Kinetics of induced crystallization during stretching and annealing of poly(ethylene terephthalate) films

G. le Bourvellec† and L. Monnerie
Laboratoire de Physicochimie Structurale et Macromoléculaire, associé au C.N.R.S., Ecole Supérieure de Physique et de Chimie Industrielles, 10 Rue Vauquelin, 75231 Paris Cedex 50, France

and J. P. Jarry
Rhône-Poulenc Films, Usine St Maurice de Beynost, 01700 Miribel, France

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The kinetics of induced crystallization is studied during uniaxial stretching of amorphous poly(ethylene terephthalate) films and annealing of oriented samples. The time scale of crystallization and the influence of orientation and temperature are determined for annealing of stretched films. During stretching, it is shown that crystallization obeys a 'forced kinetics' controlled by the strain rate and affected by the stretching temperature.

(Keywords: PET; orientation; relaxation; annealing; strain-induced crystallization; kinetics of crystallization; fluorescence polarization)

INTRODUCTION

Many studies have been done recently on the kinetics of strain-induced crystallization of poly(ethylene terephthalate) (PET)[1-6]. However, these works only deal with the rate of induced crystallization during annealing of oriented amorphous samples. The initial orientation of the material and the annealing temperature are the two parameters which control the kinetics of strain-induced crystallization, which is much faster than isothermal crystallization of isotropic samples. For example, at 120°C, the half-time of isothermal crystallization is a few minutes[7], but it becomes lower than 0.01 s for strain-induced crystallization[6]. At lower temperatures, about 90°C, isotropic PET needs several days to crystallize under isothermal conditions[8,9], whereas a few minutes are enough for strain-induced crystallization[2].

These results show that the orientation of the material has a large influence on the rate of crystallization of PET.

In a previous paper[10] it was shown that the degree of crystallinity of a sample can be accurately related to the amorphous orientation of PET films, at constant temperature.

The present work reports a study on the kinetics of strain-induced crystallization in amorphous PET films during uniaxial stretching above T_g and at a constant strain rate. It also deals with the annealing, at constant length, of oriented samples.

EXPERIMENTAL

Experimental details on sample preparation and measurements are given in ref. 10. The main points of the procedure are briefly mentioned below.

Materials

The PET films supplied by Rhône-Poulenc Recherches, have a weight average molecular weight of 39 000 and a T_g of 80°C.

Sample preparation

The samples were stretched at constant strain rate in the temperature range 80–103°C on a machine developed in our laboratory[11].

Annealing

Oriented samples were annealed at constant length in the oven of the stretching machine. After annealing, each sample was air quenched.

Density and crystallinity

The density of a sample was estimated from the average refractive index $\bar{n}$ obtained by refractometry by using the following relation[12]:

$$d = 4.047\left(\frac{\bar{n}^2 - 1}{\bar{n}^2 + 2}\right)$$

with d expressed in g cm^{-3}.

The degree of crystallinity X was determined by the relation:

$$X = \frac{d - d_a}{d_c - d_a}$$

with $d_c = 1.457$ g cm^{-3} and $d_a = 1.336$ g cm^{-3}.[13]

Amorphous orientation

The amorphous orientation of the samples was measured by fluorescence polarization with the

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† Present address: Rhône-Poulenc Recherches, Centre de Recherches de St-Fons, 85 Avenue des Frères Perret BP 62, 6990 St-Fons, France

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fluorescent molecule 4,4′-(dibenzoxazolyl) stilbene (VPBO), which is sensitive to the orientation of the amorphous chains in *trans* conformation[14]. The orientation is described by using the second moment of the orientation distribution function, $\langle P_2(\cos\theta)\rangle$, also denoted $\langle P_2\rangle$[15]:

$$\langle P_2(\cos\theta)\rangle = \langle P_2\rangle = \langle (3\cos^2\theta - 1)/2\rangle$$

where θ denotes the angle between the transition moment of VPBO and the stretching axis.

RESULTS AND DISCUSSION

Annealing at constant length of oriented samples

At a given temperature T and strain rate $\dot{\varepsilon}$, several samples were stretched at various draw ratios so that they reached different levels of orientation. After stretching, each sample was annealed at constant length at the drawing temperature. In each case, the degree of crystallinity X was determined as a function of annealing time.

The values of crystallinity and orientation after stretching at $T = 84°\mathrm{C}$ and $\dot{\varepsilon} = 0.029\ \mathrm{s}^{-1}$ are reported in *Figures 1* and *2*, respectively. The orientation is seen to decrease with annealing time when the crystallinity increases, whatever the level of orientation at the end of stretching. Therefore, the degree of crystallinity at equilibrium is not reached during stretching, since crystallization proceeds during the annealing.

Furthermore, the influence of initial orientation on the rate of crystallization can be seen. It is known that the orientation of the sample before annealing does not change the degree of crystallinity at equilibrium[3,4]. So, the curves in *Figure 1* should reach the same value after long annealing times. Thus it can be deduced from *Figure 1* that the higher the initial orientation is, the faster is the rate of crystallization.

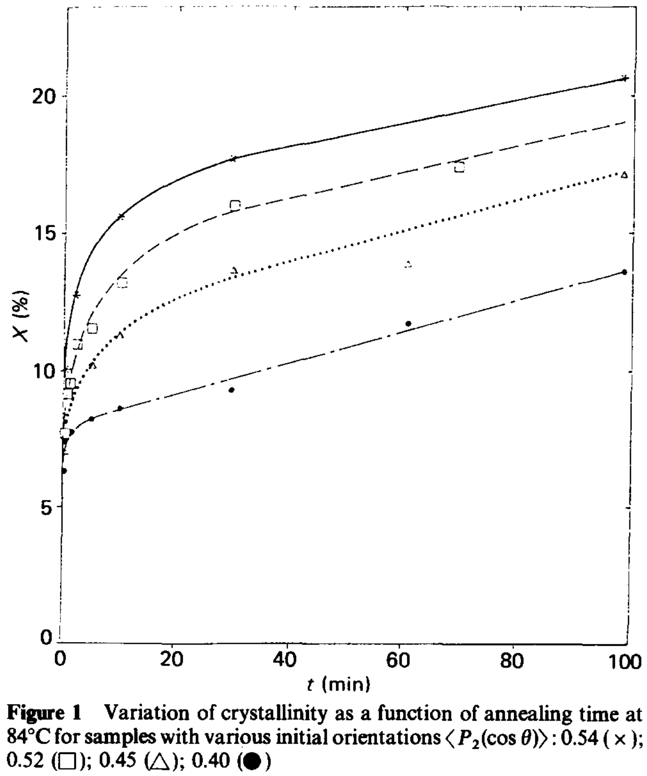

Figure 1 Variation of crystallinity as a function of annealing time at 84°C for samples with various initial orientations $\langle P_2(\cos\theta)\rangle$: 0.54 (×); 0.52 (□); 0.45 (△); 0.40 (●)

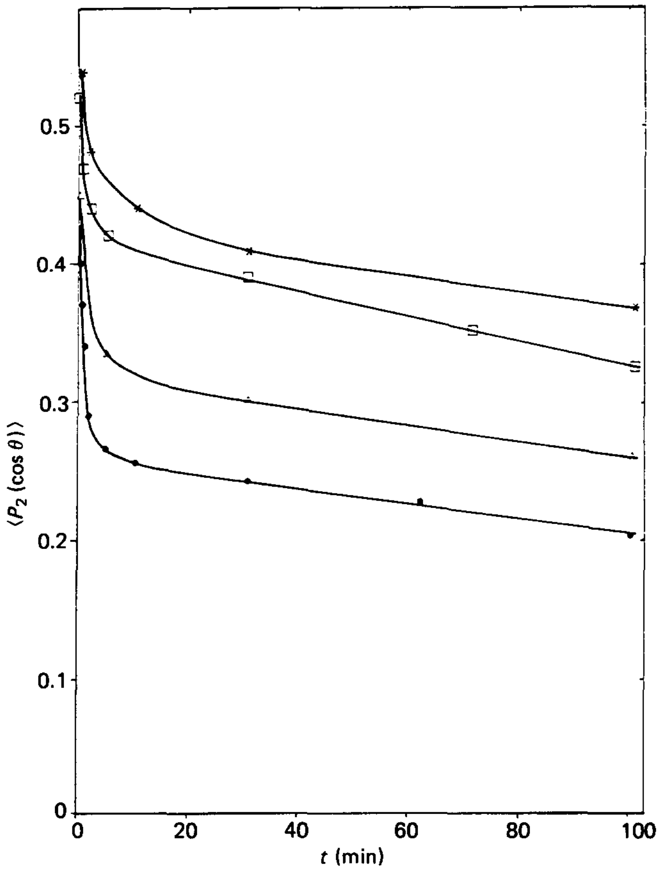

Figure 2 Variation of *trans* amorphous orientation as a function of annealing time for samples with various initial orientations $\langle P_2(\cos\theta)\rangle$: 0.54 (*); 0.52 (□); 0.45 (△); 0.40 (●)

To show more clearly the effect of temperature on the kinetics of crystallization, the evolutions of crystallinity during annealing at 84 and 96°C were compared for two samples of almost the same level of orientation (0.36 and 0.40). The results are plotted in *Figure 3*, which shows that the rate of crystallization is greater at a higher temperature. The increase with temperature of the rate of crystallization of an oriented sample, annealed at constant length, has already been observed[1–6].

This result can be attributed to the effects both of orientation and of mobility. Mobility, which increases with temperature, is larger at 96°C than at 84°C and implies faster kinetics at 96°C. On the other hand, as the crystallinity of a sample is higher at 96°C, the relaxation of orientation is perturbed by the crystallites, which act as tie points, and $\langle P_2\rangle$ decreases more slowly at 96°C than at 84°C (*Figure 4*). Therefore a larger orientation remains in the sample at 96°C, which induces a faster crystallization.

Finally, *Figure 3* shows that the growth of crystallites lasts several tens of minutes at 84°C, as well as at 96°C. This time scale of crystallization agrees with other studies performed in the same range of temperature[2,3].

Kinetics of crystallization induced during stretching

By using the previous results, it is now possible to define the kinetics of crystallization induced during stretching.

If the rate of crystallization induced during stretching is very slow compared with the time scale of stretching, no crystallization should be observed during stretching. A

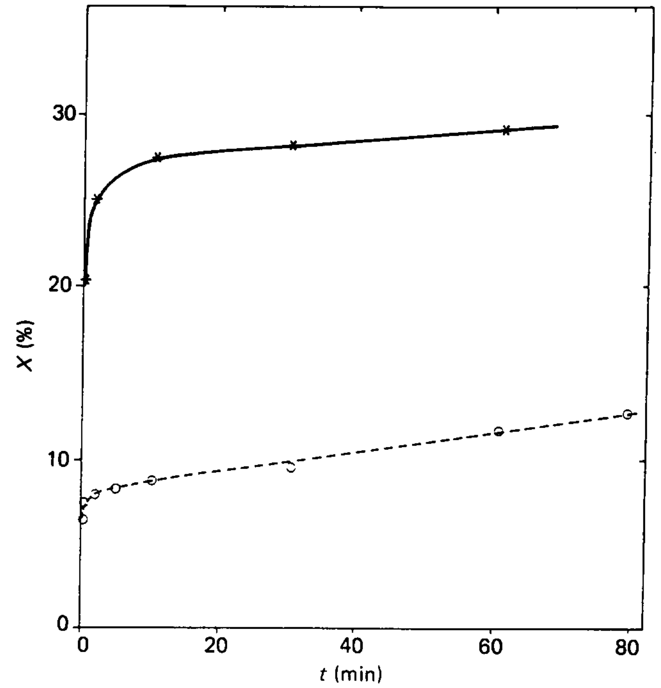

Figure 3 Variation of crystallinity as a function of annealing time at 84°C (○) and 96°C (*) for two samples with very similar initial orientations (0.36 and 0.40)

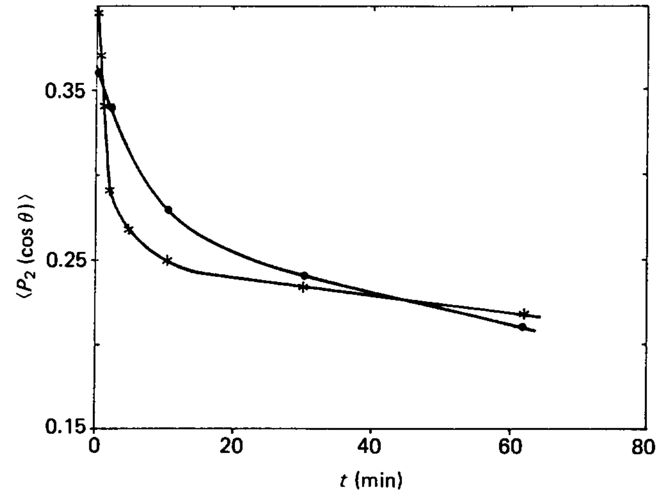

Figure 4 Variation of *trans* amorphous orientation as a function of annealing time at 84°C (*) and 96°C (●) for a sample with initial orientation of 0.36–0.40

previous work[10] demonstrates that this is not true and that the crystallinity increases with draw ratio.

The study of annealing of oriented samples showed that the crystallinity at equilibrium is not reached during stretching. Consequently, the kinetics cannot be much faster than the stretching rate.

Therefore, the rate of strain-induced crystallization can only be of the order of magnitude of drawing times. In *Figure 5*, the evolution of crystallinity is plotted as a function of time during both stretching and annealing. The solid lines correspond to crystallization during stretching at 84°C and at various strain rates. The dashed curves correspond to the crystallization during annealing of stretched samples, at constant length, and at 84°C. The difference in the rate of crystallization induced by stretching and by annealing can be seen.

At a given temperature, during stretching the crystallinity X is a function of time t. Furthermore, it has been shown in a previous paper[10] that X is also a function of the amorphous orientation $\langle P_2 \rangle$. During stretching $\langle P_2 \rangle$ is a function of time because of the strain rate dependence (*Figure 6*).

In a general way, during stretching, the crystallinity can be written as $X(\langle P_2\rangle(t),t)$ and the rate of crystallization dX/dt is given by:

$$\left(\frac{dX}{dt}\right)_T = \left(\frac{\partial X}{\partial t}\right)_{\langle P_2\rangle,T} + \left(\frac{\partial X}{\partial \langle P_2\rangle}\right)_{t,T}\left(\frac{d\langle P_2\rangle}{dt}\right)_T \qquad (1)$$

To estimate the relative contributions of the two terms, it is interesting to consider, at each time t, the change in crystallinity occurring either by proceeding with the stretching or by annealing at constant length. In the latter case, *Figure 6* shows that just after stopping the stretching at time t no significant relaxation of orientation occurs (dashed curves), in such a way that $(d\langle P_2\rangle/dt)_T$ vanishes from expression (1). Thus the slope at time t of the change in crystallinity with annealing time (*Figure 5*, dashed curves) yields an estimate of the first term in expression (1), $(\partial X/\partial t)_{\langle P_2\rangle,T}$. Data reported in *Figure 5* show that, at any time t, the slope of the change of crystallinity obtained by proceeding with stretching is much larger than that corresponding to annealing, indicating that the term $(\partial X/\partial t)_{\langle P_2\rangle,T}$ makes a negligible contribution to the kinetics of crystallization during stretching. Con-

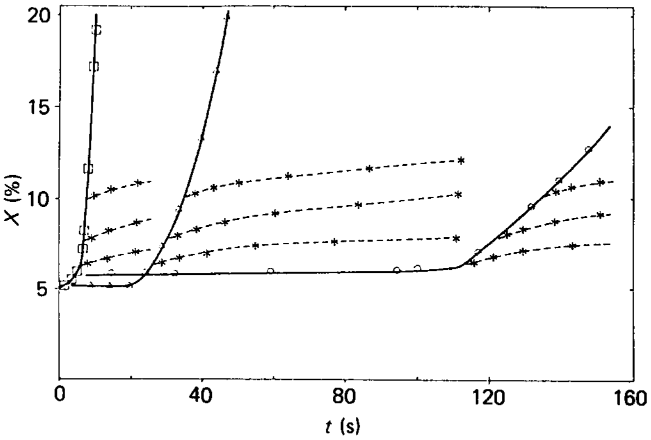

Figure 5 Variation of crystallinity as a function of time during stretching at 84°C and at various strain rates $\dot{\varepsilon}$: 0.115 s^{-1} (□); 0.028 s^{-1} (△); 0.008 s^{-1} (○); and during annealing of stretched samples at 84°C (*)

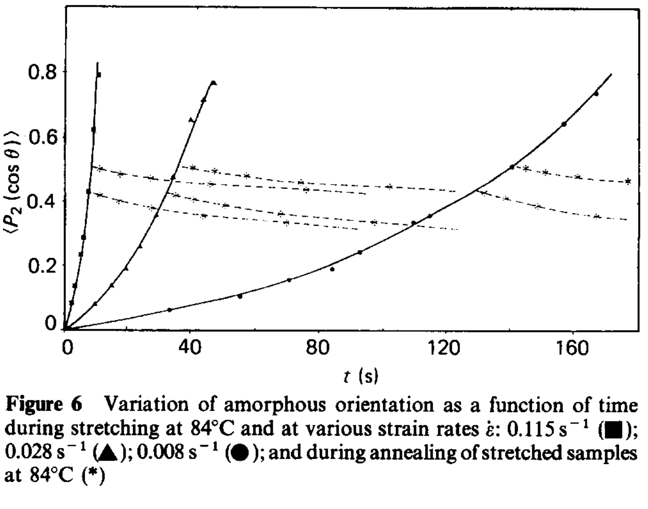

Figure 6 Variation of amorphous orientation as a function of time during stretching at 84°C and at various strain rates $\dot{\varepsilon}$: 0.115 s^{-1} (■); 0.028 s^{-1} (▲); 0.008 s^{-1} (●); and during annealing of stretched samples at 84°C (*)

sequently, expression (1) can be satisfactorily approximated by:

$$\left(\frac{dX}{dt}\right)_T \approx \left(\frac{\partial X}{\partial\langle P_2\rangle}\right)_{t,T}\left(\frac{d\langle P_2\rangle}{dt}\right)_T \qquad (2)$$

Expression (2) defines the 'forced kinetics' since the kinetics of crystallization depends on the variation of amorphous orientation during stretching, $(d\langle P_2\rangle/dt)_T$. This kinetics is affected by the strain rate $\dot{\varepsilon}$ and the temperature T.

Influence of strain rate. At constant temperature, $d\langle P_2\rangle/dt$ depends on strain rate $\dot{\varepsilon}$ as shown in *Figure 6* (solid lines), whereas $\partial X/\partial\langle P_2\rangle$ is independent of $\dot{\varepsilon}$, as shown in a previous paper[10]. From *Figures 5* and *6* (solid lines), we calculated dX/dt and $d\langle P_2\rangle/dt$ as a function of time for various strain rates. The results reported in *Figure 7* show that the variation of dX/dt is proportional to $d\langle P_2\rangle/dt$:

$$\frac{dX}{dt} = 0.627\left(\frac{d\langle P_2\rangle}{dt}\right)$$

whatever the value of $\dot{\varepsilon}$ for stretching at 84°C. This means, for a given temperature, that the kinetics of crystallization during stretching is controlled by the evolution of the amorphous orientation $\langle P_2\rangle$ and so increases with strain rate.

Influence of temperature. When temperature increases, $\partial X/\partial\langle P_2\rangle$ increases, as shown in *Figure 8*, and at constant temperature it is dependent on the level of orientation. The variation of $\langle P_2\rangle$ with time during stretching can be deduced from the variation of $\langle P_2\rangle$ with draw ratio λ as, for our experimental conditions, $\lambda = \exp(\dot{\varepsilon}t)$. As an example, we report in *Figure 9* the variation of $\langle P_2\rangle$ with time for stretching at $0.115\,s^{-1}$ and at two temperatures, 84 and 96°C. Notice that the higher the temperature, the lower is $d\langle P_2\rangle/dt$.

So the kinetics is controlled by the product

$$\left(\frac{\partial X}{\partial\langle P_2\rangle}\right)_{t,T}\left(\frac{\partial\langle P_2\rangle}{\partial t}\right)_T$$

which remains constant, as shown by the variation of crystallinity with stretching time (*Figure 10*) and *Table 1*.

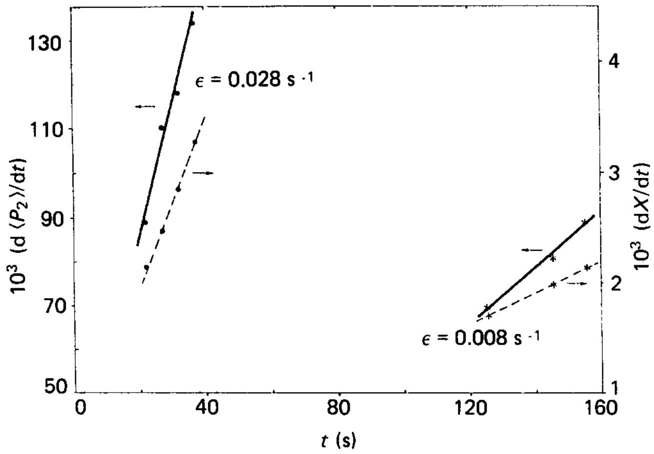

Figure 7 Variation of dX/dt (dashed curves) and $d\langle P_2\rangle/dt$ (solid curves) as a function of time of stretching at 84°C and at $\dot{\varepsilon} = 0.028\,s^{-1}$ (●); $0.008\,s^{-1}$ (*)

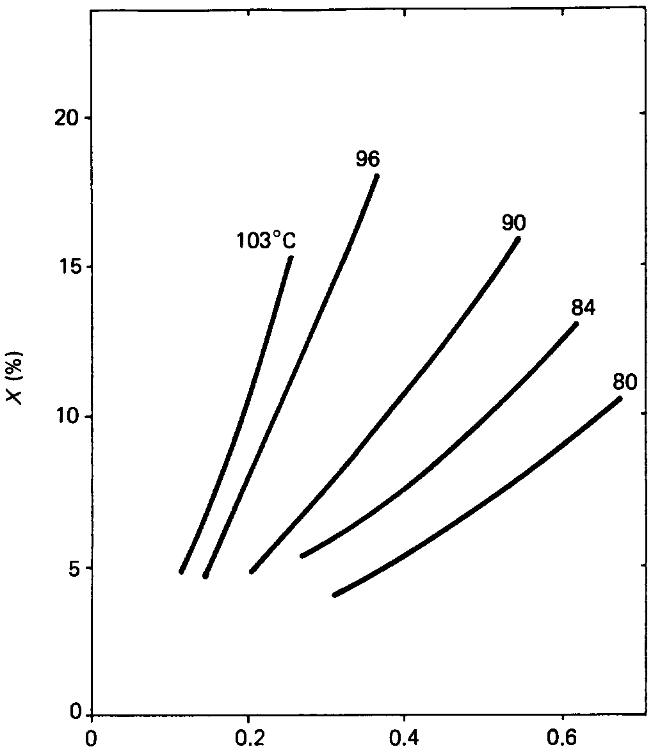

Figure 8 Relation between crystallinity and amorphous orientation for various temperatures of stretching, whatever the strain rate $\dot{\varepsilon}$ (from ref. 10)

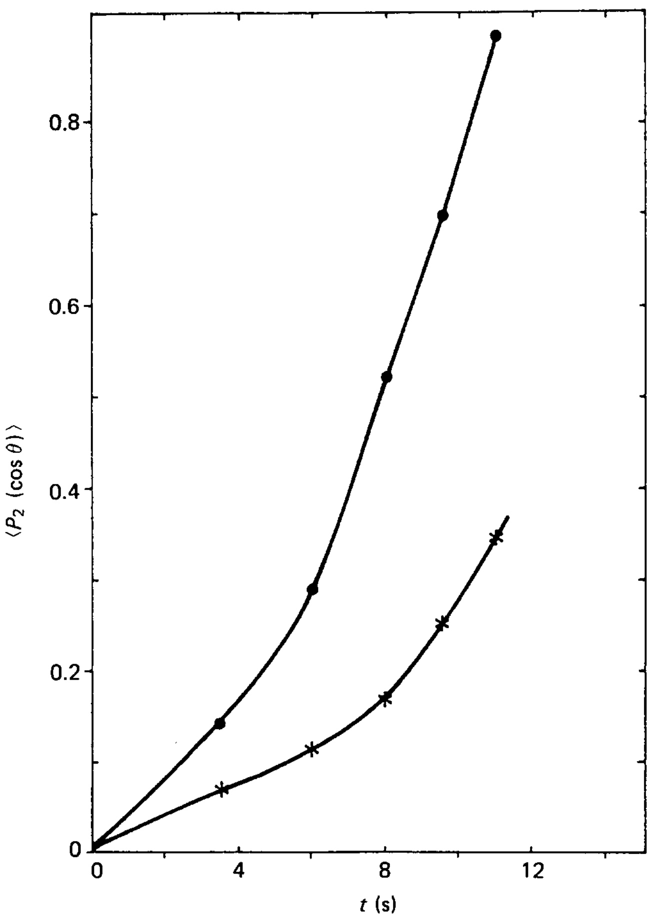

Figure 9 Variation of amorphous orientation as a function of time during stretching at $0.115\,s^{-1}$ and at various temperatures: 84°C (●); 96°C (*)

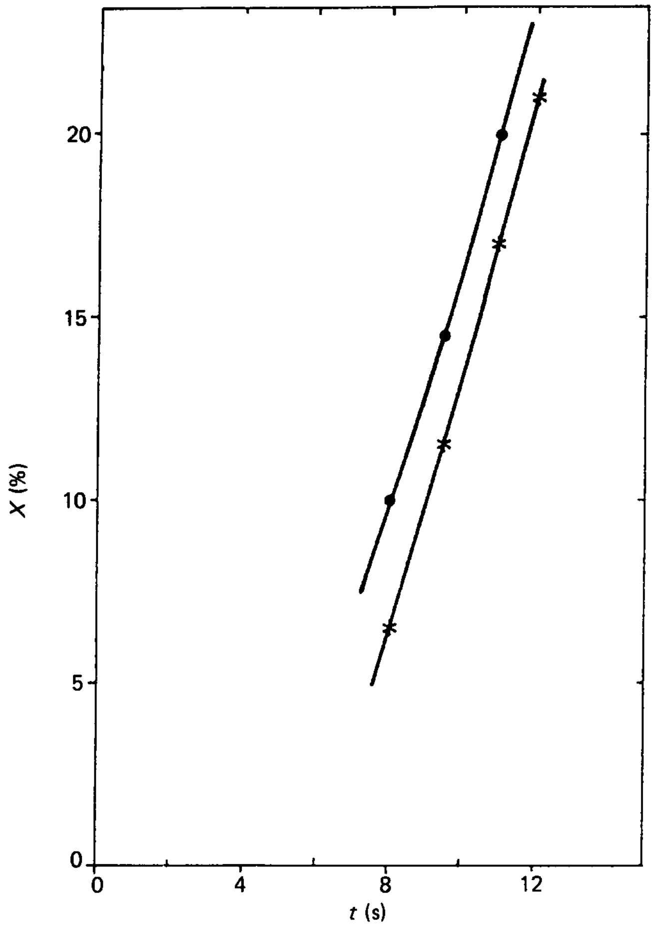

Figure 10 Variation of crystallinity as a function of time during stretching at 0.115 s^{-1} and at various temperatures: 84°C (●); 96°C (*)

The effect of temperature is just to delay the beginning of crystallization due to the relaxation of amorphous orientation during stretching, but the kinetics is not modified.

In conclusion, the variations of $(\partial X/\partial\langle P_2\rangle)_{t,T}$ and $(\mathrm{d}\langle P_2\rangle/\mathrm{d}t)_T$ imply that the rate of crystallization induced during stretching is completely controlled by the strain rate, the beginning of crystallization being delayed at higher temperatures because of a lower amorphous orientation in the material.

Table 1

T(°C)	$\left(\frac{\partial X}{\partial\langle P_2\rangle}\right)_{t,T}^{a}$	$\left(\frac{\mathrm{d}\langle P_2\rangle}{\mathrm{d}t}\right)_T^{b}$	$\left(\frac{\partial X}{\partial\langle P_2\rangle}\right)_{t,T}\left(\frac{\mathrm{d}\langle P_2\rangle}{\mathrm{d}t}\right)_T$	$\left(\frac{\mathrm{d}X}{\mathrm{d}t}\right)_T^{c}$
84	0.24	0.135	0.032	0.033
96	0.59	0.057	0.034	0.036

[a] From *Figure 9*. [b] From *Figure 10*. [c] From Figure *11*

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