Is the break in the curve giving the thermal dependence of crystal growth rate a signature of regime II→III transition?

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A combined study of the morphology and the kinetics of isothermally grown spherulites of poly(ethylene oxide) ($M_w = 20\,000$) has revealed that a break in the $\log G$ *versus* T_c plot coincides with a change in the crystallographic orientation of the leading growth face. Because, in the 'regime III→II transition', the growth front is assumed to maintain the same crystallographic orientation, we conclude that the observed break cannot be taken as the signature of such a transition.

(Keywords: crystallization temperature; nucleation theory; orientation; poly(ethylene oxide); regime transitions; supercooling; X-ray diffraction)

INTRODUCTION

It is accepted that, in a certain range of temperature, the crystallization of polymers is controlled by surface nucleation and proceeds in the polynucleation regime (or regime II). According to Hoffman[1] the distance between the *niches* on the growth front diminishes rapidly with falling crystallization temperature T_c and approaches the molecular width at a transition temperature $T_{\mathrm{II}\rightarrow\mathrm{III}}$ (ref. 2). He postulates that below this temperature a new crystallization regime occurs (regime III) and that the growth rate is proportional to the surface nucleation rate i (instead of being proportional to $\sqrt{i}$ as in the polynucleation regime). This corresponds to a marked *upward* change of the growth rate *versus* temperature curve.

Mathematically, Hoffman postulates that the nucleation barrier expressed in both regimes is:

$$\Delta\Phi = 4b\sigma\sigma_e T_m^\circ / \Delta h_f \Delta T f \qquad (1)$$

where b is the thickness of a molecular layer, $\sigma\sigma_e$ the product of the lateral and fold surface free energies, Δh_f the heat of fusion per unit volume, T_m° the equilibrium melting temperature, $\Delta T = T_m^\circ - T_c$ and $f = 2T_c/(T_m^\circ + T_c)$. In regimes II and III the growth rate can be expressed in terms of a well known equation:

$$G_{\mathrm{II}} = C_{\mathrm{II}}\beta \exp(-K_{g\mathrm{II}}/T_c\Delta T f) \qquad (2)$$

$$G_{\mathrm{III}} = C_{\mathrm{III}}\beta \exp(-K_{g\mathrm{III}}/T_c\Delta T f) \qquad (3)$$

$$K_{g\mathrm{III}} = 2K_{g\mathrm{II}} \qquad (4)$$

where C_{II} and C_{III} involve terms which with respect to the third factor are temperature-insensitive and where β is a retardation factor pertaining to the diffusion of molecules at the growth front. These equations justify the universally adopted criterion for regime transitions: in a plot of $\log G/\beta$ *versus* $1/T\Delta Tf$ a regime transition is recognized by an *increase* in the slope of the curve by a factor equal or close to 2 when passing from regime II to regime III. This condition relies heavily upon the fact that equation (1) with the same value of $\sigma\sigma_e$ is assumed to hold in both regimes, because the orientation of the growth front is assumed to be the same.

In this paper, we do not intend to discuss the predictive ability or the theoretical foundation of the standard 'theory' of polymer crystal growth[1,2] (this was done by one of us in collaboration in another paper[3]), but rather to scrutinize, in a particular experiment on the crystallization of poly(ethylene oxide) (PEO), if such a break in the $\log G$ *versus* $1/T\Delta Tf$ curve is really the signature of a regime transition (as assumed by one of us (in collaboration) in a recent paper[4]). In some respects this note is an erratum to this latter paper, because, as shown here on an experimental basis, the considered transition cannot be classified as a regime II→III transition. In fact, at temperatures of crystallization that are in the range of these two 'regimes', the growth front differs in crystallographic orientation.

EXPERIMENTAL

Poly(ethylene oxide) ($M_w = 20\,000$; $M_w/M_n = 1.1$) was purchased from Hoechst. Isothermal growth rate measurements were performed on films 10 μm thick previously melted between glass plates. Spherulitic films of PEO used in X-ray diffraction were supported between sheets of polypropylene inserted between two glass slides. The wide-angle X-ray pattern was taken at the peripheral part of a large spherulite and was recorded on planar films using Ni-filtered Cu Kα radiation ($\lambda = 0.15418$ nm).

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RESULTS

The results of growth rate measurements are very similar to those previously obtained by one of us in collaboration[4]. The log G *versus* T_c curve shows a break at 49.7°C (*Figure 1*). X-ray fibre patterns are obtained from spherulites crystallized at 48, 49, 52.5, 56, 57.5 and 58°C (see *Figure 2*).

In the patterns obtained at $T_c = 49°C$ and at lower temperatures (well within the supposedly regime III region), the (0 1 0) plane is found to be tangential to the growth front, and no evidence of a rough or ill-defined growth front appeared to be present. At higher temperatures of crystallization, above 49°C, the (1 2 0) plane becomes tangential. These results on medium-molecular-weight PEO are similar to those obtained by Hirai *et al.*[5] on a lower-molecular-weight PEO fraction. Balta Calleja and co-workers[6] have also investigated the crystal orientation within poly(ethylene oxide) spherulites. Spherulites with both b and [4 0 1] radial orientation were found (see also refs. 7 and 8). On non-isothermal crystallization of PEO of low molecular weight (6000), we have also observed successive changes in the radial orientation (unpublished results). Note, however, that in these various works, no correlation with measurement of growth rate was established, and that sometimes the crystallization conditions (temperature and molecular weight) were not reported. Unfortunately, at this time, we are not able to grow spherulites of suitable size for X-ray studies much above 58°C. Work in this direction is still in progress in our laboratory.

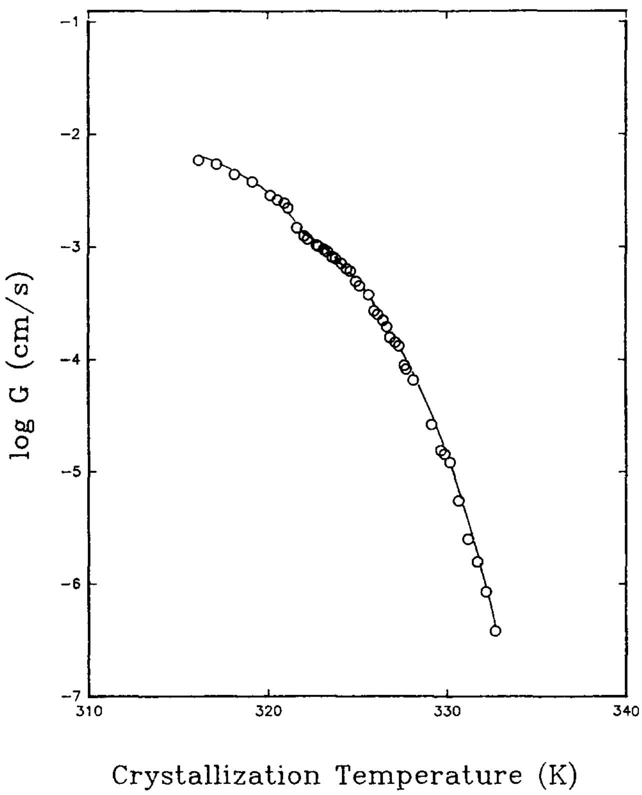

Figure 1 A plot of log G *versus* T_c for PEO from the melt ($M_w = 20\,000$; $M_w/M_n = 1.1$)

DISCUSSION

In the case of spherulites of PEO of $M_w = 20\,000$, the radial direction is not the same for temperatures of crystallization lower and higher than the temperature at which a break in the curve of log G *versus* T_c appears. Therefore the observed transition cannot be classified as a regime II→III transition, which was explained in the introduction, as this would imply that the crystallographic orientation of the growth front is the same above and below the transition point. By contradistinction, even if the standard theory of polymer crystal growth is used, the break may be explained by assuming that in the whole range of crystallization temperature the crystallization process proceeds in the polynucleation regime; on two different crystallographic planes, the product $\sigma\sigma_e$ of the lateral and fold surface free energies may not be the same, and thus the corresponding values of K_{gII} differ one from another. The graph of log G *versus* $1/T\Delta Tf$ may comprise two intersecting curves. It may be that these two curves

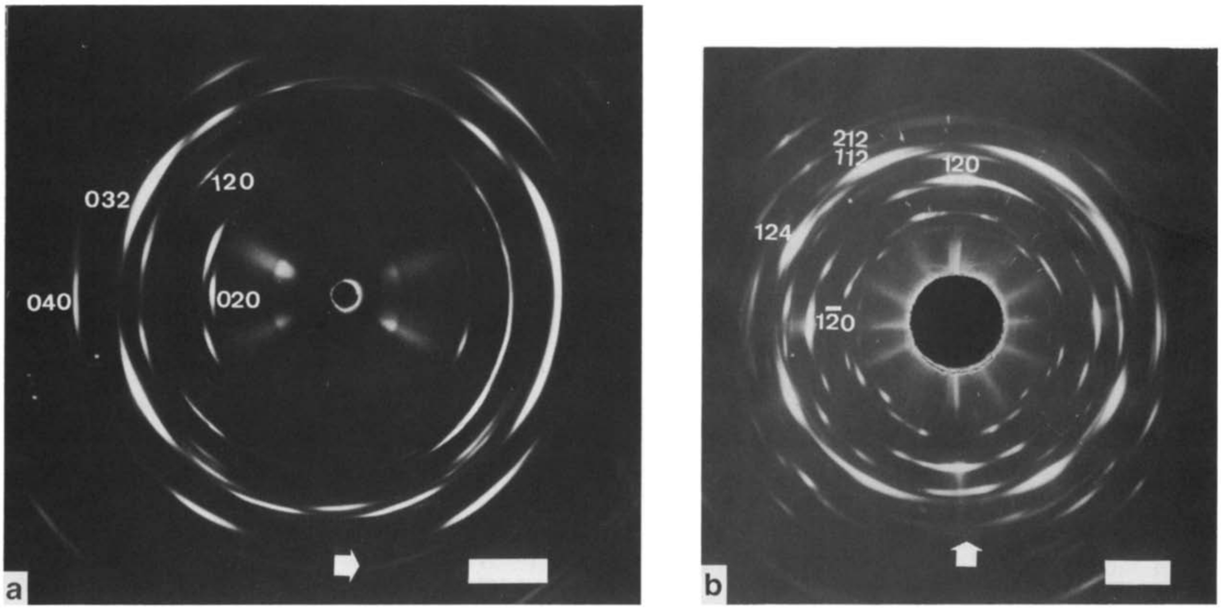

Figure 2 X-ray fibre patterns from PEO spherulites grown at (a) 48°C and at (b) 57.5°C. The arrows indicate radial growth direction; scale bar = 1 nm^{-1}

are observable at temperatures both lower and higher than the intersection point. We have made such an observation in many systems where two types of spherulites develop under the same conditions of crystallization (a well documented situation from the earlier years[9]).

Recently, in a kinetic study of the crystallization of a PEO–*p*-nitrophenol molecular complex[10], two breaks in the curve giving the thermal dependence of the linear crystal growth rate were observed. These breaks were found to correspond to an overall change in the crystal orientation within spherulites grown isothermally. This result was confirmed by fibre X-ray diffraction studies as well as from dichroic measurements using polarized Fourier transform infra-red spectroscopy.

From the present work, it appears very likely that (also for pure PEO) the change in radial crystallographic orientation is the cause of the observed break. In any case, this break cannot reveal a regime II→III transition because, from a pragmatic point of view, the practicians assume that the thermal dependence of i, the initiation rate or the rate of attachment of a stem on a substrate, the product of lateral and fold surface free energies and finally the nucleation barrier have the same values below and above a 'regime II→III' transition, justifying, in this way, the change by a factor equal or close to 2 in the slope of the $\log G$ *versus* $1/T\Delta Tf$ curve.

CONCLUSIONS

The $\log G$ *versus* T_c curve for PEO of $M_w = 20\,000$ presents a break at 49.7°C. This break is very likely due to a change of morphology and cannot be interpreted as the signature of a regime transition to the hypothetical and so-called 'regime III'.

We suggest that defenders of 'regime I and III' perform not only kinetic but also morphological studies, and more especially that they determine the crystallographic orientation of the growth front. From our point of view claims about the values of $\sigma\sigma_e$, when obtained from a regime II→III analysis, need at least further justification.

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