Amorphous orientation and induced crystallization in uniaxially stretched poly(ethylene terephthalate glycol)

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The degree of crystallinity of poly(ethylene terephthalate glycol) (PET) obtained by induced crystallization during stretching of amorphous PET films is related to the amorphous orientation of the samples. The results show the existence of a critical amorphous orientation for the beginning of crystallization. This critical orientation depends on the temperature of stretching but not on the strain rate. It is also shown that, during stretching, the crystallinity of PET is completely determined by the temperature and the level of amorphous orientation in the sample, and it increases with both parameters.

(Keywords: PET; orientation; stress-induced crystallization; fluorescence polarization)

INTRODUCTION

Stress-induced crystallization, also called strain-induced crystallization, differs from isothermal crystallization by its origin, morphology and kinetics. Induced crystallization of poly(ethylene terephthalate glycol) (PET) has been studied for a long time because its mechanical properties are largely affected by this phenomenon[1-3].

Several morphological studies have been made on induced crystallization during stretching of amorphous PET[4-11] and annealing of oriented amorphous samples[3,7-13]. Various crystalline structures are described such as twisted lamellae or fibrillar textures.

The structures developed during annealing depend basically on the initial level of orientation in the sample[3,13-15]. According to Bragato and Gianotti[15], as the initial level of orientation increases, the mechanism of crystallization changes from a three-dimensional growth, to a two-dimensional one, and finally to a one-dimensional rod-like growth at high levels of orientation. The crystalline textures, obtained by induced crystallization, have a common feature: the crystallites are oriented, contrary to the crystallites obtained by isothermal crystallization of isotropic samples.

All these morphological studies show that, compared with isothermal crystallization, the origin of induced crystallization is related to an entropic effect due to the orientation of the material[16].

The present work reports a study of the induced crystallization phenomenon in PET and shows the relation with the amorphous orientation generated in a PET film stretched above T_g at a constant strain rate.

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EXPERIMENTAL

Material

Amorphous isotropic PET films (thickness: 150 μm) were supplied by Rhone-Poulenc Recherches. The polymer was prepared and extruded in the Research Centre at St Fons. The weight average molecular weight was 39 000, as determined by viscosimetry in *o*-chlorophenol at 25°C, and T_g was 80°C, as measured by d.s.c. at 20 K min^{-1} with a Dupont 1090 analyser.

Sample preparation

Oriented samples from the commercial films were obtained on an apparatus developed in our laboratory[17], i.e. a stretching machine operating at constant strain rate, and a special oven to obtain a very good stability in temperature over all the sample (homogeneity is *ca.* 0.05°C). Five temperatures (from 80°C to 103°C) and three strain rates (0.115, 0.028, 0.008 s^{-1}) have been investigated. After the stretching, each sample was air-quenched to avoid any isothermal crystallization.

Density

The densities of the samples were estimated with the average refractive index obtained by refractometry. This technique, in polarized light, gives the refractive indices in the three directions of space and thus, the average index $\bar{n}$.

Moreover, for PET, De Vries *et al.*[18] found a linear relation between the density d and the average index $\bar{n}$

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

if d is expressed in grams per cubic centimetre. This relation is independent of the degree of crystallinity X and the level of orientation.

Degree of crystallinity

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} (ref. 19).

It is well known[20] that crystallinity can be overestimated when it is calculated with value of density measured on oriented samples, because of the increase in density of the amorphous phase with the orientation of the chains. However, Ward[21] showed that, up to a level of amorphous orientation equal to 0.3, the density of the amorphous phase of PET does not exceed 1.340, i.e. a variation of less than 0.3%, which is negligible for the determination of crystallinity.

Measurement of orientation

The technique used to determine the orientation of the samples was fluorescence polarization. For these measurements, a photostable compound, 4,4'-(dibenzoxazolyl)stilbene (VPBO), was used as the fluorescent additive in PET (*Figure 1*). This long and thin molecule has a high quantum efficiency of fluorescence. This compound was incorporated into the material during the polycondensation at a concentration of 100 ppm (by weight). The fluorescence intensities were measured by using an apparatus developed in our laboratory[22].

The orientation of the samples is described by using the second moment of the orientation distribution function, $\langle P_2(\cos\theta)\rangle$, which is easily determined by fluorescence polarization[23]. In both amorphous and semicrystalline polymers, $\langle P_2(\cos\theta)\rangle$ is representative of the amorphous orientation. However, Nobbs *et al.*[24] showed that VPBO is sensitive only to the orientation of amorphous chains in the *trans* conformation and not to the average amorphous orientation.

RESULTS AND DISCUSSION

Evolution of crystallinity during stretching

The crystallinity was measured for samples stretched at various draw ratios, λ, temperatures, T, and strain rates $\dot{\varepsilon}$. In some previous work[25], the relaxation of Young's modulus has been determined from step-strain experiments and $\log E$ has been plotted *versus* $\log 1/\dot{\varepsilon}$, instead of $\log t$, because $1/\dot{\varepsilon}$ is similar to time (*Figure 2*). This figure shows that to each stretching, characterized by a temperature and a strain rate, there corresponds a specific viscoelastic behaviour of PET, from the rubbery pseudo-plateau (80°C and 84°C) to the flow zone (103°C).

In *Figures 3* and *4* the variations of the *trans* amorphous orientation $\langle P_2(\cos\theta)\rangle$ with the draw ratio in two typical viscoelastic regions (pseudo-plateau at 84°C, intermediate and flow zone at 96°C) are shown. At 84°C, the amorphous orientation increases rapidly with λ. At 96°C, $\dot{\varepsilon} = 0.115$ and 0.028 s^{-1}, $\langle P_2(\cos\theta)\rangle$ increases more slowly. At 96°C and $\dot{\varepsilon} = 0.008$ s^{-1}, the level of amorphous orientation remains very low, which is characteristic of the flow zone.

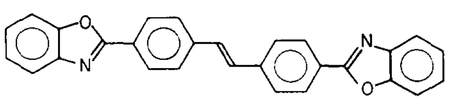

Figure 1 4,4'-(dibenzoxazolyl)stilbene (VPBO)

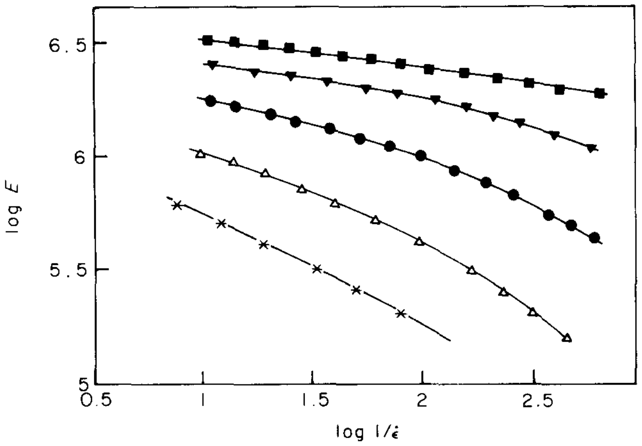

Figure 2 Relaxation of Young's modulus at various temperatures: 80°C (■); 84°C (▼); 90°C (●); 96°C (△); 103°C (*)

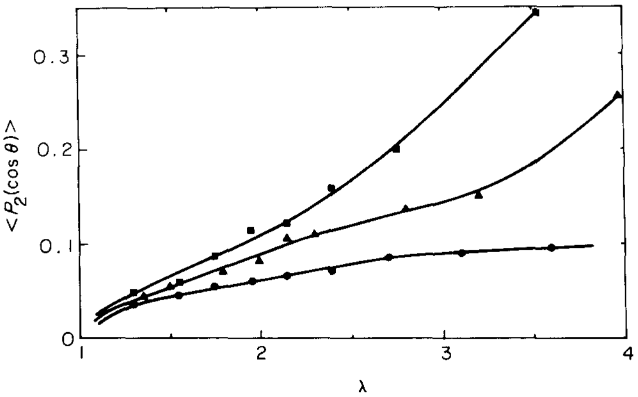

Figure 3 Evolution of amorphous orientation as a function of draw ratio at 84°C and various strain rates: 0.115 s^{-1} (■); 0.028 s^{-1} (▲); and 0.008 s^{-1} (●)

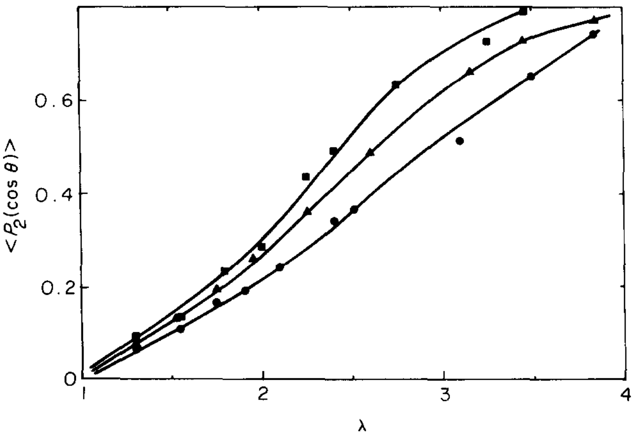

Figure 4 Evolution of amorphous orientation as a function of draw ratio at 96°C and various strain rates: 0.115 s^{-1} (■); 0.028 s^{-1} (▲); and 0.008 s^{-1} (●)

Figures 5 to *9* illustrate the evolution of the degree of crystallinity X with the draw ratio λ during a stretching under different conditions (T,$\dot{\varepsilon}$). At the lowest temperatures (80°C and 84°C), corresponding to the pseudo-plateau region, PET crystallizes from values of λ close to 2. At intermediate temperatures (90°C and 96°C),

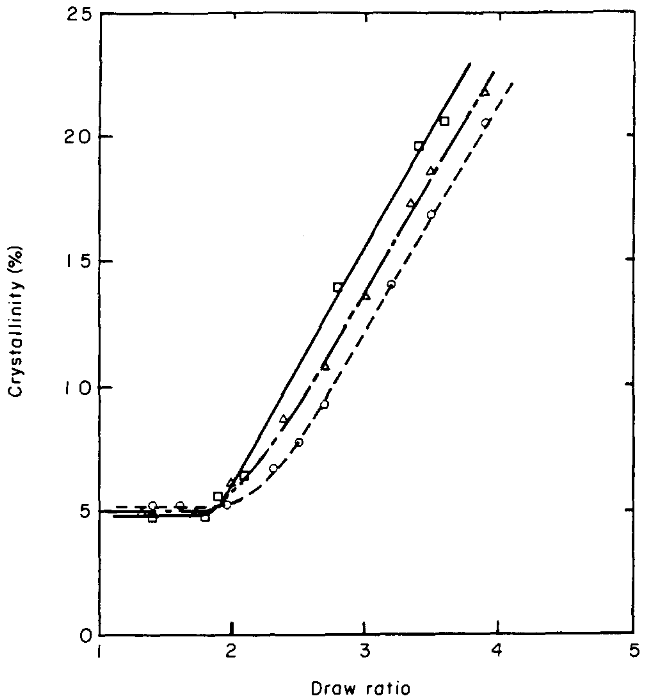

Figure 5 Variation of crystallinity as a function of draw ratio at 80°C and various strain rates: $0.115\,\mathrm{s}^{-1}$ (□); $0.028\,\mathrm{s}^{-1}$ (△); and $0.008\,\mathrm{s}^{-1}$ (○)

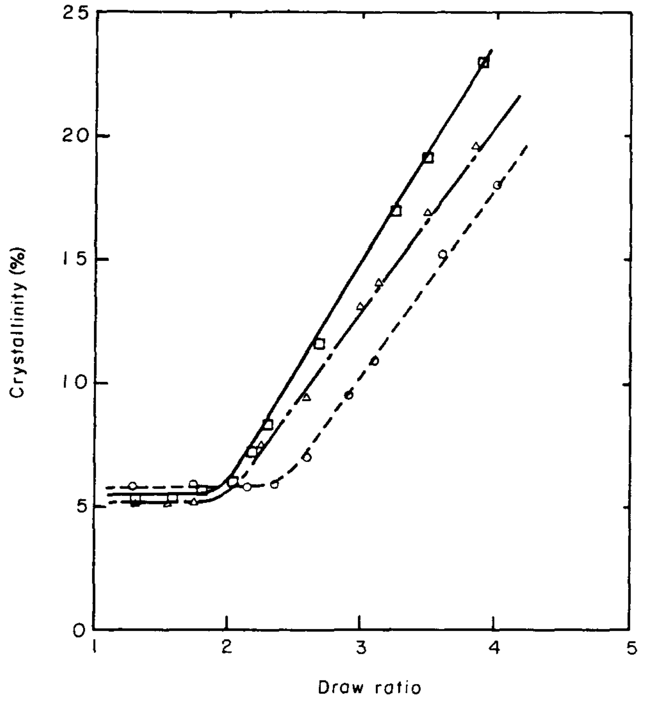

Figure 6 Variation of crystallinity as a function of draw ratio at 84°C and various stain rates: $0.115\,\mathrm{s}^{-1}$ (□); $0.028\,\mathrm{s}^{-1}$ (△); and $0.008\,\mathrm{s}^{-1}$ (○)

the beginning of crystallization is progressively shifted towards $\lambda = 3$, when $\dot{\varepsilon}$ decreases. When PET is in the flow region (96°C, $\dot{\varepsilon} = 0.008\,\mathrm{s}^{-1}$; 103°C, $\dot{\varepsilon} = 0.028\,\mathrm{s}^{-1}$ and $0.008\,\mathrm{s}^{-1}$), it does not crystallize at all, up to draw ratios close to 5.

Figures 5 to *9* show the influence of the strain rate at constant temperature. For one temperature and one draw ratio, the degree of crystallinity X increases with the strain rate $\dot{\varepsilon}$. It will be shown later that this is not due to a kinetic effect but to the relaxation of the orientation during the stretching.

In the same way, *Figure 10* shows the influence of temperature at constant strain rate. For one strain rate and one draw ratio, the crystallinity decreases when the temperature increases. This dependence of X on T will be interpreted in terms of relaxation of orientation.

Critical orientation

For every stretching that induces crystallization, it is possible to define a critical draw ratio λ_{cr}, at which induced crystallization appears. This critical draw ratio depends on the stretching parameters (T,$\dot{\varepsilon}$). The values of λ_{cr} are reported in *Table 1*.

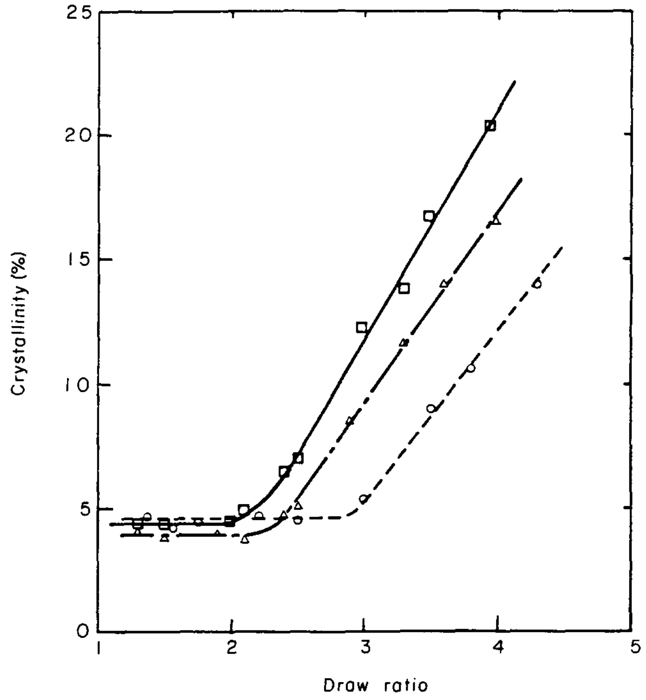

Figure 7 Variation of crystallinity as a function of draw ratio at 90°C and various strain rates: $0.115\,\mathrm{s}^{-1}$ (□); $0.028\,\mathrm{s}^{-1}$ (△); and $0.008\,\mathrm{s}^{-1}$ (○)

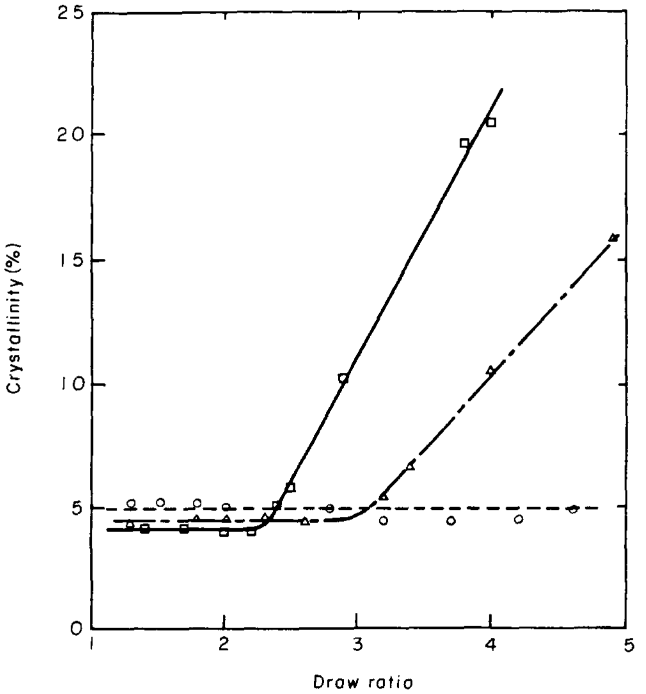

Figure 8 Variation of crystallinity as a function of draw ratio at 96°C and various strain rates: $0.115\,\mathrm{s}^{-1}$ (□); $0.028\,\mathrm{s}^{-1}$ (△); and $0.008\,\mathrm{s}^{-1}$ (○)

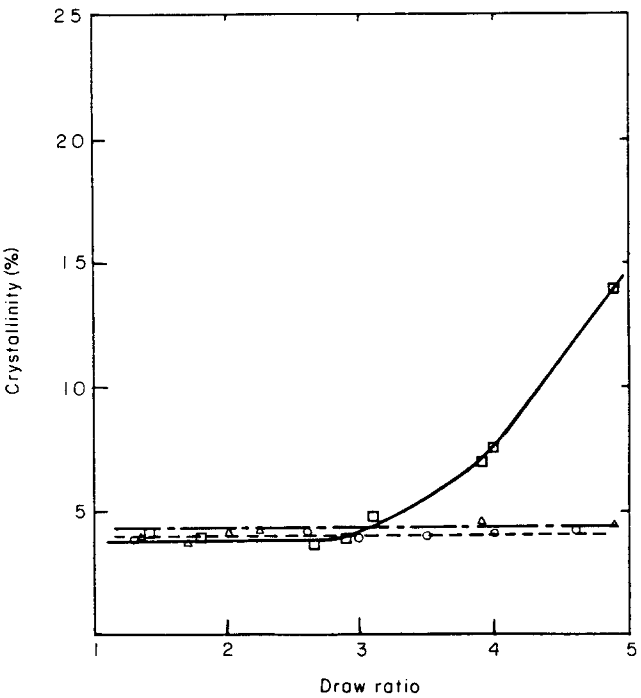

Figure 9 Variation of crystallinity as a function of draw ratio at 103°C and various strain rates: 0.115 s^{-1} (□); 0.028 s^{-1} (△); and 0.008 s^{-1} (○)

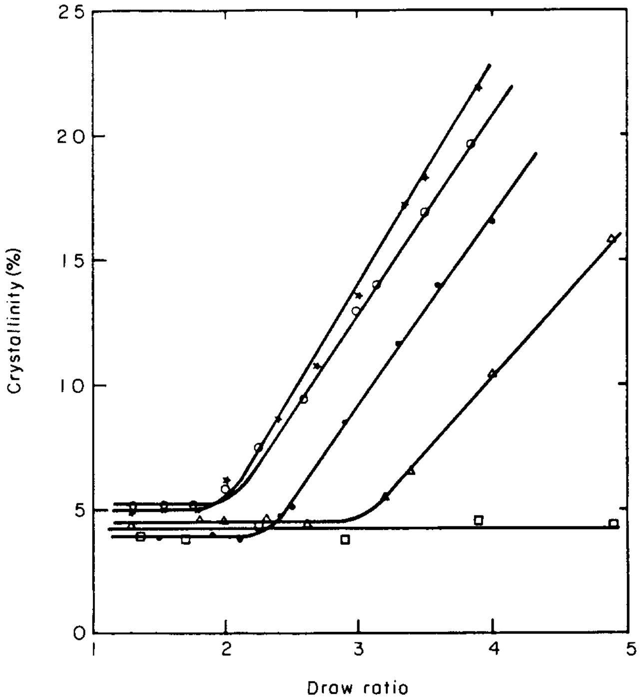

Figure 10 Variation of crystallinity as a function of draw ratio at constant strain rate (0.028 s^{-1}) and various temperatures: 80°C (★); 84°C (○); 90°C (●); 96°C (△); 103°C (□)

With the measurements of orientation by fluorescence polarization of VPBO, a critical orientation of *trans* amorphous chains, denoted $\langle P_2(\cos\theta)\rangle_{cr}$, can be associated with each critical draw ratio λ_{cr}. The values of $\langle P_2(\cos\theta)\rangle_{cr}$ are also reported in *Table 1*.

Two remarks can be made about these values of critical orientation. First, for one stretching temperature, $\langle P_2(\cos\theta)\rangle_{cr}$ remains constant, whatever the values of the strain rate. Secondly, as the stretching temperature increases, the critical orientation $\langle P_2(\cos\theta)\rangle_{cr}$ decreases. These results show that the critical orientation for the initiation of induced crystallization can be defined, independently of the strain rate, as a decreasing function of the temperature only (*Figure 11*).

The temperature appears, through the orientation, as the main parameter that determines the beginning of crystallization. The evolution of $\langle P_2(\cos\theta)\rangle_{cr}$ with temperature can be explained by the essential role of *trans* segments in the formation of nuclei[25]. The lower the temperature is, the lower is the mobility of the chains and the more the chains must be oriented to compensate for this low mobility with a larger number of amorphous *trans* chains that contribute to the formation of stable nuclei.

The strain rate has an influence only on the critical draw ratio λ_{cr}; with decreasing strain rate, the relaxation increases and the larger λ_{cr} must be, so that the critical level of orientation can be reached. At the low rates, at 103°C, the relaxation is too large during the stretching and prevents the chains from reaching $\langle P_2(\cos\theta)\rangle_{cr}$, such that no crystallization is observed.

Crystallinity and trans *amorphous orientation during stretching*

In the representation of the variation of crystallinity X with the draw ratio λ (*Figures 5* to *9*), the influence on the degree of crystallinity of the parameters temperature, strain rate and orientation is covered by the chain

Table 1 Values of critical draw ratio and critical orientation as a function of stretching parameters ($T,\dot{\varepsilon}$)

T (°C)	$\dot{\varepsilon}$ (s^{-1})	λ_{cr}	$\langle P_2(\cos\theta)\rangle_{cr}$
80	0.115	1.85	0.365
	0.028	1.90	0.360
	0.008	2.10	0.375
84	0.115	1.95	0.280
	0.028	2.05	0.285
	0.008	2.40	0.320
90	0.115	2.05	0.200
	0.028	2.35	0.195
	0.008	2.85	0.195
96	0.115	2.25	0.135
	0.028	3.10	0.150
103	0.115	3.45	0.120

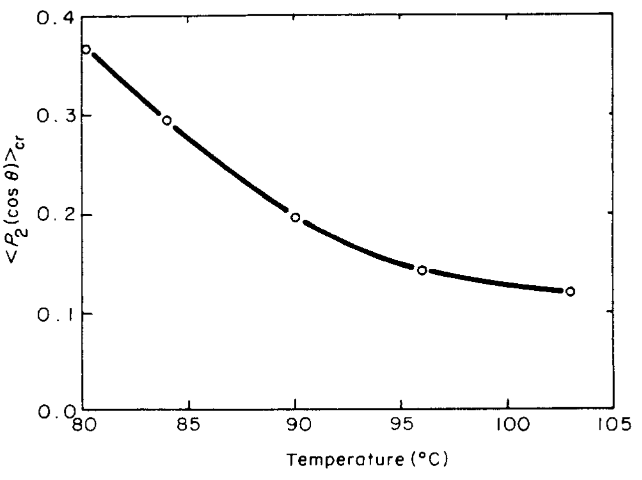

Figure 11 Dependence of the critical orientation for the initiation of induced crystallization on the stretching temperature

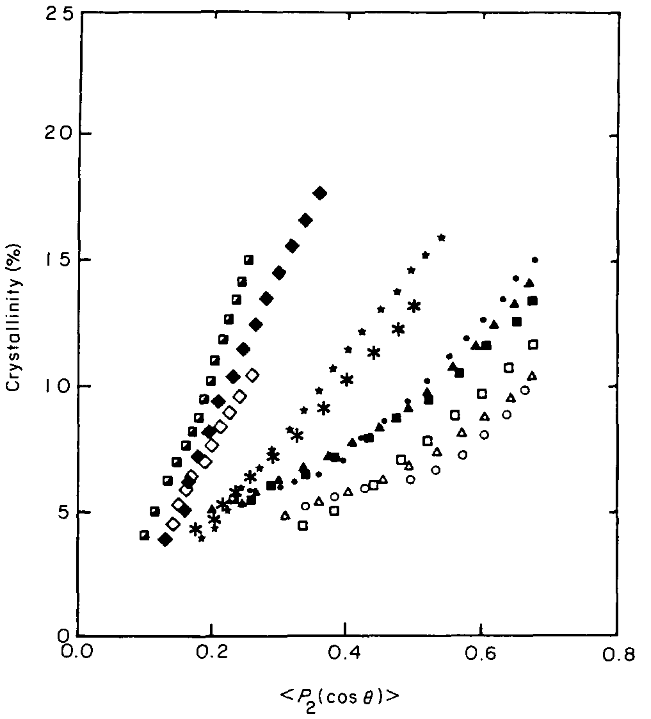

Figure 12 Relation between crystallinity and amorphous orientation in various conditions of stretching: $T=80°\mathrm{C}$ and $\dot{\varepsilon}=0.115\,\mathrm{s}^{-1}$ (□), $0.028\,\mathrm{s}^{-1}$ (△), $0.008\,\mathrm{s}^{-1}$ (○); $T=84°\mathrm{C}$ and $\dot{\varepsilon}=0.115\,\mathrm{s}^{-1}$ (■), $0.028\,\mathrm{s}^{-1}$ (▲), $0.008\,\mathrm{s}^{-1}$ (●); $T=90°\mathrm{C}$ and $\dot{\varepsilon}=0.115\,\mathrm{s}^{-1}$ (*), $0.028\,\mathrm{s}^{-1}$ (★); $T=96°\mathrm{C}$ and $\dot{\varepsilon}=0.115\,\mathrm{s}^{-1}$ (◆), $0.028\,\mathrm{s}^{-1}$ (◇); $T=103°\mathrm{C}$ and $\dot{\varepsilon}=0.115\,\mathrm{s}^{-1}$ (◪)

relaxation that occurs during the stretching. To enhance the effect of these parameters, the crystallinity has been plotted against the *trans* amorphous orientation $\langle P_2(\cos\theta)\rangle$, both generated during stretching at different rates and temperatures (*Figure 12*).

It is noticeable that one temperature T and one level of orientation $\langle P_2(\cos\theta)\rangle$ determine completely the degree of crystallinity of the sample. This degree of crystallinity is independent of the strain rate. As shown in *Figure 12*, the small variations of X with $\dot{\varepsilon}$ have no correlation from one temperature to another, and these variations must be considered to be experimental errors. For a given temperature and orientation, the lack of influence of $\dot{\varepsilon}$ has already been observed for fibre spinning and can be interpreted as the balance of two phenomena[27]. The strain rate determines the time allowed for the sample to crystallize and so, the lower is the strain rate, the higher will be the crystallinity. On the other hand, with higher strain rates, the internal temperature of the sample can increase by viscous dissipation and involves a faster crystallization. The compensation of these two effects can explain that, for one temperature and one level of orientation, the crystallinity is independent of the strain rate $\dot{\varepsilon}$.

Figure 12 shows that, for a given temperature, the higher the orientation is, the higher is the crystallinity. So, the influence of $\dot{\varepsilon}$ observed in *Figures 5* to *9* can be explained: for one temperature T and one draw ratio λ, the lower the strain rate is, the larger is the relaxation. This implies lower values of orientation and, therefore, lower degrees of crystallinity.

Moreover, *Figure 12* shows that, for a given orientation, the crystallinity increases with the stretching temperature. This influence of the temperature is well known for isothermal crystallization of an isotropic material[28,29].

In the same way, the effect of temperature observed in *Figure 10*, i.e. the decrease of crystallinity with temperature at one draw ratio, can be explained: for one strain rate $\dot{\varepsilon}$ and draw ratio λ, the higher the temperature is, the larger is the relaxation. This implies a lower orientation and then a lower degree of crystallinity.

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