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Abstract: Simulations have shown that temperature changes during the growth of lamelae/ribbons of a polymer crystal induce alterations in the thickness of the lamelar crystal. Therefore, the lamelae/ribbons would melt at different temperatures. This is demonstrated experimentally here for spherulites of Isotactic Polystyrene (iPS). The results were obtained following the melting process of selected spherulite structures through temperature scanning. The samples, in which chosen spherulites were observed, were crystallized from the melting state at successive crystallization temperatures. Observations of these spherulite melting processes were made with an optical polarized microscope, using a hot stage to apply the temperature scan.

Keywords: *Morphology, crystallization, crystalline thickness, spherulite structure, isotactic polystyrene.*

Introduction

What are the effects on the crystallites of a spherulitic structure, when the growth is made at different successive crystallization temperatures? In a spherulite, the crystallites grow radially from the center of the spherulite, following the direction of one of the crystallographic axes of the crystallites, giving rise to true ribbons[1]. What will happen to the ribbons when successive crystallization temperatures are applied?

In the literature that discusses these questions, it has been shown by simulation[2-5] that the ribbon thickness is modified as the crystallization temperature changes. Nevertheless, experimental results that prove this statement are not found. Through atomic force microscopy[6] it has been possible to see the height of the lamella and the roughness of the folded surfaces. Electron microscopy[7] has enabled the physical changes occurring during the thickening to be followed, as well as the melting of lamellar crystals. On the other hand, there are many results coming from techniques such as SAXS and WAXS[8-9], that describe the variation of average lamellar thickness with crystallization temperatures. It has been demonstrated that the thickness increases with rising crystallization temperature.

In fact the average lamellar crystal thickness (l_c) is[10-12] inversely proportional to the supercooling (ΔT) following equation 1, where A and B are constants and ΔT is given by equation 2:

$$\ell_c = \frac{A}{\Delta T} + B \tag{1}$$

$$\Delta T = T_m^{\,o} - T_c \tag{2}$$

with $T_m^{\,o}$ the equilibrium melting temperature and T_c the crystallization temperature.

Equation 1 can be deduced for a homogeneous nucleation[13,14], which will happen with low ΔT, giving rise to single crystals. Under this condition, A is given[13] by

$$A = \frac{4\sigma_e\, T_m^0}{\Delta h_f} \tag{3}$$

and B is zero. σ_e corresponds to the surface free energy of the upper and lower folded surfaces of the

A R T I G O   T É C N I C O   C I E N T Í F I C O

crystallites and Δh_f, is the bulk enthalpy of melting per unit volume in the crystallite at T_m^0. The corresponding bulk free energy of melting Δf is given[13] for low and intermediate ΔT by

$$\Delta f = \left[\frac{\Delta h_f \, \Delta T}{T_m^0} \right] \left(\frac{2 \, T_c}{T_m^0 + T_c} \right) \qquad (4)$$

where for the single crystal formation $2 T_c / (T_m^0 + T_c)$ is practically one.

On the other hand, in the case of crystallization with spherulite formation, in regime I and the high temperature part of regime II, the equation 1 must be derived on the basis of heterogeneous nucleation[14,15] (for the different regimes I, II and III, see reference 14). For the case of A in equation (3) the new deduction only incorporates the term $(T_m^0 + T_c)/2 T_c$ in the right side, when it can not be considered one. At the same time, the deduction for B on the basis of heterogeneous nucleation [14,15] gives a non zero value. For the case in which the apportion fraction ψ[15] (the fraction that contribute to the free activation energy of the total free energy of interactions for the passage of a stem from the amorphous region to the crystallite growing surface) is considered zero and if it is assumed[15] that

$$\frac{4 \, \sigma}{a_0} \rangle \Delta f \qquad (5)$$

B is given[14] by

$$B = \frac{k \, T_c}{2 \, b_0 \, \sigma} \qquad (6)$$

where σ is the surface free energy of the lateral faces of the crystallites and a_0 and b_0 are the parallel and perpendicular dimensions to the growing surface, respectively, of a stem located on the growing crystallite surface. In a more general situation, B is given[14,15] by

$$B = \frac{kT}{2 \, b_0 \, \sigma} \left[\frac{\Delta f + 4 \, \sigma / a_0}{\Delta f + 2 \, \sigma / a_0} \right] \qquad (7)$$

However, in equation 7 neither the fluctuations of the folding surfaces nor the interface regions between crystalline and amorphous regions have been taken into account.

For regimes I and II it has been shown by Lauritzen and Passaglia[16] that the fluctuations of the folding surface contribute with two terms, which have been called equilibrium and kinetic roughness[15]. The first one (d_{eq}) corresponds to the folded surface roughness at T_m^0. The second (d_{kin}) comes from the kinetic process and is given[16] by

$$d_{kin} = \frac{2 \, \sigma_{e(eq)} \, y \, T_m^0}{\Delta h_f} \qquad (8)$$

where $\sigma_{e(eq)}$ is the equilibrium surface energy of the folded surface at T_m^0 and y is the temperature coefficient of σ_e. In this sense, the surface energy of the folded surface σ_e changes in a way given[15] by

$$\sigma_e = \sigma_{e(eq)} \left(1 + y \, \Delta T \right) \qquad (9)$$

On the other hand, the interface region between crystalline and amorphous regions (d_a), which is related to the second-nearest neighbor nonadjacent reentries back into the lamella[15], has not yet received a theoretical treatment.

Finally, all these theoretical treatments apply to regimes I and II, but there is none for the case of regime III[15]. Even in the case of very high ΔT, where Mandelkern et ali.[17] have shown that there is no spherulite formation and the crystallites become oriented at random, there is also no theoretical formulations for B. Even when some of these equations are not going to be used in the present paper, they have been discussed to show which is the theoretical situation of the field which constitute in some ways the background of the work which will be presented.

The purpose of the present study was to demonstrate, from experimental data, that when a spherulite structure is grown at successive temperatures, the thickness of its ribbons varies. To this end, it was proposed to observe the melting of iPS spherulites structure previously grown at successive values of T_c. From these observations it will be shown how to get indirect information about changes in the ribbons thickness inside the spherulite, by take into account a known relation[14,15] between the melting temperature T_m of a given crystallite and its thickness l_c:

$$T_m = T_m^0 \left[1 - \frac{2 \, \sigma_e}{\Delta h_f \, \ell_c} \right] \qquad (10)$$

Experimental

The Isotactic Polystyrene (iPS) ($M_w = 3 \times 10^6$ g/mol, $M_w/M_n = 16$ and isotacticity 90%) was obtained from the Macromolecular Institute of Rio de Janeiro (IMA, UFRJ), to which the authors are indebted.

In situ imaging of the growth and melting of specific spherulites was accomplished by mounting the sample in a Linkam hot-stage between the crossed polarizing lenses of an Olympus BX50 microscope. A CCD-Iris camera was used for the video recording of the processes.

To prepare samples for study, as received iPS powder was melted in the hot stage at a scanning rate of 10°C/min from room temperature to 280°C, where it was kept for two minutes. These particular initial experimental conditions chosen are explained elsewhere[18]. Subsequently, the sample was cooled to different successive crystallization temperatures at 50°C/min. Several successive T_c were used, the samples being maintained at these T_c for different times. The passage between two successive T_c was always made at a scanning rate of 50°C/min from a lower T_c to a higher one. The idea to begin with a lower T_c, even when it can be thought to conduce to the growth of the crystallite thickness and/or to produce recrystallization at the higher T_c, was chosen due to problems coming from low nucleation rate at high temperatures together with the modification of the spherulite sizes from spherical (low T_c) to hexagonal (at enough high T_c), as it is well known. This procedure from low T_c to higher ones, nevertheless, does not prevent the observation of the evidences that wish to be shown.

After growth at different T_c of spherulite structures that will be followed during their melting, the samples were cooled again to room temperature at a scanning rate of 50°C/min. At this point, the samples were ready for the temperature scanning, at a sweep rate of 10°C/min., to observe the melting process of the selected spherulite.

This procedure led to obtain polymer samples about 10 μm thick, contained between the two glass cover slips. To obtain this sample thickness, in general, about 0.05 mg of as received polymer powder was used.

The growth and melting of a given spherulite structure through the microscope with the hot stage plate was followed, using polarized light, with the focus of the microscope kept constant. This enables the evolution of the melting process to be observed on a comparative base.

Results and Discussion

Figure1 shows successive optical micrographs of the melting process for a chosen spherulite. This was grown at various crystallization temperatures as explained in the experimental part. The regions that match these different temperatures in the growth process are visualized during the melting process in Figure 1b. The central region of the spherulite was grown for 16 h at a T_{c1} of 140°C. The second region was grown at a T_{c2} of 180°C for 2 h. Finally, the external region was grown at 210°C (T_{c3}) over 18 h. The regions are visible in Figure 1b because inter-region lines appear as a result of the different textures of the different regions. This sequence of textures shows that something has changed with the change of the growing temperature T_c. A possible interpretation of these differences of texture, based on the simulation literature[2-5], is that in each different region there is different average thickness of the ribbons even when during the stage at each higher T_c they can be grown in thickness but do not seem to be recrystallized, as will be shown later. As a consequence, the melting of these different regions will happen at different temperatures following equation 10.

It can be seen in Figure 1b to f, as expected, that the spherulite melts from inside to outside, following the regions and the corresponding initial crystallization temperatures, and consequently, the expected ribbon differences in thickness are made visible indirectly by this technique (even with the possible thickening phenomenon). This is supported by the fact that a spherulite grown only at a T_c of 140°C shows its visible melting between 220 and 223°C then, there is an increase in T_m from 220-223°C to 223-225°C for the data in Figure 1.

The melting of a given region in Figure 1 is a non-instantaneous process happening in a given temperature interval for each region, and with the intervals in part overlapping. This occurs because at each crystallization temperature there are different phenomena like the primary and secondary crystallization processes. It is well known[15] that T_m is related to T_c by an equation obtained from equations 1, 3, 7 and 10, which can be summarized by

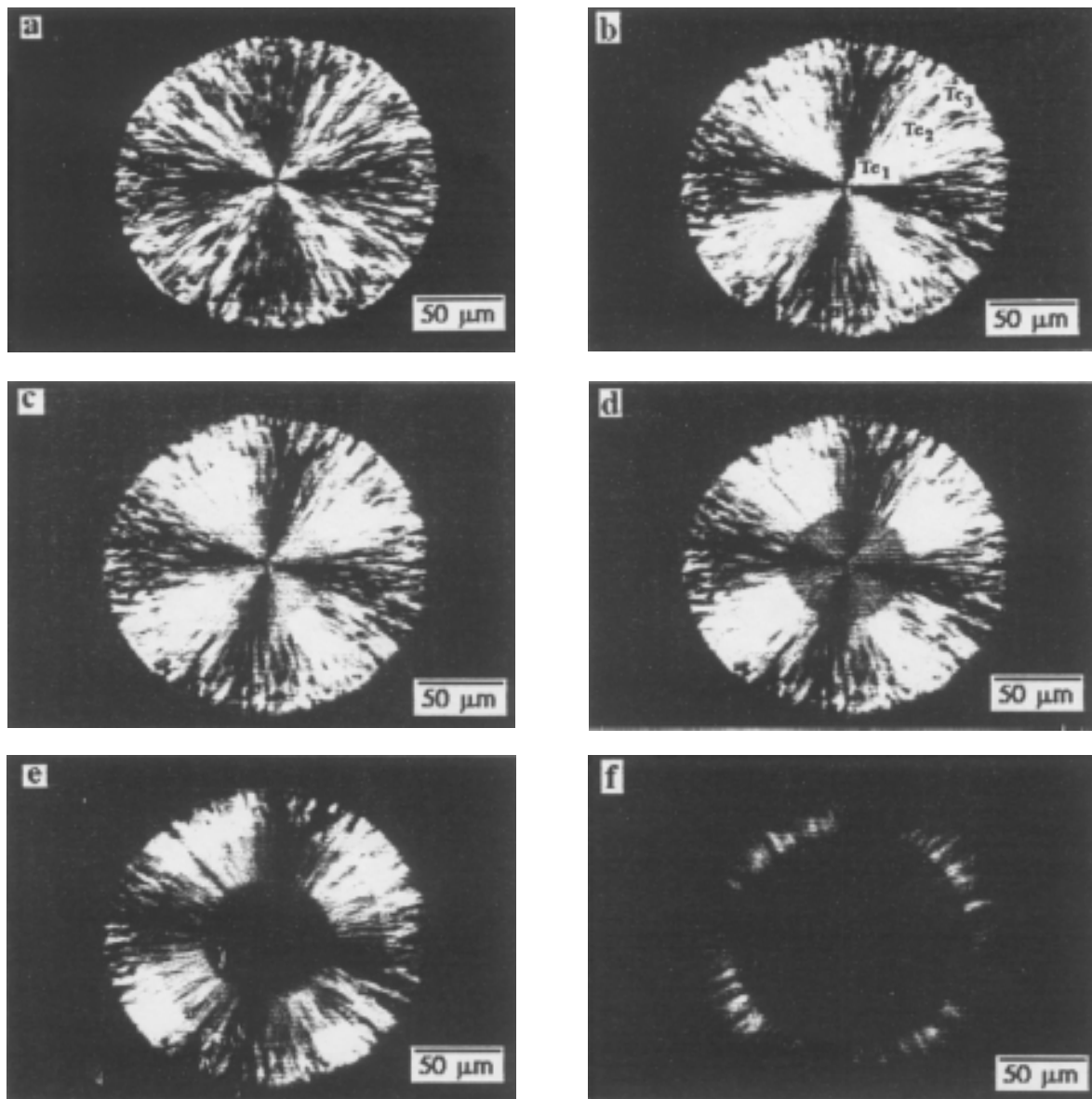$$T_m = T_m^0 \left(1 - \frac{1}{\gamma} \right) + \frac{T_c}{\gamma} \tag{11}$$

Figure 1- Sequences of micrographs obtained by optical microscopy with polarized light at distinct temperatures, during a scanning melting process. The focus is fixed throughout on the same spherulite grown at three different temperatures (see the text). Temperatures of the micrographs: (a) 25°C; (b) 223°C; (c) 224°C; (d) 225°C; (e) 226°C e (f) 227°C.

where γ is the fractional degree of thickening above the initial lamella thickness l_c at a given crystallization condition.

Typically, some ribbons (those which do not come from ramifications) are extended from the center of the spherulite to its edge. Thus, these results demonstrate the change of the thickness of these ribbons with the change in crystallization temperature. This does not mean that those ribbons which do come from ramifications of the original ribbons, do not also change in thickness as T_c changes.

For comparison, in Figure 2 is seen the melting behavior of one spherulite grown at a single temperature. In this case, the observed process is a continuous disappearance of the crystallites homogeneously over the whole observed volume of the spherulite. In this kind of spherulite there is no sign of the melt processing from the center to the edge of the structure, as in the previous process. This behavior is expected, since this spherulite would have ribbons produced under the influence of only one external crystallization temperature, even though the two phe-
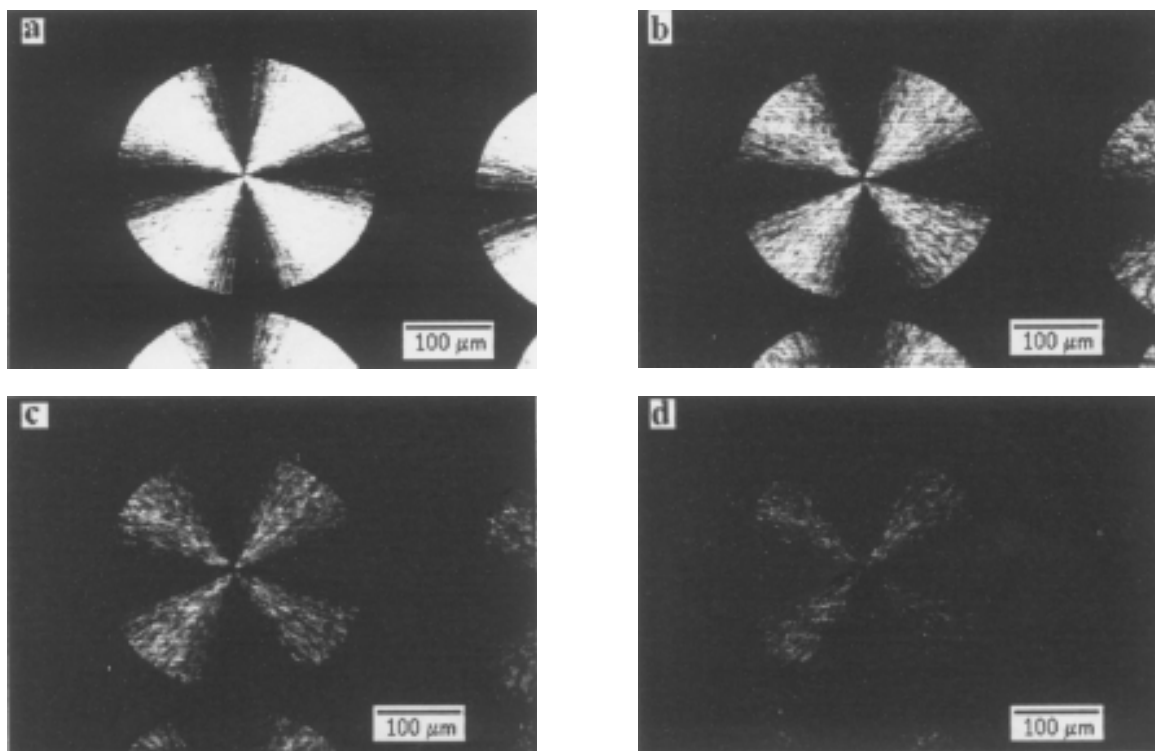
Figure 2. Sequences of micrographs obtained by optical microscopy with polarized light at distinct temperatures, during a scanning melting process. The same spherulite only grown at 150°C for 27 h is observed throughout at constant focus. (a) 25°C; (b) 220°C; (c) 221°C e (d) 222°C.

nomena are present: the primary and secondary crystallization processes[19].

Returning to the problem of recrystallizations, another significant observation in the experiments is that when the crystallization temperature increases from, for example, 140°C to 180°C, during the growth of a given spherulite, there is no observable melting process of the spherulitic region grown at 140°C neither during the temperature change nor during the permanence at the highest temperature. This can be observed in Figure 3.

The reasons of the different textures of the two regions of the spherulite shown in Figure 3, which have been called radial (internal part) and fibrillar (external part), have been discussed elsewhere[20].

Generally, it is assumed that under these circumstances the inner part of the spherulite of Figure 3 must be melted and recrystallized. Nevertheless, that is not observed. The ribbons can present one of their dimensions which arrive to be of the order of the radius of the spherulite in which it is included. This is possibly the reason by which the hoped melting fact for a lamella is not observed for ribbons. On the other hand, the melting can not occur with small increases of T_c, because the ribbon formed at a given T_c will
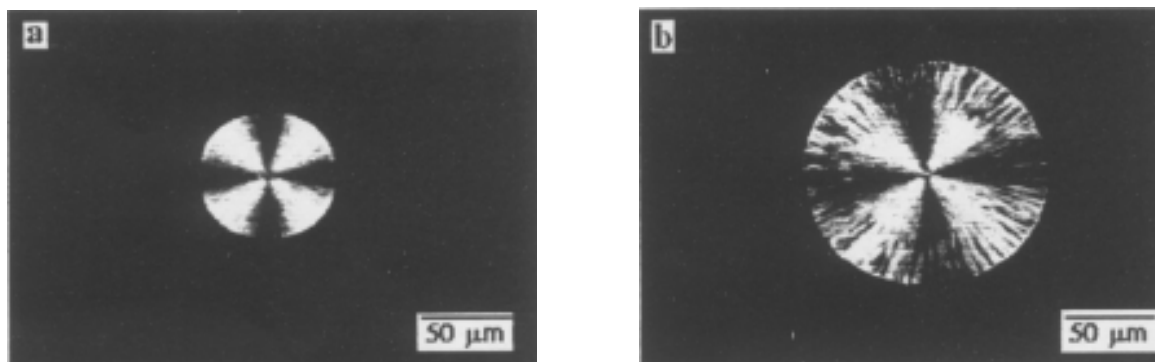

Figure 3. Micrographs of the same spherulite grown in two stages at different T_c: (a) after 16 hours at 140°C, (b) followed by 3 hours at 180°C.

melt at a T_m reasonably above that T_c. This can be related to the exothermicity of the crystallization process and the lack of thermal conductivity of the polymers, which is traduced into the fact that the local real crystallization temperature at the point where the ribbon is growing must always be higher than the external applied crystallization temperature. Nevertheless, in the literature[15] the fact that T_m is higher than T_c has always been explained only in terms of equation 10. It is possible to show from equation 10 that when B is zero (single crystal formation), T_m is equal to T_c. Hence, given that B > 0 under the spherulite formation conditions, the same equation 10 imply that T_m will be higher than T_c. These two interpretations must receive attention in the future.

Conclusions

The study of melting behavior by temperature scanning, using optical microscopy, in the case of iPS spherulites grown in successive different temperatures, demonstrates experimentally that:

i) spherulite exhibit different ribbons average thicknesses corresponding to their different growth temperatures. This was demonstrated because the different growth regions were melted at different temperatures;

ii) hence, as the crystallization temperature is changed from a lower to a higher one, each growing ribbon thickness will tend to alter from the initial thickness to the final one, as has been proposed by simulations;

iii) the increase of the crystallization temperature during the growth of a given spherulite will not always cause the previously grown region to melt and recrystallize. This will depend not only on the sizes of temperature increments but also on the value of the initial crystallization temperatures. This is closely related to the Hoffman and Weeks plot of T_m versus T_c. For the studied cases, due to the fact that the crystalline material is under the form of ribbons inside a spherulite, the recrystallization was not observed.

In the case of spherulites grown at a single temperature, the melting process occurring over a given temperature interval, was demonstrated to be homogeneous, because there is only one spherulitic region.

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