New dynamical effects in spherulitic growth

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Two unexpected phenomena have been observed during the study of the growth of α and β spherulites of a poly(ethylene oxide)–resorcinol complex: an overgrowth rate (denoted as G_i) of the fastest, namely the α-form, along the interface of the β-form, and a transformation of the β-form into the α-form, which propagates as a dynamic front at a constant rate G_t. The evidence for these two phenomena is demonstrated, and possible explanations are discussed. Measurements of the two rates, G_i and G_t, are also reported.

(Keywords: spherulitic growth; interspherulitic limit; PEO–resorcinol complex)

INTRODUCTION

It is well known[1–3] that under normal conditions of crystallization, semicrystalline polymers crystallize from the melt in the form of spherulites, i.e. spheres whose radii increase with time, and which originate from nuclei. Their sizes range from a few nm to several μm, depending upon the density of the nuclei. The chain axis of the macromolecules is always found to be tangentially oriented within these crystalline aggregates. At a microscopic level, spherulites are composed of a lamellar type morphology, consisting of a two-phase system with crystalline and amorphous components[4,5]. As sample preparations for polarized optical microscopy observations are usually in the form of thin films of polymer which are sandwiched between glass slides, the spherulites are therefore diametral cross-sections of the normally three-dimensional objects. Sometimes, this procedure allows us to obtain quite large spherulites, since the production of thinner cross-sections involves a natural reduction in the number of nuclei. Nucleation can be induced by quenching in liquid nitrogen, in order to obtain spherulites with sizes ranging from 10 μm to 10 mm.

In melt crystallization, the growth rate is defined and measured as the velocity of advancement of circular fronts. Hence, the larger the spherulite, the more precise is its growth rate determination. Some semicrystalline polymers can exhibit several crystal modifications, depending upon the experimental conditions. For example, poly(ethylene oxide) (PEO) usually crystallizes in a 7/2 helical conformation[6], but can crystallize in a *trans*-planar conformation[7] in a stretched sample. It is also possible to reversibly, or irreversibly, transform one form into another by changing the experimental conditions (such as stretching, heating, drying, etc.), e.g. as seen with poly(oxacyclobutane), which can exist in any one of three crystal modifications[7]. In more common examples, it is possible to obtain at least two different types of spherulites during the same sample preparation. Isotactic polypropylene is a good example, of this, since four distinctly different types of spherulites can be grown from the melt, and at least two of these at the same temperature[8,9]. Generally, a particular form can be favoured by using the appropriate operating conditions. In addition, different growth rates can be measured for the different allotropic forms, and this gives a good implication of typical shapes for the interspherulitic boundaries[4,10,11].

Poly(ethylene oxide) and resorcinol form a molecular complex with a 2/1 stoichiometry (i.e. two PEO monomer units for one resorcinol molecule)[12–14]. This paper deals with two different morphologies (denoted hereafter as the α- and β-form) for the molecular complex formed between these two components. The experimental preparation conditions have been described elsewhere[15]. In these experiments, we used PEO ($M_w = 35\,000$) which was obtained from Hoechst, and resorcinol, which was obtained from Aldrich, to prepare the molecular complex. In addition to the classical experimental study of the thermal dependence of the growth rates, which provides fascinating results arising from the different polymorphs, the experiments have also revealed two unexpected phenomena. First, an interfacial growth rate was observed which can be described as an overgrowth rate of the α-form spherulites when they are in contact with the slower growing β-form spherulites. The relative rate increase depends upon the temperature. This can be several tens of percents at low temperatures, which becomes increasingly less significant at elevated temperatures, and eventually becomes essentially undetectable above a certain temperature. Secondly, a transformation of the β-form into the α-form, which occurs when a β-form spherulite encounters an α-form spherulite, was found. At high temperatures, this transformation process follows a dynamic front, which propagates at a constant rate within the β-phase. This rate increases with temperature. Some results about spherulitic growth and interspherulitic limits will be recalled prior to the presentation of these specific new results.

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USUAL GROWTH RATES, INTERSPHERULITIC LIMITS

As we are only interested in a macroscopic description of the spherulitic growth, the following simple equation (in spherical coordinates) may suffice:

$$r = Gt \tag{1}$$

where r is the radius of the spherical front of the growing spherulite, G is the growth rate, and t is the time which has elapsed after the nucleation event. A two-dimensional growth pattern can be modelled by the parametric equation of the crystallization front in cartesian rectangular coordinates:

$$(x-x_0)^2+(y-y_0)^2=[G(t-t_0)]^2 \tag{2}$$

where (x_0, y_0) represents the position of the nucleus which has started to grow at time t_0. The crystallization stops when two spherulites encounter each other, the consequence of which is the formation of an interspherulitic limit. It is quite evident that the loci of encounter of simultaneously nucleated and identical objects are the mediatrices of the lines between the centres (*Figure 1a*). It is easy to obtain simultaneously nucleated spherulites by quenching samples of the PEO–resorcinol complex in liquid nitrogen (*Figure 1b*). When nucleation events take place at different times, the interspherulitic boundary is a branch of a hyperbole, whose focuses are the centres of nucleation. The delay between two nucleation events is an invariant feature, which when multiplied by the growth rate, gives a characteristic difference length. The geometrical locus of the encounter of the spherulites is the point at which the difference in the lengths of the radii is this characteristic length. This is clearly the definition of an hyperbole. In bipolar coordinates, the equation then becomes:

$$r_1-r_2=G(t_2-t_1) \tag{3}$$

where r_1 and r_2 are the radii of the spherulites and t_1 and t_2 are, respectively, the times at which they are nucleated. *Figure 1c* shows schematically the hyperbolic shape, whereas *Figure 1d* presents an experimental case in which nucleation began at different times, in all cases for the PEO–resorcinol molecular complex. A more extended treatment of this case can be found elsewhere[11].

In order to introduce the main objective of this paper, we have still to learn how the interspherulitic boundaries exist between spherulites with two different morphologies, which grow at different rates during the same preparation; details concerning these limits can also be found in the above mentioned paper[11], although the subject was first introduced by Point[3] in 1953. Let us define the problem: the two morphological species, referred to hereafter as α and β (α defines the fastest allotropic form) are characterized by the radial growth rates, G_α and G_β, respectively. These rates depend upon the crystallization temperature. The nucleation of the slow β spherulite defines the initial time 0 and the origin of the cartesian coordinates (0, 0), whereas the α spherulite nucleates at time t_α, at a distance d (at the position of

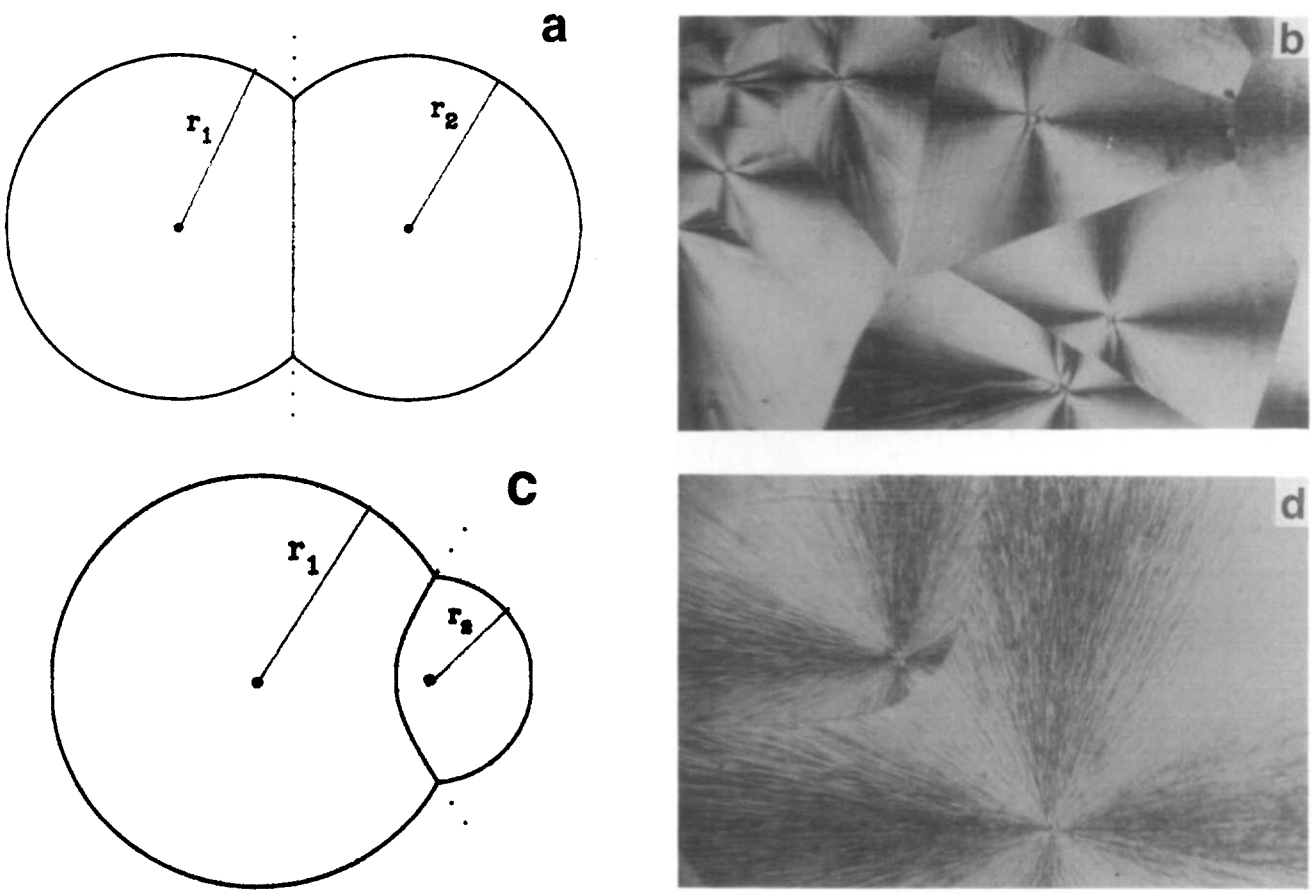

Figure 1 Impingement of spherulites of the PEO–resorcinol complex with the same morphology: (i) simultaneously nucleated, (a) schematic representation of the limit, and (b) micrograph showing mediatrices between the α-spherulites and; (ii) nucleated at different times, (c) schematic representation of the hyperolic limit and (d) micrograph showing a part of the hyperbole

coordinates $(-d, 0)$) from the β nucleus. The problem of the locus of encounter of the α and β fibres is in its first part almost identical to a problem resolved by Descartes concerning optics. The equation of this locus (also known as a Cartesian oval) in bipolar coordinates states that the delay between nucleation events is the invariant feature of the problem, which yields to give:

$$\frac{r_\alpha}{G_\alpha} - \frac{r_\beta}{G_\beta} = -t_\alpha \tag{4}$$

Figure 2a presents an illustration of this equation, while *Figure 2b* shows the encounter of α and β spherulites in the PEO–resorcinol system. It is, however, clear that when the α fibres become tangential to the spherulitic limit, the Cartesian oval cannot remain as the solution of the problem, since the α fibres cannot produce a second encounter (see *Figure 2a*). We define, therefore, a 'tangence time', t_t, and 'tangence coordinates', after which we need a new equation for the α–β interspherulitic limit. After tangence has occurred, it is evident that crystallization of both species can continue in the 'shaded side', represented by the dashed lines, in *Figure 2a*. It is observed that the tangence point constitutes a new growth centre for the α fibres and that this is also the case for all of the successive encounter sites. This observation corresponds to an old idea in solid-state physics which states that each new part of a crystalline aggregate constitutes a centre for further crystallization. These centres are both the cause and the limit of the curve itself. The problem is reduced to finding the equation of a curve having the following properties: during a small time interval dt, the radius r_β increases its length by an amount dr_β $(= G_\beta\, dt)$, and the length of the arc of the limited curve increases by $G_\alpha\, dt$, which is also equal to (see the right-angle triangle construction in *Figure 2d*)

$$\sqrt{(r_\beta\, d\psi)^2 + dr_\beta^2} = G_\alpha\, dt \tag{5}$$

where r_β and ψ are polar coordinates centred on the β nucleus. Equation (5) can be easily transformed in the

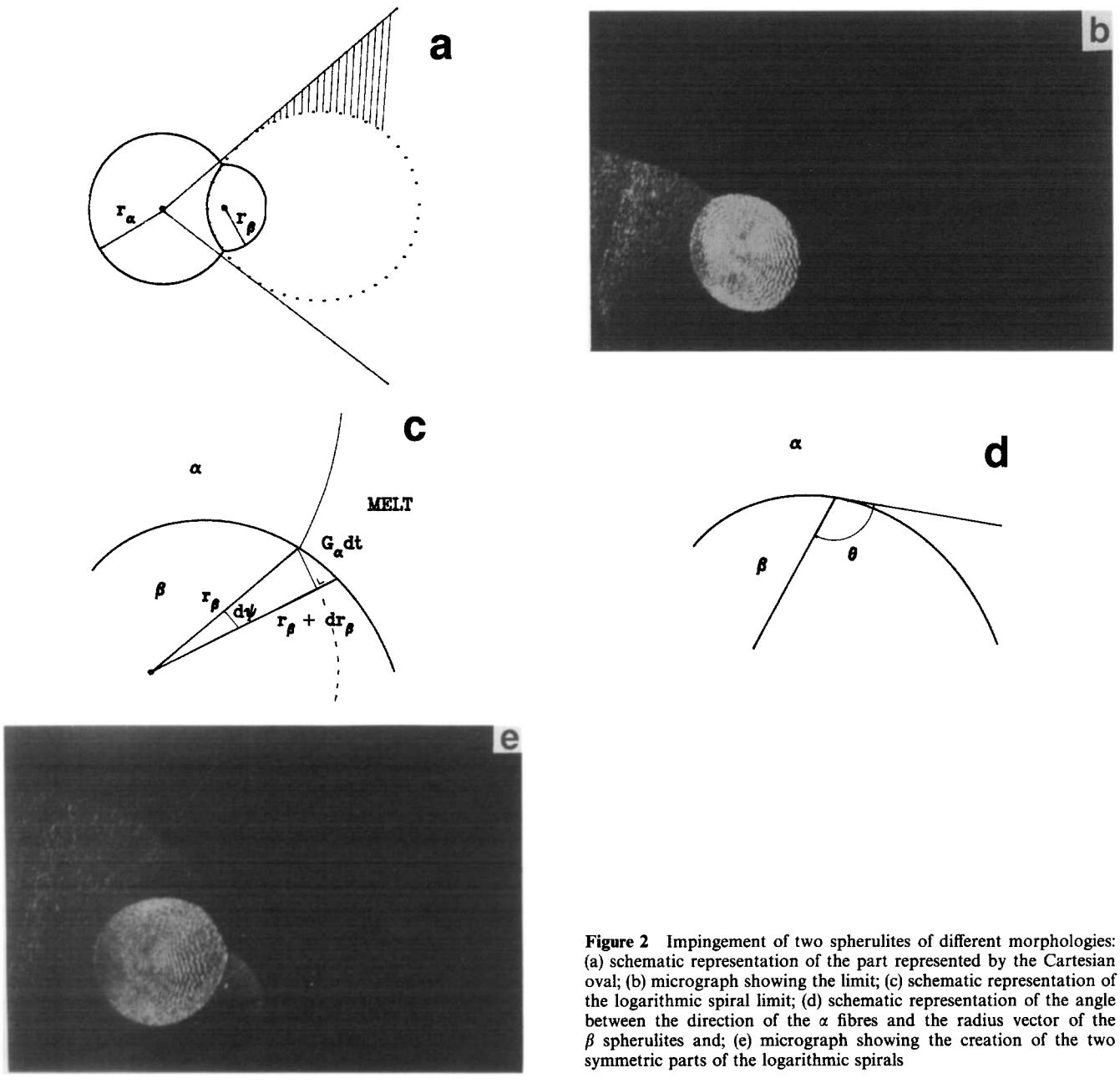

Figure 2 Impingement of two spherulites of different morphologies: (a) schematic representation of the part represented by the Cartesian oval; (b) micrograph showing the limit; (c) schematic representation of the logarithmic spiral limit; (d) schematic representation of the angle between the direction of the α fibres and the radius vector of the β spherulites and; (e) micrograph showing the creation of the two symmetric parts of the logarithmic spirals

following differential equation:

$$\frac{dr_\beta}{r_\beta} = \pm d\psi \sqrt{\frac{G_\beta^2}{G_\alpha^2 - G_\beta^2}} \quad (6)$$

The trivial solution of equation (6) defines what is called the logarithmic spiral, a curve studied by several famous physicists, including Descartes, Torricelli and Bernoulli[16]. Among the properties of this special curve, we can mention that the angle θ, between the radius vector having its origin on the β nucleus and the tangent to the curve (which is also the direction of growth of the α fibres), is a constant obeying the relationship:

$$\cos\theta = -\frac{G_\beta}{G_\alpha} \quad (7)$$

(see *Figure 2d*). This relationship can be used to determine graphically the ratio G_β/G_α from a micrograph of a fully crystallized preparation. It is also possible to measure the cumulative arc length as a function of the radius vector length in order to determine the same ratio[17]. This ratio can be compared to the ratio obtained by direct measurement of the linear growth rates G_α and G_β. Such an approach provides a test for the self-consistency of the experimental data. *Figure 2e* shows a typical example of spiral boundary formation. The mathematical description of the α-form growth front in the shaded side will be shown later when considering envelope curves.

INTERFACIAL OVERGROWTH RATE

The two following departures from the behaviour presented in the preceding section appear from examination of *Figure 3a*. First, the α fibres are not tangential to the spiral part of the interspherulitic boundary. Secondly, we observe a prominent growth front for the α-form nucleated in the shaded side with respect to the circular growth front of the α spherulite. From this second experimental fact, a quite surprising behaviour is deduced: the α-form front near the β spherulite, made of fibres which are not coming straight from the α primary nucleus, is however advanced compared to normal (straight) α-form radial fibres, despite the fact that the path is longer. Further detailed studies of this type of growth have indeed shown an unusual phenomenon occurring at the interface between the two growing fronts: this point (which, in reality, separates the α-form, the β-form and the melt) progresses at a rate G_i ('i' = interface), which is greater than G_α. It should be noted that this feature does not seem to agree with the classical view, which establishes that each new site along the β–α interface simply constitutes a new α nucleus. We therefore need to reconsider equations (5)–(7) previously stated, and to define a way to measure this new rate G_i:

(i) The Cartesian oval part remains unchanged while the curve is generated at a rate (the usual ds/dt in mathematical textbooks) greater than G_i. Indeed, this rate is infinite at the initial contact, and decreases afterwards.

(ii) The logarithmic spiral part begins precisely when the Cartesian oval is grown at a rate which becomes equal to G_i. This condition defines a particular point whose coordinates can be evaluated by an analytical treatment of equation (4) in its cartesian parametric form (stating that $ds/dt = G_i$).

However, as there is no real need to know these coordinates exactly, this will not be discussed further in this paper. The polar coordinates centred on the β nucleus (for this point) are defined as r_β^c and ψ^c at the time t^c. After the above defined point, the interspherulitic α–β boundary is created in the same way as discussed previously, except that G_α is replaced by G_i in equations (5)–(7). It should be noted particularly that the angle θ between the tangent to the curve and the radius vector (see *Figure 3b*) is slightly modified, such that

$$\cos\theta = -\frac{G_\beta}{G_i} \quad (8)$$

The graphical method already described thus allows us to determine this ratio G_β/G_i, and then to obtain G_i, if G_β is known. This is particularly useful since a direct dynamic measurement of G_i is very difficult to carry out.

Let us now remark that the first clue concerning the existence of the interfacial overgrowth rate, is the non-tangency of the α fibres to the spiral. Therefore, the angle between these fibres and the tangent to the spiral remains unchanged along the curve. This suggests the use of this invariant property to determine a combination of growth rates. The angle γ (see *Figure 3b*) can be related to G_α and G_i. Indeed, the α fibres are perpendicular to the α growth front, and for a short time interval dt, the right-angle triangle construction yields the relationship

$$\cos\gamma = \frac{G_\alpha}{G_i} \quad (9)$$

As G_α, G_β, θ and γ can be independently measured, it is still possible to check the consistency of the experimental data and to determine G_i by two different methods.

Experimental data pertaining to the angles θ and γ

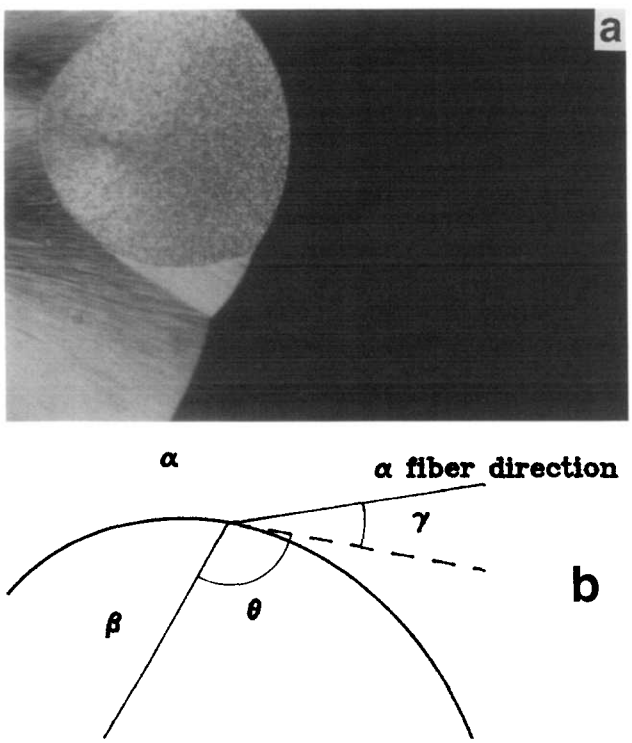

Figure 3 (a) Experimental evidence for the interfacial overgrowth rate: α fibres are not tangential to the spiral, and the α growth front near the α–β interface is advanced compared to the circular part of the α growth front. (b) Definition of the angles used to estimate G_i

were measured on micrographs of samples crystallized at various temperatures. The results are summarized in *Table 1*. G_i was computed from dynamically measured values of G_α and G_β, using the ratios obtained from the values of θ and γ. It is an interesting exercise to decide the best experimental way to determine G_i. At the highest temperatures (> 50°C), measurement of θ yields erroneous estimates of G_i (as it is absurd to obtain G_i values which are lower than G_α values). Comparing G_i to G_α, the measurement of γ certainly allows a better accuracy, as confirmed by examination of *Figure 4*, when looking at dispersion of the data.

Now, what if we consider the physical meaning of this unexpected G_i rate? Tentative explanations, taking into account a possible heat-source effect at the crystallization front, or an epitaxial growth of the α-form onto the β-form, with the latter acting as a substrate, do not seem

Table 1 Experimental data obtained from micrographs of samples of the PEO–resorcinol complex crystallized at various temperatures

T (°C)	G_α (μm s^{-1})	G_β (μm s^{-1})	θ (°)	γ (°)	G_i^a (μm s^{-1})	G_i^b (μm s^{-1})	G_t (μm s^{-1})
27.5	3.2	2.54	122	38	4.8	4.1	–
30	4.21	2.94	123	36	5.44	5.2	–
32.5	6.1	3.57	122	37	6.74	7.63	–
35	6.84	4.27	118	29	9.09	7.86	–
37.5	8.38	4.79	116	35	10.9	10.2	–
40	11.12	4.95	114	32	12.1	13.1	–
42.5	13.41	5.7	111	32	15.8	15.8	–
45	15.44	6.09	111	28	16.9	17.5	4.1
47.5	17.8	6.5	108	24	21	19.5	4.2
50	20.5	7.13	–	21	–	21.9	5.9
52.5	24.1	7.36	112	19	19.6	25.5	7.1
55	27.1	7.72	110	11	22.6	27.5	8.5
57.5	30.9	8.35	–	–	–	–	11.3
60	32.8	7.79	107	17	26.6	34.3	12.5
62.5	34.2	3.3	–	–	–	–	14.3
65	35.4	3.3	–	–	–	–	17.1

[a] Obtained from measurement of θ
[b] Obtained from measurement of γ

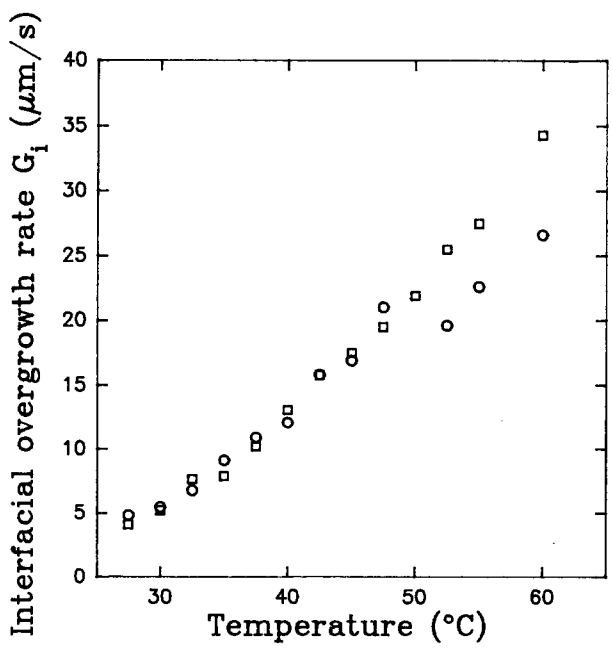

Figure 4 Interfacial overgrowth rate G_i, as a function of temperature, calculated from measurement of the θ (○) and γ angles (□)

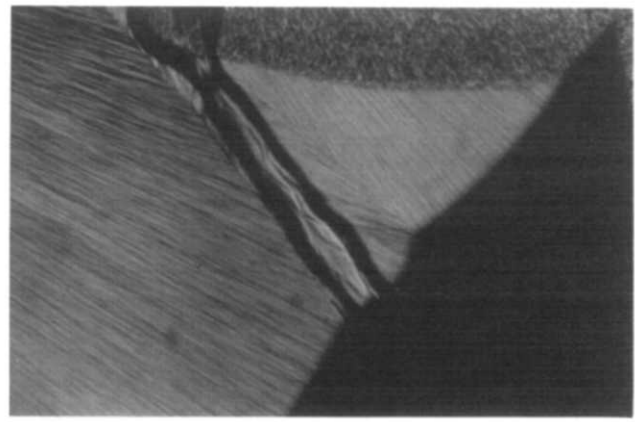

Figure 5 Micrograph showing the occurrence of the interfacial overgrowth phenomenon along elongated air bubbles

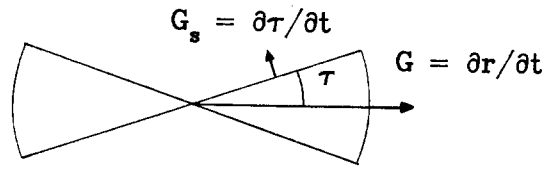

Figure 6 Schematic representation of spherulitic crystallization at early stages of growth, with the existence of an angular growth rate G_s

plausible. Indeed, in the first case, one would expect a drastic change in this effect, together with the absolute value of G_α, whereas the second view implies a microscopic description of the spherulitic growth process with highly speculative considerations. Moreover, the interfacial overgrowth rate was also observed along elongated air bubbles, which were sometimes found in the samples (as shown in *Figure 5*). Thus it seems clear that the β-form does not have a direct influence on the interfacial overgrowth phenomena. The only remaining parameters which can play a major role are, therefore, the melt properties (viscosity, molecular weight, etc.) and the spherulite growth mechanism of the α-form. Melt properties can be different near to the α–β interface, where there could be mechanical effects such as flow, viscosity change, orientation of marcomolecules, mechanical waves due to the crystallization front, etc. The spherulite growth mechanism could also interfere if we consider how it is nucleated and how it develops. At the early stages of crystallization, it is recognized that spherulites develop first as rodlike entities, evolving into sheaves before they finally become spherical[18,19]. As the sheaf can be approximated by a conic sector, Stein and Misra[20] have introduced an angular growth rate, $G_s = \delta\tau/\delta t$ (where τ is the half-apex angle of the cone), which is different from the radial growth rate (see *Figure 6*). This simple model is of interest in proposing another explanation for G_i. Indeed, we could consider the growth of the α-form along the β spherulite as being permanently at an early stage of crystallization in a sector between the α fibre direction and the tangent to the β spherulite. The angular extension of this melt sector is thus $\gamma + \theta - 90°$, with values obtained in our experiments which were of the order of 30 to 70°. Such values indicate that angular growth, which should be characterized by a high value of G_s, could be the origin of the interfacial growth rate G_i. In other words, the microscopic mechanism of the growth of the spherulites

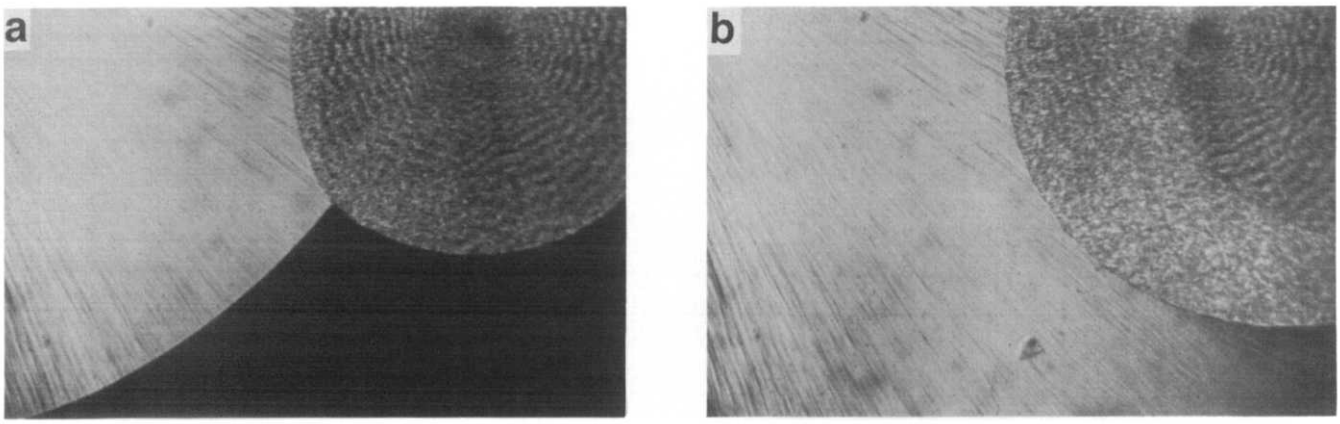

Figure 7 Successive micrographs (a) and (b) of the transformation of the β-form into the α-form. The transformation is induced by the α-form and propagates as a dynamic front

at early stages of crystallization, could be related to the corresponding mechanism of the growth of the α-form along either the β-form or bubbles in our system. This introduces the need for a detailed morphological study of both the α nuclei and the α–β interface, work on which is currently in progress.

From another point of view, it should be noted that the interfacial overgrowth effect has been observed in samples of the PEO–resorcinol complex which have been prepared from PEO materials having different molecular weights (ranging from 6000 to 200 000). Therefore, a systematic study of the influence of the molecular weight of PEO must also be undertaken.

TRANSFORMATION RATE

The second unexpected phenomenon which was observed in the PEO–resorcinol system was the transformation of the β-form into the α-form. The existence of different types of spherulites for a given polymer is not unusual. For example, poly(ethylene adipate) crystallizes from the melt as negatively birefringent spherulites at temperature lower than 25°C, as banded spherulites in the temperature range 25–40°C and as positively birefringent spherulites at temperature higher than 40°C[21]. In the case of the PEO–resorcinol molecular complex, α and β spherulites can be simultaneously obtained over a large range of crystallization temperatures. The transformation of one particular morphology into another is often a slow process, occurring, for example, over a few hours, and is influenced by changes in the crystallization conditions, such as temperature, pressure, moisture content, imposed stresses, etc.

The particular feature of the transformation observed in the β-form of the PEO–resorcinol complex is that it is mainly induced when a β spherulite meets an α spherulite. The transformation takes place as a dynamic front, moving at a constant rate. *Figure 7* shows an example of the propagation of this transformation at different stages. This propagation mode is particularly valid for temperatures above 40°C. Below this temperature, the transformation is much slower and can take a few tens of minutes. This transformation rate is denoted by G_t and can be easily measured. As the front is visible near the α–β boundary, it is also possible to deduce a 'cosinus law', such as those given by equations (8) and (9), and as illustrated in *Figure 8*. We thus have

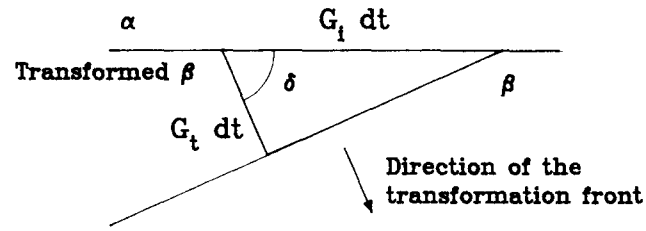

Figure 8 A schematic visualization of the δ-angle between the tangent of the α–β interface and the normal to the transformation front

$$\cos\delta = \frac{G_t}{G_i} \tag{10}$$

As it is difficult to measure the angle δ with any accuracy, we choose to measure G_t by a conventional optical microscopy method. The results are summarized in *Table 1* as a function of the crystallization temperature. These results show a continuous and significant increase in G_t, even at temperatures above 60°C, after which G_β decreases, whereas G_α approaches its maximum value. It was impossible to measure G_t above 65°C, where the transformation is quasi-instantaneous.

We have previously mentioned that the nature of the transformed β phase is equivalent to the α-form, an observation which is based upon the following arguments.

At temperatures greater than 55°C, G_t is greater than G_β. We have used this information to perform the following simple experiment. A barrier of β spherulites was obtained in a sample preparation. Against one side of this barrier, an α spherulite is encountered, thus yielding a transformation front inside the barrier. As the propagation of this front is faster than the advancement of the β front in the melt, the transformation front overtakes the melt. We then clearly observe the inrush of the α front, which propagates at a rate G_α, into the melt. This deduction was corroborated by the following experiment: a stress applied to the sample induces the transformation. We then observe a quasi-instantaneous 'nucleation' of an α-form spherulite along a β-form spherulite.

This raises some interesting questions concerning the nature of the α phase which is obtained from the transformation. For example, how does the orientation,

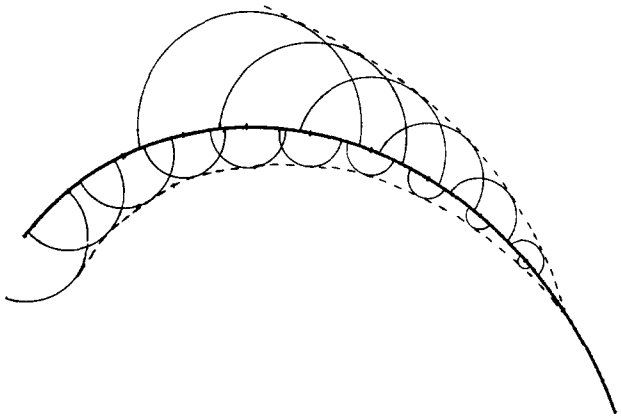

Figure 9 A schematic representation of the crystallization and transformation fronts as an envelope of the corresponding family of circles

disorder and crystallinity compare to those of the α spherulites which are obtained directly under the same temperature conditions? This suggests numerous further investigations. In order to give an insight into the complexity of the problem, we should mention that the visual appearance of a sample observed under polarized light indicates a perfection process which takes place over a period of a few weeks at room temperature.

The following final section is devoted to a mathematical description of the shape of the transformation front. The transformation begins when an α-form spherulite encounters a β-form spherulite. We can consider that on each occasion the α melt interface progresses along the β spherulite, creating a circle of growing radii which is emitted at each of the three-phases points. We consider, therefore, the envelope of a family of circles whose centres (with coordinates $x(u)$, $y(u)$) are along the logarithmic spiral, and whose radii are $G_t(t-u)$, where u is the time at which the circles are created (see *Figure 9*). It is possible to write an analytical expression for this family of circles, for $t_i < u < t$, under the form $\phi(x, y, t, u) = 0$. The classical way to find the envelope of a family of plane curves is to eliminate a certain parameter (in this case u) by using the following:

$$\frac{\partial \phi(x, y, t, u)}{\partial u} = 0 \qquad (11)$$

The complete analytical development of equation (11) has been achieved by Noël[22]. It should be noted that the same treatment allows us to obtain the shape of the growth front of the α-form in the shaded side (*Figure 9*), since we can consider this front as resulting from the emission of circles of radii $G_\alpha(t-u)$ outside the logarithmic spiral. A further description of this analytical procedure, and a numerical implementation of the same, allowing the simulation–visualization of both the interfacial overgrowth and transformation phenomena, will be discussed elsewhere[23].

CONCLUSIONS

The following two new phenomena, occurring in the spherulitic growth process of a PEO–resorcinol molecular complex, have been proved experimentally: (i) an interfacial overgrowth and (ii) a dynamic transformation front. When direct observations are not possible, the only way to detect the first phenomenon is to observe the departure of the α fibres away from the tangent direction of the α–β interface. The measurement of this angle yields an estimate of the interfacial overgrowth rate, G_i. The physical interpretation of these two effects emphasizes the major factors governing spherulitic growth rates, i.e. the melt properties and the microscopic mode of crystallization. Studies of the overgrowth and the transformation, in relation to the experimental conditions, could thus give further valuable information towards our understanding of polymer crystallization from the melt.

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