

Crystallization kinetics of oriented poly(ethylene terephthalate) from the glassy state

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Crystallization kinetics of oriented poly(ethylene terephthalate) have been studied in a temperature range close to T_g . It has been shown that orientation of the amorphous phase promotes a substantial increase in crystallization rate. This effect, in turn, depends on the crystallization temperature: the higher the temperature, the stronger is the effect of orientation. From experimental results it was possible to make an estimation of parameters describing quantitatively the crystallization kinetics in the oriented state.

INTRODUCTION

In the field of technology of plastic materials, a complete understanding of the phenomena of orientation and disorientation associated with the solidification process is of great importance for the prediction of structure and properties of the material. In the case of semicrystalline polymers, the final structure of the product is, in general, the result of a number of operations in which crystallization and orientation take place simultaneously. Typical examples are melt spinning, hot drawing, thermal treatment of drawn fibres, extrusion of films etc.

A number of papers concerning various effects observed during the crystallization of polymers in oriented or deformed states has been published. In ref 1 a review of the present knowledge in this field is given. The observed effects can be divided into three groups related to thermodynamics, kinetics and morphology, respectively. A thermodynamic description, first presented by Flory², was extended by Kobayashi and Nagasawa³ and recently by Ziabicki⁴. These theories predict an increase of the equilibrium melting temperature mainly due to the decreased entropy content of the deformed macromolecular system. On a qualitative basis this effect was confirmed with experiments performed on crosslinked rubbers^{5,6}.

Very few papers dealing directly with a quantitative evaluation of kinetic parameters for uncrosslinked polymers have been published so far. It has been demonstrated that crystallization rate increases remarkably on increasing the orientation or deformation of macromolecular chains⁷⁻⁹, but the data obtained from these experiments show quite different results, even for the same polymer. The effect of orientation on kinetics was first discussed by Dunning¹⁰ in terms of crystallization kinetic theory and was later improved by other authors^{3,11}. As the agreement between theory and experimental data is only qualitative, it seems necessary to devote some effort to measurements that could provide quantitative parameters.

There is direct experimental evidence that molecular orien-

tion also strongly affects the polymer morphology. The effect consists mainly of a gradual transition from spherulitic to non-spherulitic morphology¹²⁻¹⁵. It is known that the orientation of crystals in crystallized samples depends on the orientation of the amorphous material prior to crystallization¹⁶⁻¹⁹ but the organization of polymer crystals obtained under molecular orientation is not fully understood.

From the above considerations it seems that the present level of knowledge in this field is inadequate as far as the importance of the effects of molecular orientation on the phase transition is concerned.

In the present paper our attention is given to the quantitative evaluation of the effect of molecular orientation on crystallization half-times for poly(ethylene terephthalate) (PET). In principle, we can expect that the magnitude of the effect discussed above may depend upon crystallization temperature. To check this possibility, our experiments were performed at different temperatures.

EXPERIMENTAL

PET was chosen mainly because of its low crystallization rate in the unoriented state as well as for its relatively high T_g . Due to these properties we were able to obtain amorphous preoriented samples using a melt spinning technique and to terminate crystallization after an appropriate time of thermal treatment by quenching. PET samples were prepared by melt spinning using the same conditions of spinning head and variable take-up velocities. The characteristics of the original filaments are shown in *Table 1*. It can be seen that samples PET 1 and PET 2, spun at relatively low take-up velocities, show very low densities corresponding to zero crystallinity. Sample PET 3 shows a slight increase of density which might indicate low crystallinity; no crystallinity, however can be seen in X-ray diagrams. Hence it can be argued that the observed increase of density may be connected with some order in the amorphous phase, rather than with the formation of real crystals. The consequence of increasing

Table 1 Characteristics of the initial material

Sample	Take-up velocity (m/min)	Density ρ (g/cm ³)	Crystallinity X_v	Birefringence $\Delta \times 10^3$	Orientation factor, f_a
PET 1	1250	1.336	0.00	8.9	0.032
PET 2	2000	1.336	0.00	12.3	0.044
PET 3	3000	1.342	0.04	33.8	0.123*

* Computed using the assumption $X_v = 0$

Table 2 Asymptotic values of absolute crystallinity (X_v) of oriented samples at various temperatures

T (°C)	PET 1	PET 2	PET 3
95	22.1	24.0	24.9
100	29.3	29.3	29.3
105	30.6	30.6	32.2
110	31.4	31.8	32.2
115	32.2	32.2	32.2

take-up velocity consists of a substantial increase in birefringence. Since all these fibres can be considered as amorphous, the differences in birefringence are directly related to the amorphous orientation. The orientation factors of the amorphous phase, computed from birefringence, are also reported in Table 1.

Densities

Densities of the fibres were determined using a density gradient column filled with CCl₄ and n-heptane mixture at room temperature. All samples were degassed under vacuum for 4 h before immersion in the column.

Absolute crystallinities, X_v

Absolute crystallinities were evaluated from densities using the relation

$$X_v = \frac{\rho - \rho_a}{\rho_c - \rho_a}$$

It is well known²⁰ that an overestimation can arise when density measurements are used to evaluate the crystallinity level in deformed samples. Since we are dealing with slightly oriented fibres in which, as shown in Table 1, the density of the amorphous polymer is still comparable with that of the isotropic material, application of the previous relation seems to be acceptable. The values of $\rho_c = 1.457$ and $\rho_a = 1.336$ g/cm³ were taken from ref 21.

Relative crystallinities, X_r

Relative crystallinities for each crystallization run were calculated by dividing the absolute values by the asymptotic values reported in Table 2.

Birefringence

Birefringence measurements were made using both a Reichert polarizing microscope equipped with Ehrsingaus compensator and a PZO interferometric head connected to

a polarizing microscope of the same manufacture. Results obtained by both methods are consistent.

Orientation factors

Orientation factors were estimated on the basis of Stain's equation²².

$$\Delta = X_v \Delta_c^0 f_c + (1 - X_v) \Delta_a^0 f_a + \Delta_f$$

On the assumption that no voids are present in fibres spun at moderately high take up velocities, form birefringence was always neglected. In the case of the initial samples ($X_v = 0$) the orientation factor of the amorphous phase is:

$$f_a = \frac{\Delta}{\Delta_a^0}$$

where $\Delta_a^0 = 0.275$ as reported by Dumbleton²³.

X-ray diffraction

X-ray patterns were recorded using a flat camera with pinhole collimation with Ni-filtered CuK α radiation.

Crystallization technique

Crystallization of samples was carried out in an oven with forced circulation of air heated to the appropriate temperature (T_c). Fibres were wound on a metal frame as tightly as possible without additional deformation. After appropriate times at T_c , samples were instantaneously quenched in a bath containing a mixture of ice, water and NaCl.

The range of T_c we explored (95° – 115°C) was chosen so that slow enough crystallization would ensure effective quenching.

RESULTS AND DISCUSSION

Curves illustrating the dependence of density on time for various crystallization temperatures are presented in Figure 1. This Figure is for the sample PET 2, which exhibits the intermediate value of initial amorphous orientation. The trend in the curves is similar to that for the remaining PET samples: in all cases the typical sigmoidal shape was observed. It is evident that crystallization half-times ($t_{1/2}$) decrease with increasing temperature. This behaviour can be understood

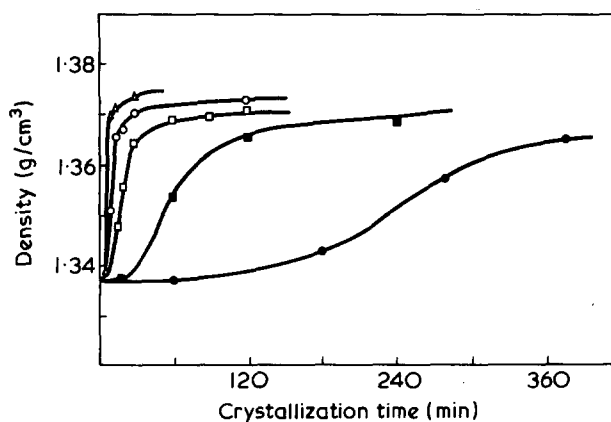


Figure 1 Density as a function of time for PET 2. ●, $T = 95^\circ\text{C}$; ■, $T = 100^\circ\text{C}$; □, $T = 105^\circ\text{C}$; ○, $T = 110^\circ\text{C}$; △, $T = 115^\circ\text{C}$

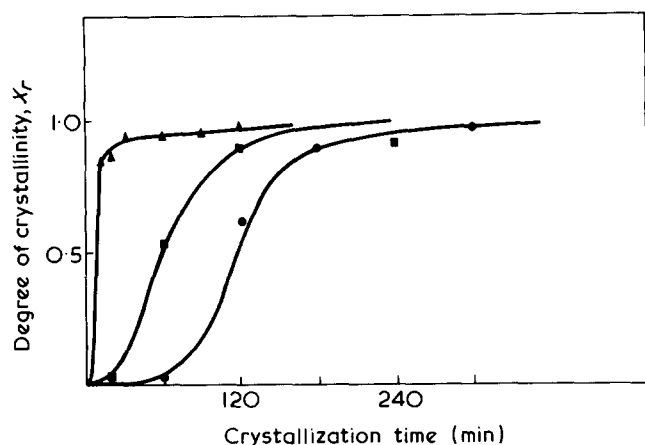


Figure 2 Relative crystallinity as a function of time at $T_c = 100^\circ\text{C}$. ●, PET 1 ($f_a = 0.023$); ■, PET 2 ($f_a = 0.044$); ▲, PET 3 ($f_a = 0.123$)

Table 3 Crystallization half-times of oriented PET at various temperatures

T ($^\circ\text{C}$)	$t_{1/2} \times 10^{-3}$ (sec)		
	PET 1 $f_a = 0.032$	PET 2 $f_a = 0.044$	PET 3 $f_a = 0.123$
95	17.19	14.40	1.92
100	7.02	3.54	0.48
105	4.80	0.84	0.36
110	0.90	0.66	0.18
115	0.60	0.30	—

taking into account that experiments were carried out in a range of temperature very close to T_g , i.e. below the temperature at which maximum crystallization rate appears.

The effect of molecular orientation on crystallization rate is evident from Figure 2 where X_r is plotted as a function of time at constant temperature for variously oriented PET samples. It may be seen that the higher the molecular orientation, the shorter is the half-time, indicating an increase of crystallization rate. The same regularity was observed at all temperatures under investigation.

On a qualitative basis, the same results have also been reported in the literature, both in theoretical^{3,4,10} and experimental^{7,17,18,24-26} papers.

In Table 3 the effects of temperature and molecular orientation on crystallization half-time are summarized. As was previously mentioned, we observe that for each molecular orientation, $t_{1/2}$ strongly decreases with increasing T_c . It is also noted that at each temperature, lower values of $t_{1/2}$ are observed for higher orientation factors. It is well known that the crystallization rate dependence on temperature can be represented by a bell-shaped curve^{27,28}. This shape was explained taking into consideration two processes having opposite temperature dependence, viz. the formation of nuclei, controlled by supercooling, and the transport of chain segments to the growing crystals.

Hoffman²⁹ has derived an equation involving a number of parameters not easy to evaluate from experiments. Unfortunately, these parameters do not remain constant over a wide range of crystallization temperatures. For this reason, Hoffman's equation can only be applied to processes occurring not too far from the melting point of the polymer. To avoid this difficulty Ziabicki¹ has proposed a three parameter

Gaussian equation to achieve the best fit to the existing experimental data. It was proved that for a number of polymers this empirical equation can be applied in the full temperature range between T_g and the melting temperature. The equation reads:

$$\frac{1}{t_{1/2}(T)} = \frac{1}{t_{1/2}^*} \exp \left\{ \frac{-4 \ln 2 (T - T^*)^2}{D^2} \right\} \quad (1)$$

where $t_{1/2}^*$ is the minimum half-time corresponding to maximum crystallization rate at the temperature T^* , and D is the half-width of the Gaussian curve.

In the case of PET these parameters are¹:

$$t_{1/2}^* = 42 \text{ sec}; T^* = 190^\circ\text{C}; D = 64^\circ\text{C} \quad (1a)$$

The Gaussian approximation for unoriented polymer is shown in Figure 3 together with the best fit of the experimentally obtained half-times for oriented PET. We can see that, for all temperatures, experimental curves lie above the Gaussian estimate of the reciprocal half-time for an unoriented polymer.

It has been shown¹¹ that, in the case of uniaxial deformation, the effect of orientation on crystallization rate can be represented by the equation:

$$\frac{1}{t_{1/2}(f_a)} = \frac{1}{t_{1/2}(0)} \exp(Af_a^2 + Bf_a^3 + \dots) \quad (2)$$

Applying equation (2) we can extend equation (1) to the cases of crystallization of oriented systems¹. For small orientations the higher terms in the expansion (2) can be neglected and the crystallization rate reads:

$$\frac{1}{t_{1/2}(T, f_a)} = \frac{1}{t_{1/2}^*} \exp \left\{ \frac{-4 \ln 2 (T - T^*)^2}{D^2} \right\} \exp(Af_a^2) \quad (3)$$

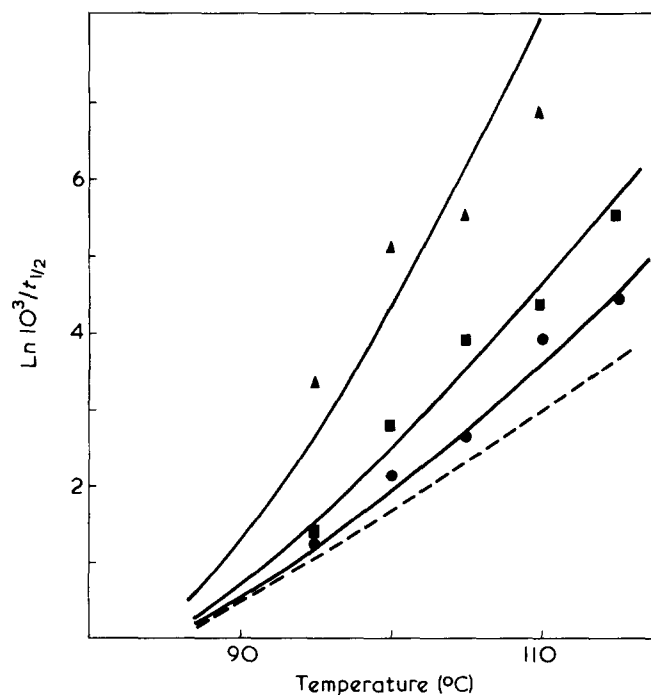


Figure 3 Crystallization rate dependence on temperature ($t_{1/2}$ in min). ●, PET 1; ■, PET 2; ▲, PET 3; (---), obtained from equation (1) for unoriented polymer

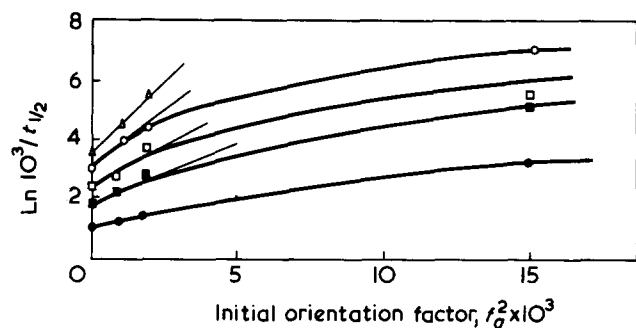


Figure 4 Crystallization rate dependence on initial orientation factor of the amorphous phase. ●, $T = 95^\circ\text{C}$; ■, $T = 100^\circ\text{C}$; □, $T = 105^\circ\text{C}$; ○, $T = 110^\circ\text{C}$; △, $T = 115^\circ\text{C}$

Table 4 Values of parameter A , at different temperatures

T ($^\circ\text{C}$)	A
95	210
100	370
105	570
110	725
115	940

From the logarithmic plot of equation (3) a linear dependence between the half-times and the square of the orientation factor could be foreseen. In Figure 4 our experimental data are presented in this logarithmic form. The points representing half-times for unoriented PET were estimated according to equation (1).

The parameter A , describing the sensitivity of crystallization rate towards amorphous orientation factor, can be evaluated from the initial slopes. The values obtained are listed in Table 4.

It is evident from Figure 5, that A increases with increasing crystallization temperature. The dependence can be expressed in mathematical form using the equation¹:

$$(\Delta T)^3 A(T) = C_1 + C_2 \Delta T \quad (4)$$

where $\Delta T = T_m^0 - T_c$, and T_m^0 is the equilibrium melting temperature in the unoriented state.

Assuming $T_m^0 = 284^\circ\text{C}$ according to Ikeda³⁰, our experimental data were fitted to the above equation using the linear regression method. As indicated by the correlation coefficient ($r^2 = 0.991$) equation (4) gives a good description of the temperature dependence of A .

The values of the parameters C_1 and C_2 obtained from this fitting are: $C_1 = 3.09 \times 10^{10} \text{ K}^3$; $C_2 = -1.55 \times 10^8 \text{ K}^2$.

It should be noticed however, that the constants C_1 and C_2 in equation (4), theoretically derived by Ziabicki^{1,4}, are both positive while our C_2 appears to be negative.

The figures reported here for A might somehow be affected by our assumption about the crystallization rates of unoriented PET. According to our investigations, equation (1) describes correctly a number of experiments reported by various authors; hence we consider that predictions made on the basis of this equation are more reliable than any single set of data arbitrarily chosen from literature.

If the crystallization kinetics of our polymer in the unoriented state deviates somehow from the estimate based on

equation (1) with the above mentioned constants (equation 1a), then the values of parameter A would be different; we believe, however, that such an effect should not be too significant. Moreover, if deviations affecting parameter A do exist, we presume that the temperature dependence of A will still be correct.

The values of A reported in ref 1 for PET are higher than those obtained in the present work. The value $A = 1000$ at 95°C reported by one of us¹⁸ was obtained using PET from a different source. For that sample it was shown that equation (1) with the constants (equation 1a), did not hold true.

It can be seen in Figure 4 that with increasing f_a the half-time of crystallization levels off. This deviation from linearity may indicate that to express adequately crystallization rate dependence we should also consider higher terms in the series expansion (equation 2). For evaluation of any higher coefficient it would, however, be necessary to accumulate much more data than we could at present obtain.

On the other hand one has to take into account that relaxation of molecular orientation may be associated with the crystallization, as was shown in ref 18. This relaxation can also be responsible for the observed deviations. Indeed, in the present work, variations of birefringence on time were observed. Typical examples are depicted in Figure 6 showing birefringence changes for PET 1 and PET 3 samples.

The birefringence depends both on crystalline and amorphous orientations; we can therefore expect that the observed variations should also be related to changes of amorphous orientation. This was already demonstrated¹⁸ for PET crystallized at 95°C . In the case of PET 1 and PET 2, birefringence decreases with time and, for high temperatures, it assumes negative values. A completely different behaviour appears on crystallizing PET 3 samples having relatively high initial orientation. In the latter case a remarkable increase of birefringence was observed.

Variations of birefringence can be explained on the basis of X-ray diagrams (see Figures 7a and 7b), showing different types of crystal orientation for PET 2 and PET 3 samples. From the patterns it can be argued that in the case of PET 2 the maximum distribution of c -axis is tilted with respect to the fibre axis. The tilt angle depends on temperature and on crystallization time. From such textures we can derive small positive, as well as negative values of birefringence. The X-ray pattern of PET 3 shows a preferred orientation of

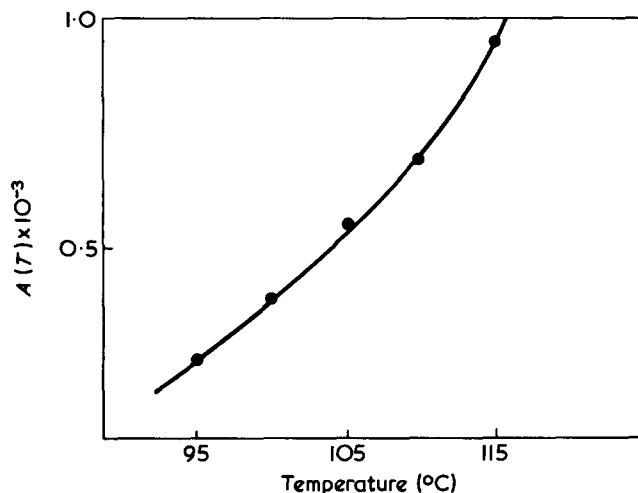


Figure 5 Temperature dependence of the parameter A

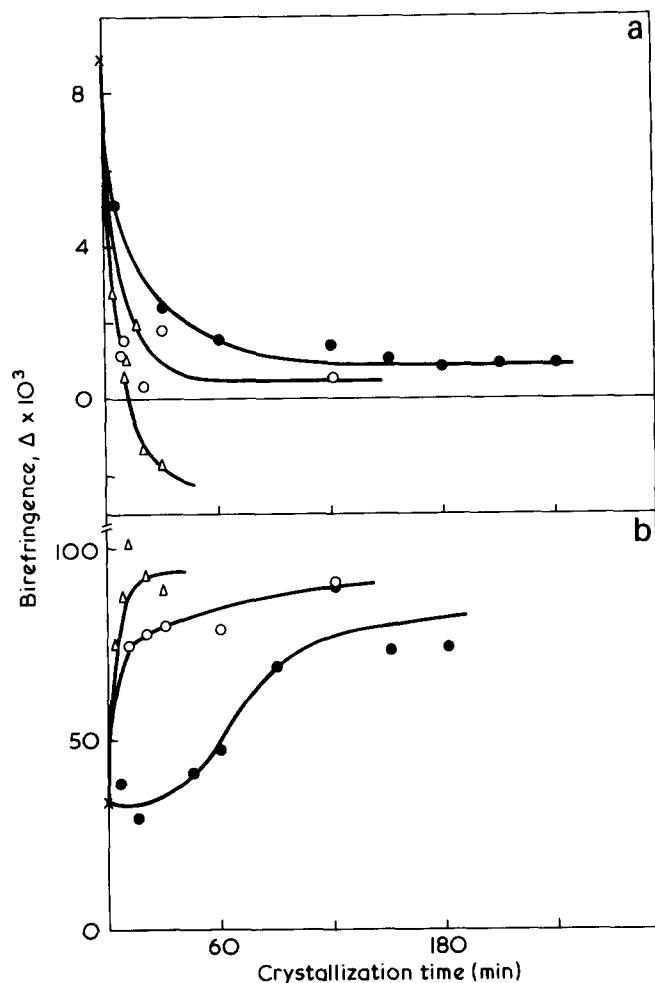


Figure 6 Birefringence as a function of time for two PET samples. (a) PET 2; (b) PET 3. ●, $T = 95^\circ\text{C}$; ○, $T = 110^\circ\text{C}$; △, $T = 115^\circ\text{C}$

the c -axis almost parallel to the fibre. Since there are indications^{16,18,31} that the orientation factor of the crystal phase is much higher than that of the amorphous phase from which crystals are formed, the strong increase of birefringence in PET 3 can be understood.

CONCLUSIONS

Summarizing the results presented in the previous sections we can conclude that the orientation of the amorphous phase plays a very important role in crystallization. Our experimental data seem to fit Ziabicki's phenomenological equation (equation 4). From this agreement a quantitative evaluation of parameters has been possible. The fact that both constants C_1 and C_2 in the equation for $A(T)$ derived by Ziabicki should be positive and C_2 obtained from the best fit of our data is negative, indicates that the consistency is purely coincidental and equation (4) should be considered as purely empirical when applied to our data. In fact equation (4) was derived for the temperature region close to the equilibrium melting temperature and was not expected to describe the situation at low temperatures as studied in this paper. It was shown that the parameter A increases with crystallization temperature and hence the effect of molecular orientation on crystallization rate becomes stronger at higher temperatures.

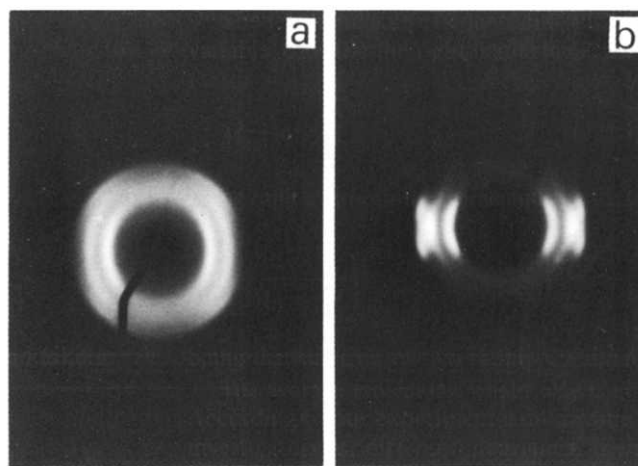


Figure 7 X-ray patterns of PET samples crystallized at 95°C for 120 min. (a) PET 2; (b) PET 3

Since this study was performed over a relatively narrow range of low temperatures, our values for the parameters probably cannot be applied safely to an extrapolation over a range of higher temperatures. They also should not be used to predict effects produced by very high orientation.

The orientation of the amorphous phase changes with time during crystallization, and because of this effect the actual instantaneous orientation factors may be different from the initial one. This fact might cause incorrect estimation of parameters. To improve this situation one should measure separately both amorphous and crystal orientations and carry out a more sophisticated analysis of the results. This work is currently being followed up in our laboratories.

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