + \frac{\pi}{8} E_a \varepsilon_c^2 \left(\frac{s}{L}\right) + \frac{\pi}{16} E_a \varepsilon_c^2\right] L^3 \tag{6}$$

Critical crystal size and shape

The critical values of s and L are found when $\Delta F = 0$. Equation (6) shows that for $\Delta F = 0$ we have a quadratic equation in s/L which can be written as

$$A\left(\frac{s}{L}\right)^2 - B\left(\frac{s}{L}\right) - \frac{B}{2} = 0$$

This has the solution

$$\frac{s}{L} = \frac{B \pm \sqrt{B^2 + 2AB}}{2A} \tag{7}$$

where we need consider the positive root since s/L must be >0.

The requirement for a crystallite to remain in the extended phase after processing is therefore given by

$$\frac{s}{L} < \frac{B + \sqrt{B^2 + 2AB}}{2A} \tag{8}$$

where

$$A = \frac{\rho_0}{m}(T\Delta S - \Delta U)$$

and

$$B = \frac{\pi}{8} E_a \varepsilon_c^2$$

Calculation of the critical value of s/L

To estimate A we require the density of the β form unit cell (1340 kg m^{-3}) and the mass of a monomer unit (0.22 kg divided by Avogadro's number) together with values for ΔS and ΔU. The question of the entropy difference between the two states is difficult. At a simple level there would appear to be no configurational entropy change if a crystallite in the extended form relaxes homogeneously to the α form. In this case the only contribution to the value of A is from ΔU. However Al-Jishi and Taylor[18] examined the transition between the two forms and suggested that there *is* a small entropy contribution to the free energy which is related to the vibrational modes of the tetramethylene segments although they did not quantify it. In view of the uncertainty therefore we first take the simple option and calculate A ignoring the entropy term.

Yokouchi *et al.*[3] carried out calculations on the theoretical unit cells and suggested a value of -25 kJ mol^{-1} of monomer for ΔU. This leads to a value of ~150 MPa for A. On the other hand Tashiro *et al.*[17] and Al-Jishi and Taylor[18] quote quite different values of -1.34 and -1.2 kJ, respectively. These figures lead to a value of ~10 MPa.

There is also another way of obtaining an estimate of A. Since it has been shown that the plateau in the 4GT stress–strain curve corresponds to the crystal phase transition, and that highly crystallized 4GT can be approximated by a series model, it is a reasonable assumption that the area under the plateau region of the curve corresponds to the energy required to transform the crystalline phase. We then have

$$A = \frac{\bar{\sigma}\Delta\varepsilon}{\chi_c}$$

where σ is the average stress along the plateau, $\Delta\varepsilon$ is the length of the plateau and χ_c is the crystallinity. Substituting typical values gives

$$A = \frac{80 \times 0.1}{0.4} = 20\,\mathrm{MPa}$$

We have therefore concluded that a realistic value for A is in the region of 20 MPa.

The value of B is more readily estimated. The Young's modulus of amorphous 4GT is ~4 GPa, and the strain in the crystallite is ~0.1. Hence B is of the order of 20 MPa.

These considerations lead to the conclusion that A and B can be considered to be of similar magnitude. Referring back to equations (7) and (8) it is then predicted that:

$$\frac{s}{L} \leqslant \frac{A + \sqrt{2A^2}}{2A}$$

i.e.

$$\frac{s}{L} \leqslant 1$$

This prediction is consistent with the results reported above.

Preparation of the stable extended phase

From the assumed model it can be seen that a crystallite of volume $\frac{1}{4}\pi L s^2$ occupies an effective exclusion zone of volume $\pi L(s/2 + w)^2$. With $w = L/2$, the proportion of crystalline phase χ_β is given by:

$$\frac{s^2}{(s + L)^2} \tag{9}$$

If $s/L < 1$ we have $\chi_\beta < 0.25$.

This result is consistent with the observation that the samples containing the stable β form are of low crystallinity. For example, Lu and Spruiell[9] reported a maximum of 19% β form.

The most stable β form crystallite size

The free energy is a function of both the lateral and longitudinal dimensions of a crystallite (equation (6)). By differentiating with respect to s and L separately and equating each derivative to zero the turning points of the curve are obtained. We have

$$\frac{\partial}{\partial s}(\Delta F) = -2AsL + BL^2 = 0 \tag{10}$$

and

$$\frac{\partial^2}{\partial s^2}(\Delta F) = -2AL$$

so that ΔF has a maximum:

$$\frac{s}{L} = \frac{B}{2A}$$

i.e. for the estimated values of A and B:

$$\frac{s}{L} = 1/2$$

and crystallites of this shape would be stable in the extended β conformation. Next

$$\frac{\partial}{\partial L}(\Delta F) = -As^2 + 2BsL + \tfrac{3}{2}BL^2$$

and

$$\frac{\partial^2}{\partial L^2}(\Delta F) = 2Bs + 3BL$$

Substituting $A = B$ and stipulating that s/L is positive shows that ΔF has a minimum at $s/L \sim 2$, i.e. crystallites with this shape are least likely to remain in the extended β conformation.

CONCLUSIONS

It has been confirmed that certain processing conditions produce the stable β crystalline form of poly(butylene terephthalate) in oriented samples. X-ray diffraction studies show that in these instances the crystallites are of small dimensions and are poorly connected to the bulk material. A simple theoretical model which shows that the stability of the crystallites depends on their shape is based on the idea that relaxation to the α form can involve a smaller reduction in the free energy of the crystallite than the increase associated with deformation of the adjacent amorphous regions.

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