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

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(Received 3 May 1993; revised 20 July 1993)

We have studied the crystallization of poly(ethylene terephthalate) during drawing at temperatures of 83, 90 and 96°C and at strain rates in the range 0.01–2.1 s^{-1}. Decreasing strain rate shifts the onset of crystallization to higher draw ratios and reduces the rate at which crystallinity increases with draw ratio, an effect that becomes more pronounced as draw temperature increases. When the degree of crystallinity is plotted against draw time, it becomes apparent that the effect of changing strain rate is simply to shift the curves along the log-time axis. The shift factor and the strain rate are related by a power law, and the value of the exponent, which reflects the rate of molecular relaxation at the draw temperature, rises with temperature at an increasing rate. Due to strain-rate/draw-time superposition, empirical equations permit prediction of the degree of crystallinity and the crystallization rate at any strain rate or temperature in the range studied from knowledge of draw time or draw ratio. The study also reveals that increasing draw temperature does not necessarily increase the draw ratio for onset of crystallization λ_c as previously supposed: at sufficiently high strain rates, λ_c decreases with increasing draw temperature.

(Keywords: poly(ethylene terephthalate); crystallization kinetics; draw temperature)

INTRODUCTION

Our recent studies of crystallinity development during drawing of poly(ethylene terephthalate) (PET) at 90°C showed that crystallization proceeds in two regimes[1]. There is a low stress regime (regime 1) in which stress increases slowly with draw ratio and crystallinity increases relatively fast, and a high stress regime (regime 2) in which stress increases rapidly and crystallinity increases slowly. Decreasing strain rate shifts the onset of crystallization to higher draw ratios[1-3] and reduces the rate at which crystallinity increases with draw ratio[1]. This is because reducing strain rate increases the time available for orientational relaxation and, therefore, increases the draw ratio required to attain the critical orientation for crystallization[3,4]. The onset of regime 2 occurs at a characteristic level of crystallinity, which is independent of strain rate. We believe that regime 1 involves the formation of a crystallite network which, at the characteristic crystallinity level, becomes sufficiently effective to sharply increase the stress generated during drawing[1].

In reference 5 we reported that, for a draw temperature of 90°C, plots of crystallinity versus draw time at various strain rates $\dot{\varepsilon}$ can be shifted along the log-time axis to superpose each other, and that the shift $A_{\dot{\varepsilon}}$ is given by:

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

where $n = 1.11$ and C depends on the reference strain rate chosen. As will be demonstrated in the present study, the exponent in equation (1) is related to the rate of molecular relaxation at the draw temperature. If the crystallinity versus draw ratio relationship were independent of strain rate, n would equal unity. The faster the relaxation, the greater is the delay in crystallization onset, and the more n exceeds unity. Our previous studies also showed evidence that the effect of molecular relaxation on crystallinity development is to some extent offset by the time-dependent nature of crystallization[5]. Thus, in the absence of molecular relaxation — in a highly crosslinked network for example — one could envisage n becoming less than unity. That is, decreasing strain rate might shift the onset of crystallization to lower draw ratios, due to greater time available for crystallization.

In the present study we investigate crystallization of PET at draw temperatures in the range 83–96°C, with particular regard to strain-rate/draw-time superposition and the temperature-dependent behaviour of n.

EXPERIMENTAL

Material

Amorphous, undrawn PET film was supplied by Goodyear. It has a number-average molecular weight of 21 000 (intrinsic viscosity of 0.66 dl g^{-1}), a density of 1337 kg m^{-3}, and a thickness of 0.253 mm. The film was of high clarity, and did not contain TiO$_2$ or other additives.

Deformation

The amorphous PET film was drawn at constant width (pure shear) in the furnace of an Instron tensile tester at temperatures of 83, 90 and 96°C, and at various nominal strain rates (0.0104, 0.0208, 0.0417, 0.104, 0.417 and

$2.08 s^{-1}$). At the end of drawing the sample was immediately air quenched by opening the furnace door. The specimen geometry and further details of the drawing procedure have been described previously[1].

Density and crystallinity

The density ρ of the film specimens was measured at 23°C in a density gradient column containing n-heptane and carbon tetrachloride. The volume fraction crystallinity was estimated from:

$$\chi = \frac{(\rho - \rho_a)}{(\rho_c - \rho_a)} \quad (2)$$

with the crystalline density $\rho_c = 1457 \text{ kg m}^{-3}$ and the amorphous density ρ_a taken as the measured density of the undrawn film. It cannot be assumed that ρ_c remains constant, but measurement of lattice spacings by X-ray diffraction indicates that it does so for the range of deformation conditions applied in this study. The values of χ reported in this study represent an average of at least three density determinations.

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Figure 2 Influence of draw temperature on development of crystallinity at strain rates of (a) $0.042 s^{-1}$ and (b) $2.08 s^{-1}$
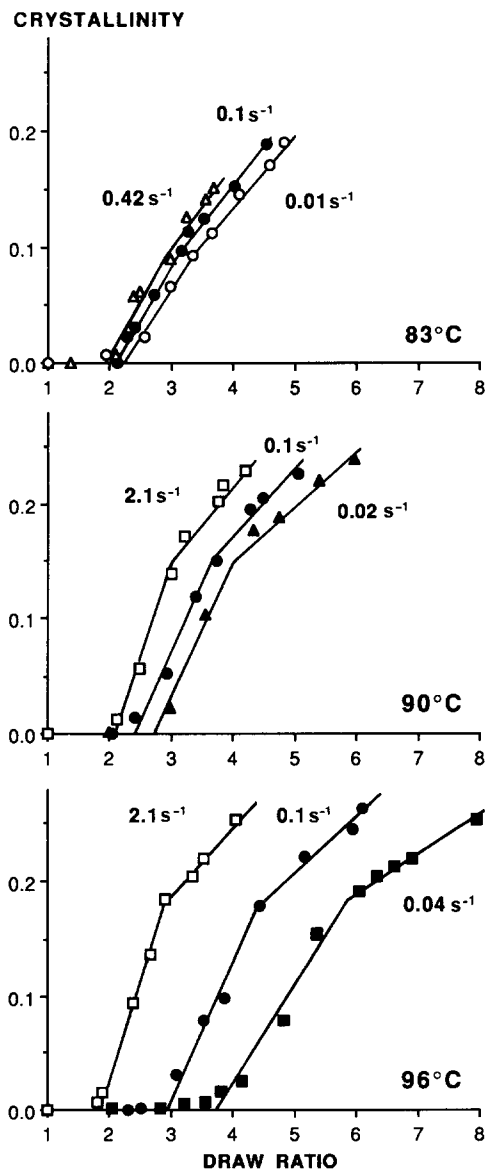

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Figure 1 Volume fraction crystallinity *versus* draw ratio at various strain rates and draw temperatures. For clarity, not all strain rates have been included in the figure
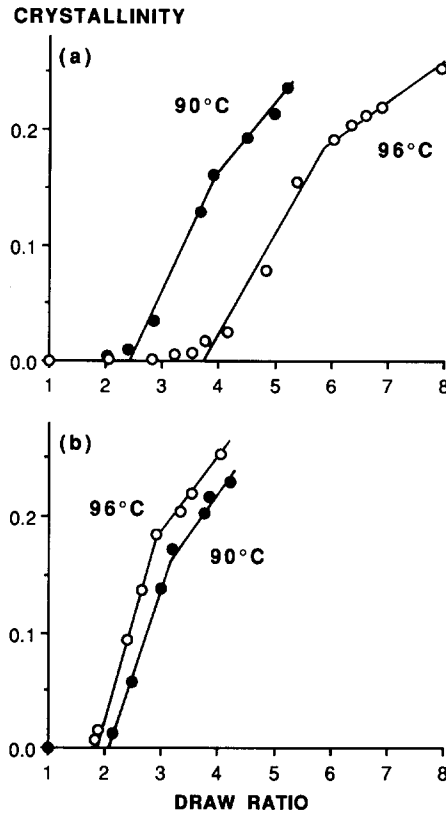
RESULTS AND DISCUSSION

Crystallinity development

Our previous studies, using a draw temperature of 90°C, have confirmed that decreasing strain rate shifts the onset of crystallization to higher draw ratios and reduces the rate at which crystallinity increases with draw ratio. The influence of draw temperature on these strain-rate effects is apparent from *Figure 1*. Higher temperature enhances the rate of orientational relaxation, resulting in a more pronounced shift of the crystallinity curves as strain rate changes. It can also be seen that the change in slope (from regime 1 crystallization to regime 2 crystallization[1]) occurs at a higher level of crystallinity, and becomes more pronounced, as draw temperature increases. These phenomena will be discussed more quantitatively later.

Until the present study, experimental investigations of the influence of draw temperature on crystallinity development have been performed at strain rates of $<0.2 s^{-1}$, and it was observed that increasing temperature always delays the onset of crystallization to higher draw ratio[2,3]. At low strain rates ($< \sim 1 s^{-1}$), this behaviour is confirmed by our data, as shown for example in *Figure 2a*. We have discovered, however, that when strain rate is sufficiently high, increasing temperature shifts the onset of crystallization to lower draw ratios (*Figure 2b*). We believe that this is because higher temperatures not only increase the rate of orientational relaxation, but also enhance the rate of crystallization at a given level of amorphous orientation. It has been shown, for example, that higher temperatures reduce the critical orientation required to induce crystallization[3]. Thus, when the time available for relaxation becomes very short
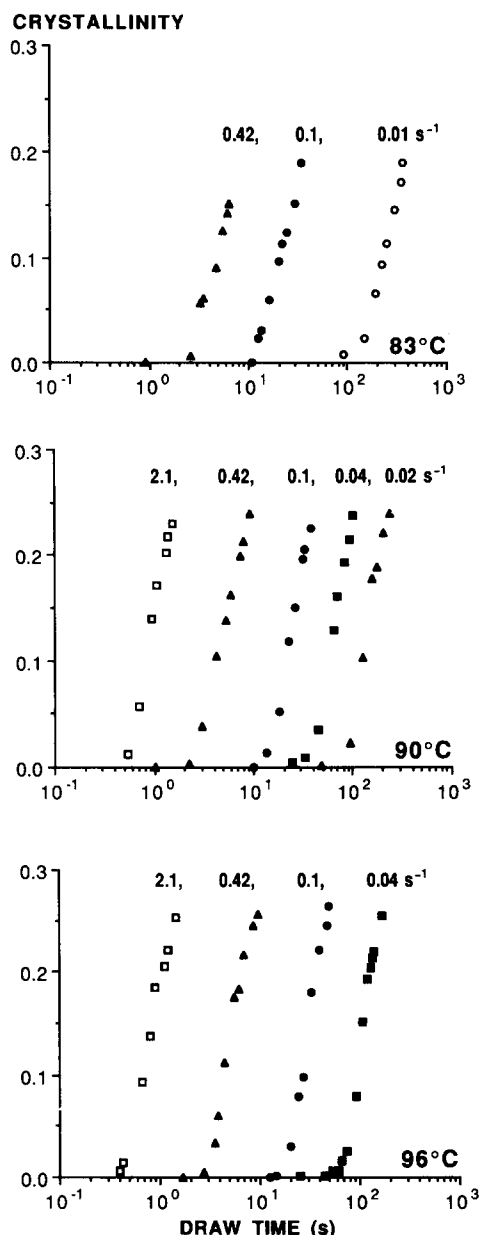
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Figure 3 Crystallinity *versus* draw time at various strain rates and draw temperatures

can be defined by:

$$n = 1.3553 \times 10^{-3} T_d^2 - 0.22775\, T_d + 10.615 \qquad (83 \leqslant T_d \leqslant 96)$$

$$(3)$$

It is interesting to notice that with the Goodyear film of the present study, n is 1.095 when $T_d = 90°C$, which is somewhat lower than the value of 1.11 obtained from the Rhône-Poulenc film of an earlier study[5]. This may reflect the fact that the Goodyear film has a slightly higher molecular weight (i.v. = 0.66 dl g^{-1}, compared with 0.60 dl g^{-1} for the Rhône-Poulenc film), which would be expected to reduce the rate of molecular relaxation. The influence of molecular weight on n is currently being investigated in detail.

In reference 5, we showed that strain-rate/draw-time superposition permits prediction of the level of crystallinity at any strain rate from knowledge of the elapsed time during drawing. The equations used in
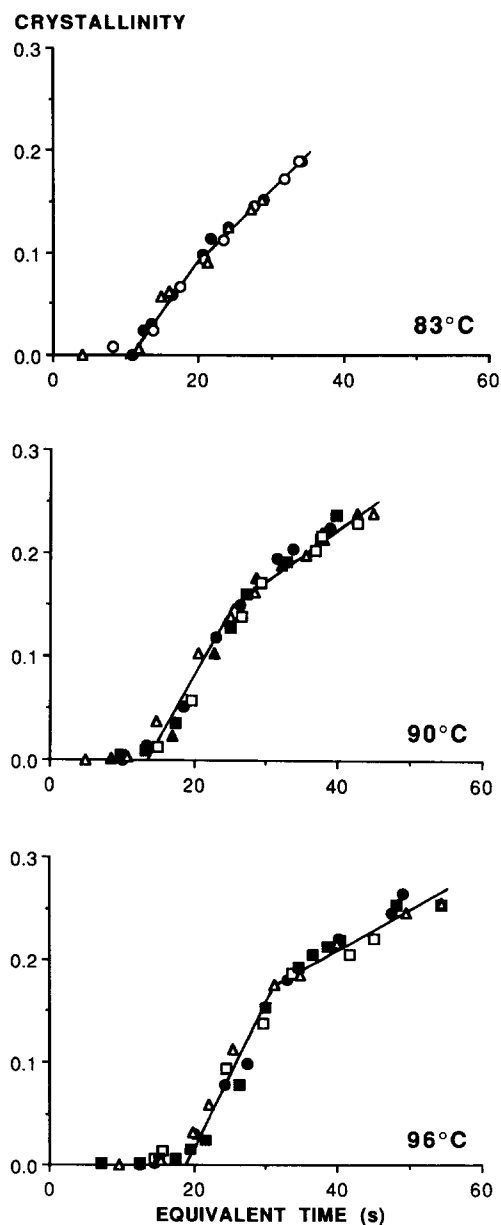
(at high strain rates), the crystallization effect dominates. Other evidence of competition between relaxation and crystallization in oriented PET has been reported by Peszkin *et al.*[6] and by Hamidi *et al.*[7].

Strain-rate/draw-times superposition

Figure 3 shows crystallinity *versus* log-time at draw temperatures of 83, 90 and 96°C. For each temperature, the crystallinity–time curve at the strain rate of 0.1 s^{-1} was arbitrarily chosen as the reference, and the curves of higher and lower strain rate were shifted to superpose it. *Figure 4* shows the superposed data on a linear time-scale, and *Figure 5* reveals that at all three temperatures the shift factor can be described by equation (1), where n now depends on draw temperature. *Figure 6* shows that n, and hence the severity of the relaxation effect, rises with temperature at an increasing rate. In order to permit approximate prediction of n at any draw temperature T_d in the range 83–96°C, we have chosen a curve shape that

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Figure 4 Crystallinity *versus* draw time at various temperatures, in which the data at higher and lower strains have been shifted to superpose the data at the reference strain rate of 0.1 s^{-1}
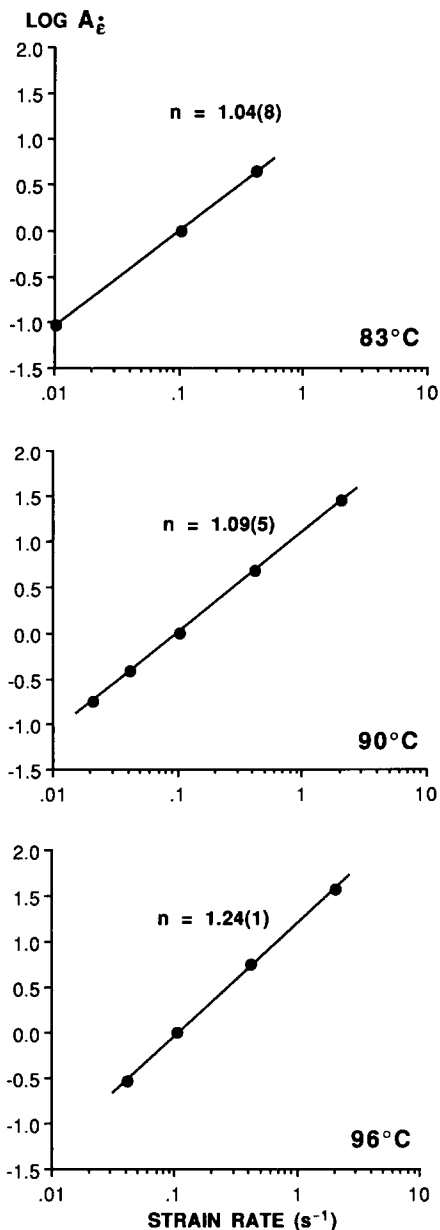
Figure 5 Relationship between shift factor $A_{\dot{\varepsilon}}$ and strain rate at various draw temperatures
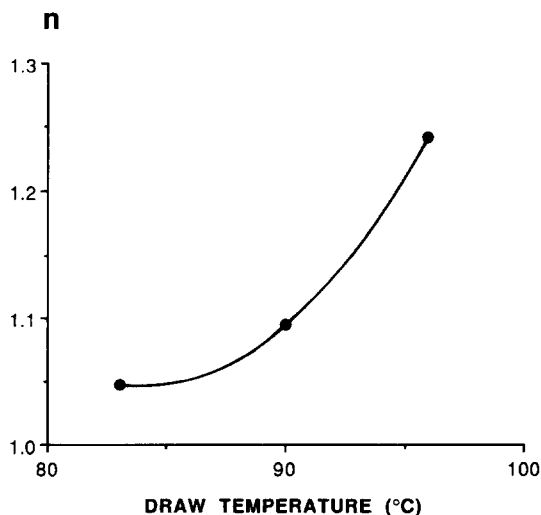
reference 5, for $T_d = 90°C$, can now be generalized to take into account the temperature effects observed in the present study. Thus, volume fraction crystallinity in regimes 1 and 2 is given by:

$$\chi_1 = \left(\frac{d\chi_1}{dt_{eq}}\right)_{T_d} (tA_{\dot{\varepsilon}} - t_1) \qquad (t_1 \leqslant tA_{\dot{\varepsilon}} \leqslant t_2)$$

$$\chi_2 = \left(\frac{d\chi_2}{dt_{eq}}\right)_{T_d} (tA_{\dot{\varepsilon}} - t_2) + \chi_2^0(T_d) \qquad (tA_{\dot{\varepsilon}} \geqslant t_2) \qquad (4)$$

where t is the real time, t_1 is the equivalent time for onset of crystallization, t_2 is the equivalent time for onset of regime 2 and χ_2^0 is the characteristic level of crystallinity at the onset of regime 2. *Figure 7* shows that χ_2^0 has a linear dependence on T_d, such that:

$$\chi_2^0 = 6.41 \times 10^{-3}T_d - 0.43 \qquad (5)$$

The temperature dependence of the crystallization rate in regimes 1 and 2, $d\chi_1/dt$ and $d\chi_2/dt$, is discussed in the following section.

Crystallization rate

Since we know that:

$$A_{\dot{\varepsilon}} = C\dot{\varepsilon}^n$$

it follows that the crystallization rate in regime 1 or 2 can be given by:

$$d\chi_{1,2}/dt = K_{1,2}\dot{\varepsilon}^n \qquad (6)$$

as demonstrated by our data in *Figure 8*. It happens that K, the crystallization rate at $\dot{\varepsilon} = 1\,s^{-1}$, has a linear relationship with T_d in both regimes 1 and 2 (*Figure 9*) such that:

$$K_1 = 7.48 \times 10^{-3}T_d - 0.518 \qquad (7)$$

$$K_2 = 0.22 - 1.76 \times 10^{-3}T_d \qquad (8)$$

It should be emphasized, however, that the relationship between $d\chi/dt$ and T_d is not linear at all strain rates. In fact, as can be seen in *Figure 10*, the linear relationship is exceptional. The complex relationships between $d\chi_1/dt$ and T_d clearly arise from the temperature dependence of n, which causes the curves of $d\chi_1/dt$ to cross each other (*Figure 8*).
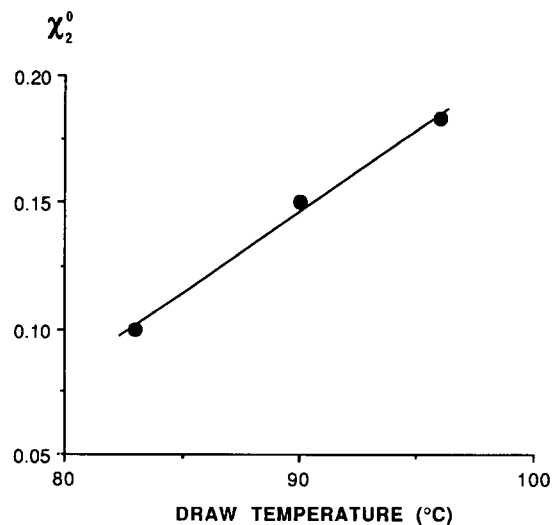

Figure 6 Influence of draw temperature on n

Figure 7 Influence of draw temperature on the characteristic level of crystallinity at onset of regime 2, χ_2^0
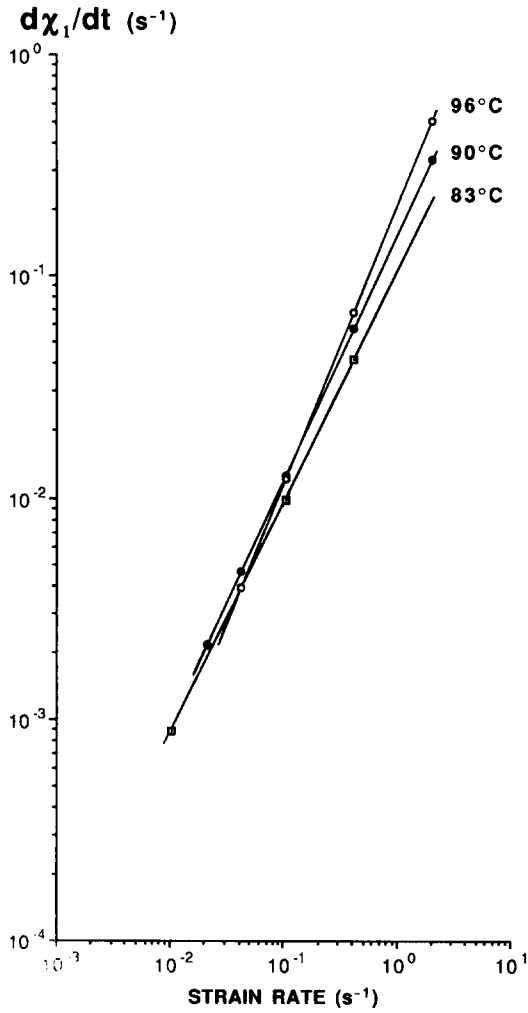
Figure 8 Crystallization rate in regime 1 as a function of strain rate at various draw temperatures
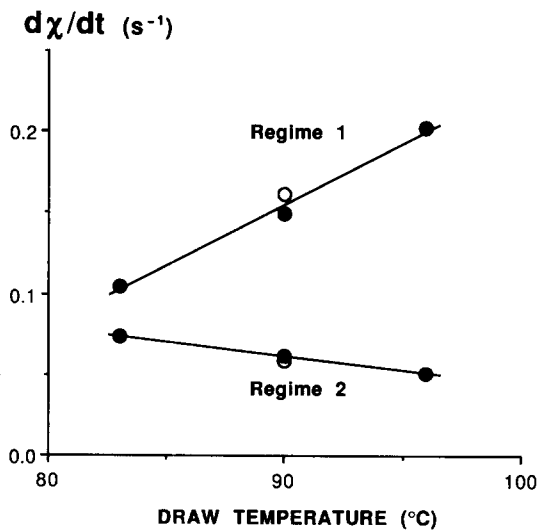
temperatures enhance the rate of crystallization at a given level of molecular orientation so that when the time available for orientational relaxation is short (at high strain rates), $d\chi_1/dt$ increases with temperature. However, higher temperature also enhances the rate of orientational relaxation, so that when there is sufficient time available (at lower strain rates), higher temperatures are more effective at reducing $d\chi_1/dt$. Consequently, higher temperatures result in a faster decrease of $d\chi_1/dt$ with decreasing $\dot\varepsilon$ (i.e. higher n), causing the curves of $d\chi_1/dt$ *versus* $\dot\varepsilon$ to cross each other.

The same arguments can of course be applied to crystallization in regime 2. It is interesting to notice from *Figure 11*, however, that in regime 2 the influence of temperature on $d\chi_2/dt$ is largest at low strain rates, and the curves do not cross each other until the strain rate exceeds $2\,s^{-1}$. This is because the higher the temperature the more pronounced is the decrease in crystallization rate at the onset of regime 2.

Figure 9 Crystallization rate *versus* draw temperature in regimes 1 and 2 at a strain rate of $1.0\,s^{-1}$. (●) Goodyear film of the present study; (○) Rhône-Poulenc film of a previous study[5]

Figure 8 demonstrates that at sufficiently high strain rates $d\chi_1/dt$ increases with temperature and that this trend gradually reverses as strain rate is decreased. This can be explained in physical terms as follows. Higher
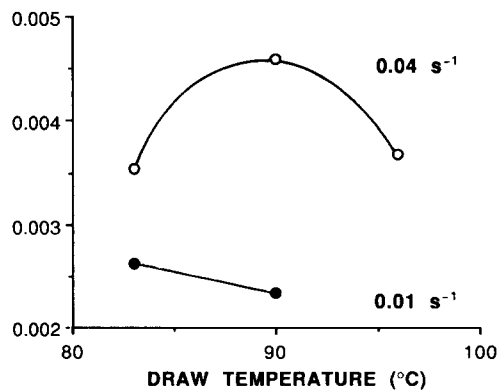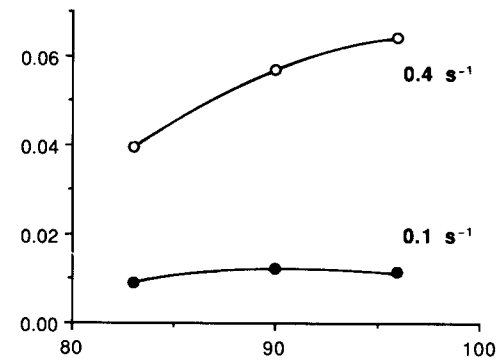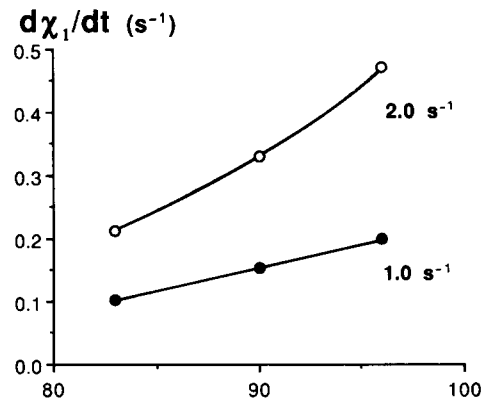

Figure 10 Crystallization rate in regime 1 as a function of draw temperature at various strain rates. The data points were calculated using equations (1), (6) and (7)
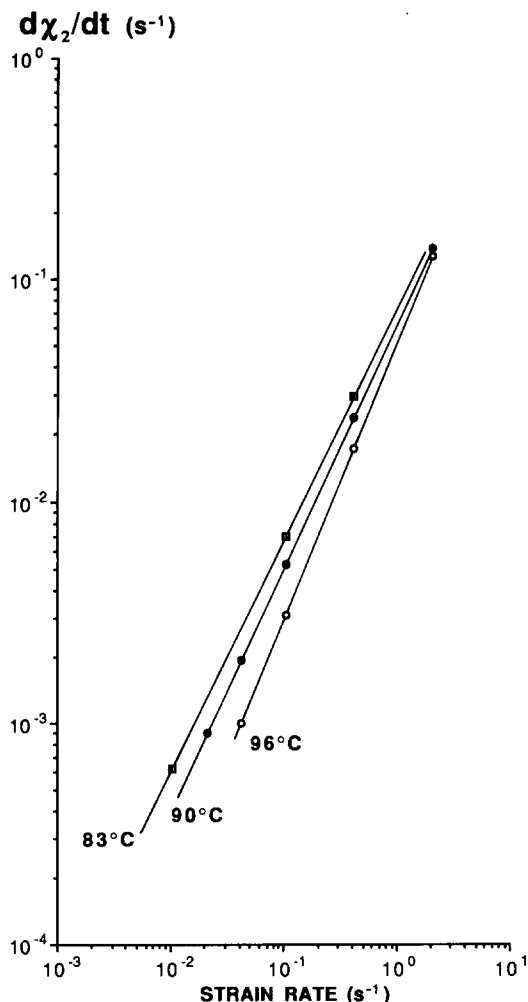
Figure 11 Crystallization rate in regime 2 as a function of strain rate at various draw temperatures
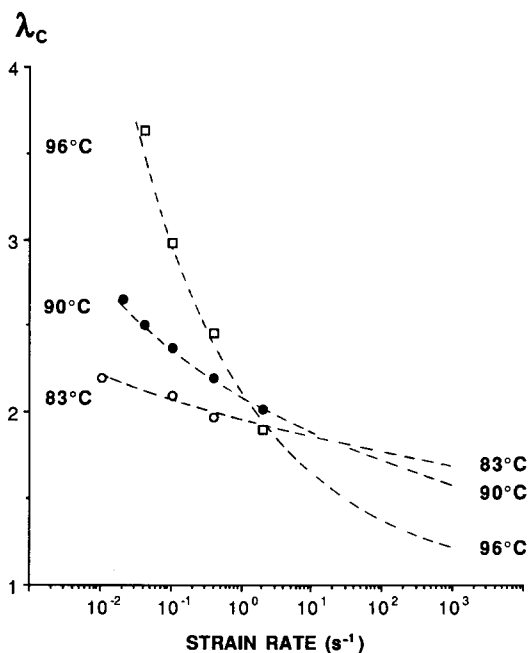

Figure 12 Influence of draw temperature and strain rate on the draw ratio for onset of crystallization λ_c, showing experimental data and calculated curves

Clearly, the curves cross-over and then diverge as strain rate increases, predicting that the decrease in λ_c with increasing temperature would become very pronounced at strain rates of $10\,s^{-1}$ and higher. Since some commercial processes draw at rates of $20–30\,s^{-1}$, this phenomenon would be of practical significance.

ACKNOWLEDGEMENTS

Predictions at higher strain rates

It is apparent that the equations obtained permit prediction of crystallinity at any strain rate or temperature within the range studied. However, it would also be interesting to use these equations to predict the effects of increasing strain rate beyond the experimental range examined so far, even though the validity of the results would be uncertain. As mentioned earlier, previous investigations of the influence of T_d on crystallinity development were performed at strain rates of $<0.2\,s^{-1}$ and showed that increasing temperature delays the onset of crystallization to higher draw ratio[2,3]. However, our experimental results indicate that at sufficiently high strain rates, increasing temperature can shift the onset of crystallization to lower draw ratios (*Figure 2b*). From the empirical equations given above, the draw ratio for onset of crystallization λ_c was determined for the three T_d values at various strain rates within the experimental range ($\leqslant 2\,s^{-1}$) and beyond it ($>2\,s^{-1}$), as shown in *Figure 12*.

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