Crystallization kinetics during hot-drawing of poly(ethylene terephthalate) film: strain-rate/draw-time superposition

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We have investigated the influence of strain rate during hot-drawing of poly(ethylene terephthalate) on the kinetics of overall crystallization and of crystal growth normal to the 010 and 100 planes. Drawing was at 90°C and at various strain rates between 0.01 s^{-1} and 2.1 s^{-1}. We found that changing strain rate simply shifts the crystallization rate curves along the log time axis, that the shift factor and the strain rate are related by a power law, and that the value of the exponent reflects the relative influence of two effects of molecular mobility: relaxation of orientation and enhancement of crystallization. The relative importance of these two effects was found to be different in different crystallographic growth directions: normal to the 100 planes, they almost exactly compensate each other; normal to the 010 planes, the relaxation effect dominates. By defining an 'equivalent time' for crystallization, degree of crystallinity at any strain rate can be predicted from knowledge of either draw time or draw ratio. A similar treatment permits prediction of crystallite size.

(Keywords: poly(ethylene terephthalate); crystallization kinetics; relaxation; strain rate; hot-drawn film)

INTRODUCTION

This paper continues our investigations of stress-induced crystallization during hot-drawing of poly(ethylene terephthalate) (PET) film[1], by focusing on its time-dependent characteristics. The influence of strain rate on crystallization is potentially complex, since it can have two competing consequences: decreasing strain rate increases time available for molecular interactions favourable to crystallization as well as molecular relaxations unfavourable to crystallization. The present study, however, reveals simple relationships between crystallization kinetics and strain rate, which depend on the relative importance of the relaxation and crystallization effects.

EXPERIMENTAL

Amorphous, undrawn PET film ($\bar{M}_n = 19\,000$, intrinsic viscosity = 0.60) was supplied by Rhône Poulenc. Drawing was carried out on an Instron tensile tester at 90°C and at nominal strain rates of 2.08, 1.04, 0.417, 0.0208 and 0.0104 s^{-1}. The aspect ratio of the sample was such that segments in the centre of the film did not change width during drawing. Thus structural characterization was carried out on specimens deformed in pure shear (constant width). The volume fraction crystallinity χ was estimated from density measurements using a density gradient column. Crystallite size normal to the 010 and 100 planes was determined by wide-angle X-ray scattering analysis, using profile-fitting procedures. Further details of the experimental procedures and the material are given in the previous paper[1].

RESULTS AND DISCUSSION

Strain-rate/draw-time superposition

Plots of crystallinity *versus* draw time are shown in *Figure 1a* for the five strain rates $\dot{e}$ studied; in *Figure 1b*, four of them have been shifted to superimpose the curve for the strain rate of 0.01 s^{-1}. Clearly there is excellent superposition. Moreover, it is apparent from *Figure 2* (solid line) that the shift $A_{\dot{e}}$ can be very precisely described by:

$$A_{\dot{e}} = C\dot{e}^n \qquad (1)$$

where $n = 1.11$ and, for the arbitrary reference strain rate $\dot{e}_0$ of 0.01 s^{-1}, $C = 165$.

It was shown in the previous paper[1], and by others[2,3], that decreasing strain rate delays the onset of crystallization to higher draw ratios due to relaxation of orientation during drawing. The magnitude of the relaxation effect is reflected in the value of n, and would be expected to depend on draw temperature. If induction and development of crystallinity were dependent only on strain level, and not on strain rate, there would be a linear ($n = 1$) relationship between $A_{\dot{e}}$ and $\dot{e}$ (*Figure 2*, broken line). Further insight into the significance of n emerges from a study of crystal growth kinetics.

Crystallite widths were measured normal to the 010 and 100 planes at different draw ratios and at three strain rates (Figure 7 in ref. 1). In *Figures 3* and *4*, crystallite width is plotted *versus* draw time. Considering that there is higher experimental scatter in these data than in the crystallinity data, the superposition is quite acceptable.

It is evident from *Figure 5*, however, that the nature of the power law relationship between $A_{\dot{e}}$ and $\dot{e}$ depends

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on the crystallographic direction of growth. For crystallite width normal to the 010 planes, $W(010)$, the relationship is almost the same as that for overall crystallization, whereas for $W(100)$, n is very close to unity. This result seems to suggest that crystallization normal to the 100 planes is essentially independent of strain rate and dependent only on the level of macroscopic strain (see also Figure 7 in ref. 1). However, in view of the significant strain-rate dependences of orientation development[3,4], overall crystallization, and $W(010)$ growth, we do not believe that the linear relationship between $A_{\dot{e}}$ and $\dot{e}$ for $W(100)$ arises from direct dependence of $W(100)$ growth on strain level. We suggest that it results from a balance of two opposing effects of thermally induced molecular mobility. On one hand, thermal mobility causes relaxation of orientation during drawing; on the other, it promotes crystallization by increasing the frequency with which suitable chain segments arrive in attachable vicinity of the crystal surface or nucleus. An example of the latter phenomenon in PET is the decrease in critical orientation for induction of crystallinity with increasing draw temperature[3].

When the relaxation effect dominates, decreasing strain rate delays the onset of crystallization to higher strains and reduces the rate at which crystallinity increases with

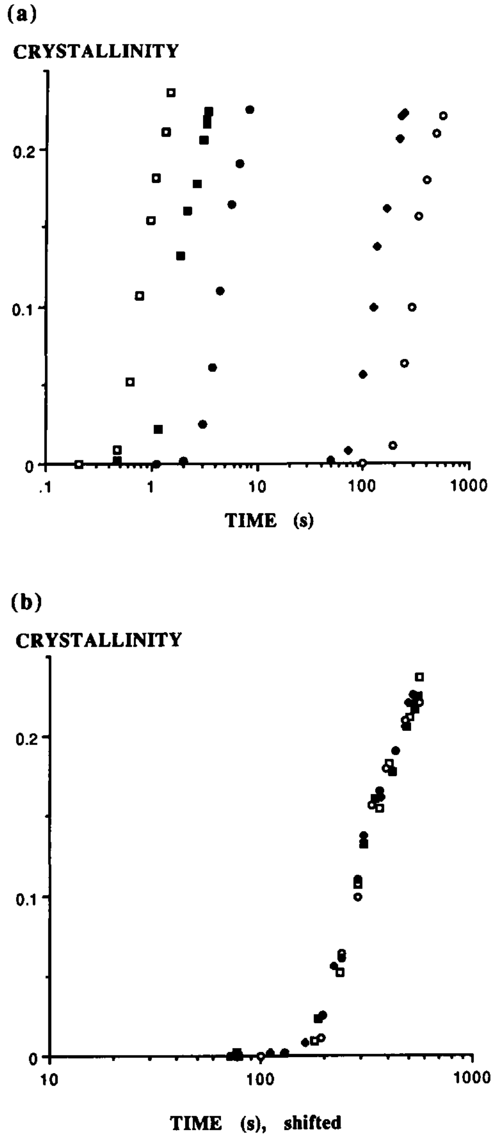

Figure 1 Crystallinity *versus* draw time for five strain rates: 2.1 (□); 1.0 (■); 0.42 (●); 0.02 (◆); 0.01 s^{-1} (○). (a) Real time and (b) shifted to superimpose the 0.01 s^{-1} strain rate data

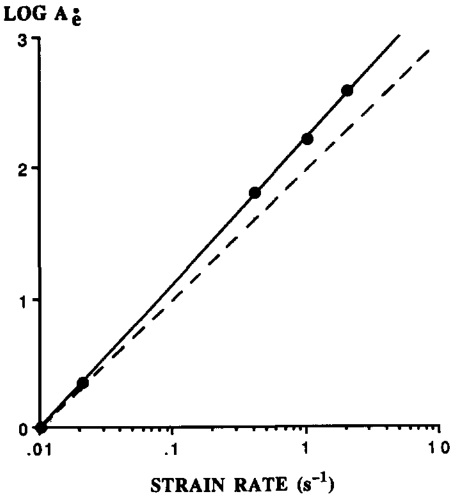

Figure 2 Relationship between shift factor $A_{\dot{e}}$ and strain rate, from the crystallinity data of *Figure 1*, giving $n = 1.11$. If the draw ratio dependence of crystallinity were independent of strain rate, n would be unity (– – –)

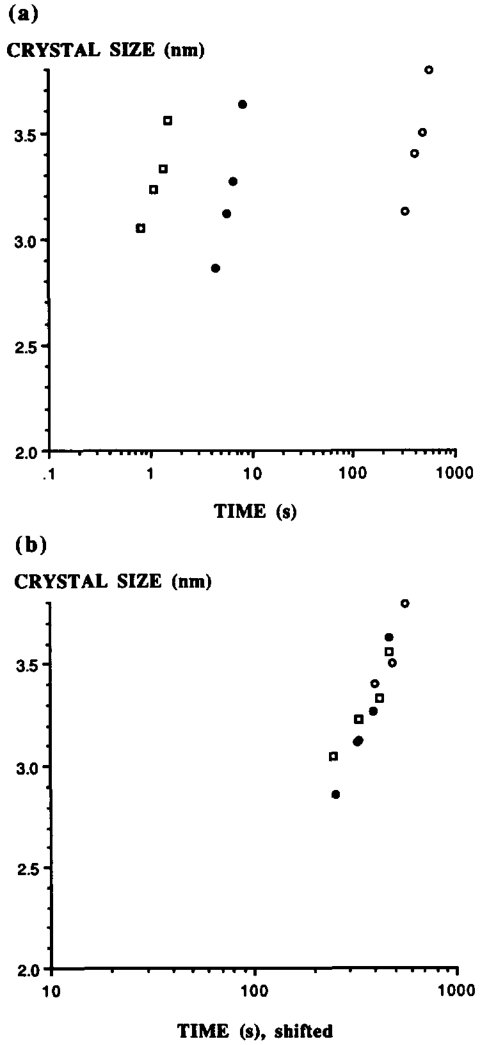

Figure 3 Crystallite width normal to the 010 planes *versus* draw time at three strain rates: 2.1 (□); 0.42 (●); 0.01 s^{-1} (○). (a) Real time and (b) shifted to superimpose the 0.01 s^{-1} data

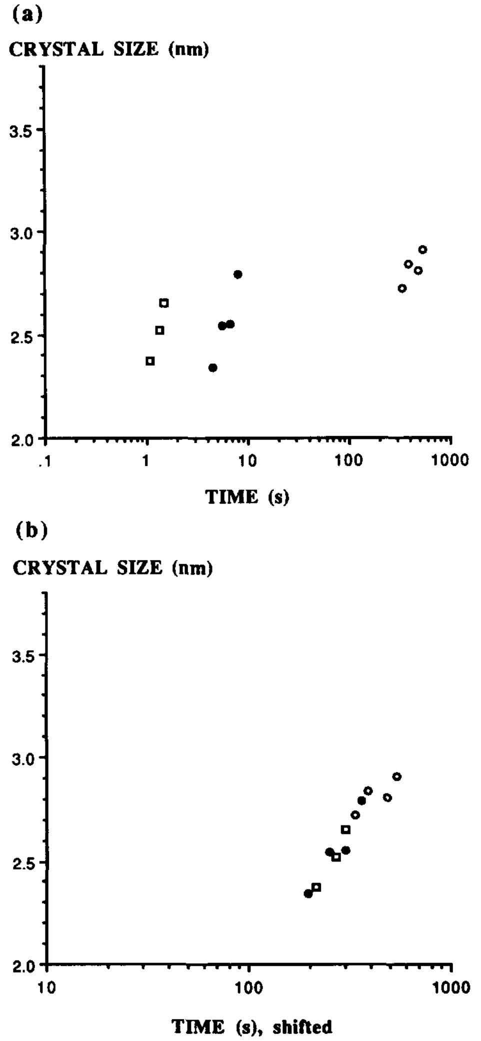

Figure 4 Crystallite width normal to the 100 planes *versus* draw time at three strain rates: 2.1 (□); 0.42 (●); 0.01 s^{-1} (○). (a) Real time and (b) shifted to superimpose the 0.01 s^{-1} data

strain level (Figure 5 in ref. 1). In this case, n is >1. If the crystallization effect were dominant, decreasing strain rate would shift the onset of crystallization to lower strains and would increase the rate at which crystallinity develops with strain level. In this case, n would be <1. An exact balance of these effects would give $n = 1$.

From the dependence of n on the growth face of the crystal, we deduce that there are local variations in the relative importance of the two mobility effects and that they arise from the nature of the molecular interactions in different growth directions. Normal to the 010 planes, n is >1, indicating that $W(010)$ growth is influenced more by molecular orientation, and therefore by relaxation effects, than by segmental mobility in the vicinity of the surface. Thus, increasing the time available during drawing results in a slower increase in $W(010)$ as a function of strain level due to the predominance of the relaxation effect. Normal to the 100 planes, segmental mobility makes a larger contribution to growth, being sufficient to exactly counteract the influence of orientational relaxation. Therefore, in the case of $W(100)$, $n = 1$ does not arise from time independence on a molecular level, but from the equivalence of two opposing time-dependent phenomena.

It follows that, for overall crystallization, $n = 1.11$ is an average of various values of n which depend on growth direction: since n for $W(100)$ is <1.11, n must exceed this value in some other growth direction. The nucleation stage may also have a characteristic value of n.

'Equivalent time' for crystallization

Equation (1) implies that we can predict the level of crystallinity at any strain rate from knowledge only of the elapsed time during drawing. To do this, we define an 'equivalent time' for crystallization as the time at some reference strain rate that would produce the same level of crystallinity as is produced at any other strain rate at the real time. In *Figure 6* the shifted data are shown as a plot of crystallinity *versus* equivalent time, on a linear scale, for the reference strain rate of 0.01 s^{-1}. Volume fraction crystallinity in the two crystallization regimes[1], regimes 1 and 2, is then given by:

$$\begin{aligned} \chi_1 &= \frac{d\chi_1}{dt_{eq}}(tA_{\dot{\varepsilon}} - t_1) \qquad && t_1 \leqslant tA_{\dot{\varepsilon}} \geqslant t_2 \\ \chi_2 &= \frac{d\chi_2}{dt_{eq}}(tA_{\dot{\varepsilon}} - t_2) + 0.15 \qquad && tA_{\dot{\varepsilon}} \geqslant t_2 \end{aligned} \tag{2}$$

where t is the real time, t_1 is the equivalent time for the onset of crystallization and t_2 is the equivalent time for the onset of regime 2. Note that 0.15 is the characteristic level of crystallinity at the onset of regime 2 (see ref. 1). A similar treatment would permit prediction of crystallite size.

Implications for higher strain rates

In some commercial processes, PET film is drawn at strain rates in the range 20–30 s^{-1}. It is therefore tempting to use equations (1) and (2) to predict the development of crystallinity at higher strain rates, beyond our present experimental capabilities.

Figure 7 shows predicted values of crystallinity *versus* draw time at 20 and 30 s^{-1}, compared with the experimental data at 2.1 s^{-1}. More interesting is the predicted relationship between crystallinity and draw ratio at these strain rates (*Figure 8*). Increasing strain rate from 2 to 20 s^{-1} decreases the draw ratio for onset of crystallization from ~1.9 to 1.7, but increasing strain

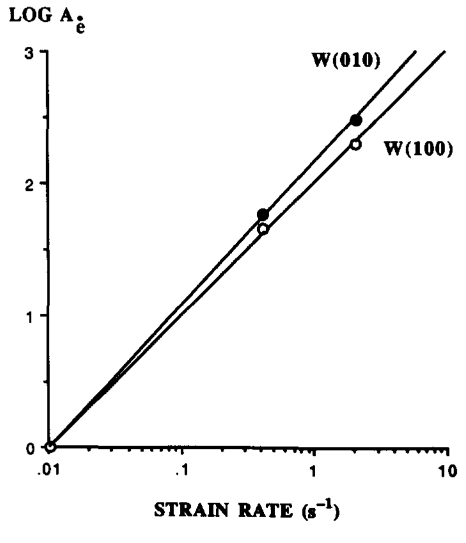

Figure 5 Relationship between shift factor $A_{\dot{\varepsilon}}$ and strain rate for crystallite growth normal to the 010 and 100 planes. For $W(010)$, $n = 1.08(5)$; for $W(100)$, $n = 1.00(5)$

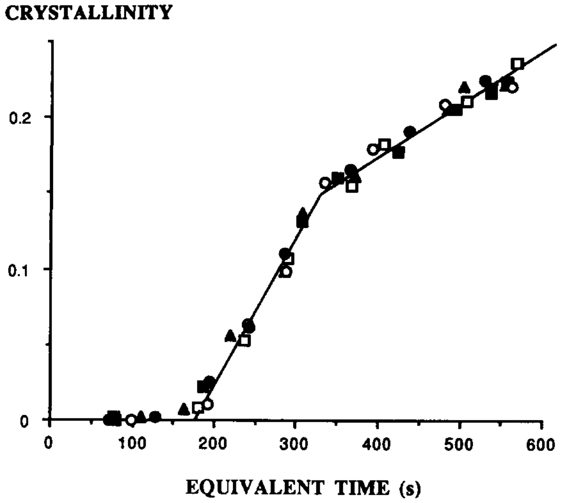

Figure 6 Crystallinity *versus* equivalent time at the five strain rates, for the reference strain rate 0.01 s^{-1}

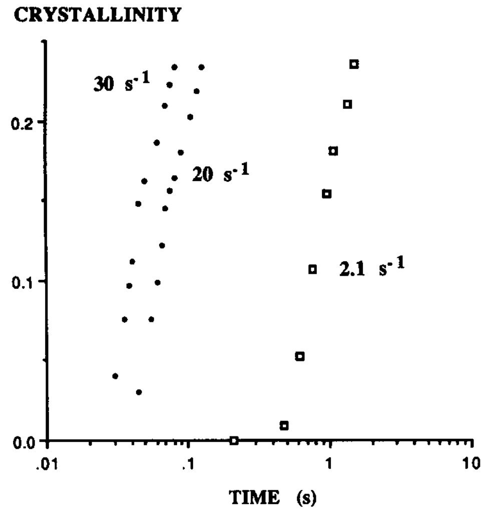

Figure 7 Crystallinity *versus* draw time for strain rates 30 and 20 s^{-1}, as predicted from equations (1) and (2), together with experimental data for strain rate 2.1 s^{-1}

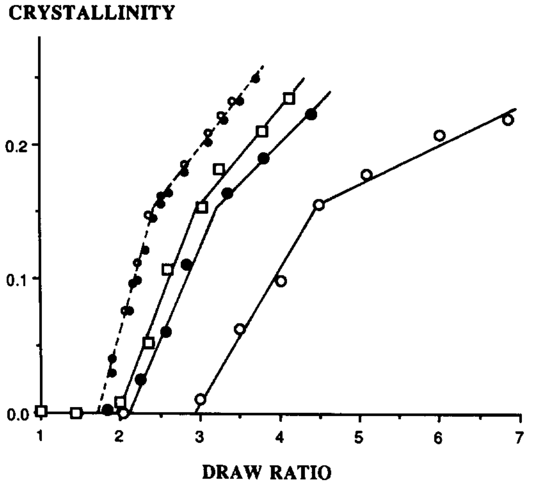

Figure 8 Crystallinity *versus* draw ratio for strain rates 30 and 20 s^{-1} (○, •), as predicted from equations (1) and (2), together with experimental data for strain rates 2.1 (□), 0.42 (●) and 0.01 s^{-1} (○)

rate from 20 to 30 s^{-1} has a negligible influence on the entire crystallinity–strain relationship.

It may be argued that at these high strain rates, significant adiabatic heating might influence the $A_{\dot{e}}$ *versus* $\dot{e}$ relationship, and invalidate the predictions in *Figure 8*. It is possible, however, that there are simple relationships between the strain rate, the rise in temperature, and the influence of the temperature rise on molecular mobility, such that this effect is already accounted for in the value of n.

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