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LECTURE TEXT

Growth of spherulites: foundation of the DSC analysis of solidification

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Abstract Solidification is a practically and theoretically important issue, since it allows to design experimental conditions for desired material properties and also to discuss basic relationships between thermodynamics, kinetics and morphology. In this article, an overview on the crystallization theory and on the main traditional techniques to determine the crystallization rates, under constant and variable external temperature, is provided. The differences and similarities of isothermal and non-isothermal crystallization mechanisms are highlighted in the framework of the nucleation and growth theory, also by comparisons of the differential scanning calorimetry (DSC) peaks. The origin, broadness and symmetry of DSC peaks are explained in detail by considering the need for heat removal from the solid front and the coalescence of grains that originated in several points of the liquid phase. Although impingement is responsible for the general slowdown of crystallization, it is shown that the growth rate of a spherulite in the initial stage of coalescence continues to increase up to a maximum even if with a rate of change (i.e., a growth "acceleration") lower than that before impingement.

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Introduction

Solidification is a macroscopically observable phenomenon familiar to everyone, since it is often exploited in the everyday life. Most of the industrial processes involve recrystallization after fusion, which allows to give the desired shape and properties to materials by means of appropriate temperature programs. The solidification rate is an important parameter not only because it determines the production speed of goods and, hence, their cost but also because for particular uses very short times of crystallization may be required.

It is worth noting that the crystallization rate of a sample is expressed by the mass (or volume) of substance that solidifies in a time unit [1, 2]. The crystallization rate depends on the solidification conditions and, especially for low conductivity substances as polymers, on the mass. In fact, if the rate of the heat propagation was infinite, nucleation for homogeneous systems with only one solid phase would be equally probable in any point of samples, independently of the mass [1]. Instead, the rate of heat propagation, even high as it is, is not infinitive but depends on thermal properties of materials and, consequently, solidification cannot occur simultaneously in the whole mass of a specimen unless very thin films of a high thermal conductivity metal are used. As crystallization proceeds, two things happen: the number of crystals increases (i.e., nucleation is taking place), and the size of the crystals increases (i.e., growth is taking place) [3]. Depending on both nucleation and growth of crystals, the rate of

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crystallization from melt is not constant (even at constant temperature) but depends on time. An average value (the so-called overall crystallization rate), for a definite mass under specific temperature conditions, may be obtained by the ratio between the final mass of solid and the whole time needed for crystallization. Since the crystallization dynamics within a sample depends on the distance from the cooled walls, especially for low thermal conductivity substances, morphology also depends on the volume and changes from the external to the interior parts of specimens.

Solidification needs the displacement of the atoms or molecules of the prior liquid phase in specific positions of crystalline lattices, through mass and heat transport. The well-known equation:

$$\Delta G_{\text{system}} = \Delta H_{\text{system}} - T\Delta S_{\text{system}}$$

valid at constant values of temperature and pressure, allows understanding why processes occurring with an entropy decrease (i.e., with $\Delta S_{\text{system}} < 0$), as solidification, must be exothermal (i.e., $\Delta H_{\text{system}} < 0$) and are favoured at low temperatures. Indeed, according to thermodynamics, any system at definite temperature and pressure transforms in the direction that entails a Gibbs free energy decrease of the system. Therefore, assuming $\Delta S_{\text{system}} < 0$, to have $\Delta G_{\text{system}} < 0$ it must be $\Delta H_{\text{system}} < 0$ and, moreover, $\left| \Delta H_{\text{system}} \right| > -T\Delta S_{\text{system}}$. In a more general form, the second law of thermodynamics establishes that every real process entails an increase of the total entropy, including the entropy of the environment in which the evolving system is placed. Intuitively, we may say that the entropy of a confined system may decrease provided that the entropy diminution of the system is exceeded by an entropy increase of the entire universe, i.e., provided that heat is simultaneously transferred from the system to the surrounding. At a specific pressure, the temperature T_m at which $\Delta H_{\text{system}} = T_m\Delta S_{\text{system}}$ and,   therefore, $\Delta G_{\text{system}} = \Delta H_{\text{system}} - T\Delta S_{\text{system}} = 0$, is the equilibrium melting temperature: at $T > T_m$ the liquid is the stable phase, and at $T < T_m$ the stable phase is the solid. Practically, solidification does not occur at the melting temperature but only at lower temperatures.

In conclusion, spontaneous solidification of a liquid system may occur only by exothermal processes at temperatures below the equilibrium melting point. This latter is defined, under a specific pressure, as the temperature at which the rate of molecular attachment to a solid equals the rate of detachment so that the solid and the liquid phases can coexist and the ratio between the amounts of the two phases remains indefinitely unchanged. The equilibrium melting temperature also corresponds to the melting temperature of an ideal perfect crystal with infinite thickness, since the presence of imperfections, impurities and surfaces causes a decrease of the theoretical melting point [4]. Defining the difference between the melting and the crystallization temperatures as "undercooling", the free energy change (also referred to as "driving force for solidification") for liquid–solid transformations is approximatively proportional to the undercooling (or supersaturation) [1, 3, 5, 6]. The actual rate of thermodynamically possible transformations is regulated, through their mechanism, from kinetics, which is strictly interconnected with thermodynamics. When the solid and the liquid phases are in equilibrium, the macroscopically measurable crystallization rate is zero since new solid material is not produced [3]. Reliable predictions of the crystallization rate at temperature below the equilibrium melting temperature have to be based on an appropriate model for the crystallization mechanism. The most used and realistic model for solidification consists in the mechanism of nucleation, growth and growth cessation because of impingement.

This model considers solidification to begin with the formation of crystalline embryos which, because of their high dispersion and surface energy, cannot cause a real free energy diminution of the whole solid–liquid system, at least until their size remains very small. Only embryos that achieve a minimum size (the so-called critical size) are allowed to grow irreversibly [7], whereas smaller nuclei will re-dissolve in the melt because of their high surface and free energy. In order to reach the critical size and actually grow, nuclei need an extra energy (activation energy) to overcome the kinetic barrier and, finally, to contribute effectively to a free energy decrease of the system [8]. The activation energy measures the enthalpy difference between the rate-controlling group in the melt near the crystal surface and in the activated state [8]. It is a measure, then, of the ease of molecular rearrangement that must take place during the growth process. This rearrangement is difficult to picture in detail, but may include rotation and breaking or stretching of bonds [8]. According to the theory, the free energy difference between the solid and the liquid phases is positive or null at temperatures $T \geq T_m$ and becomes negative at temperature below T_m, decreasing with increasing undercooling (i.e., decreasing temperature). The growth rate, then, is zero at the liquidus, increases to a maximum and then decreases as the activation energy term begins to dominate [8]. In other words, the crystallization rate of crystals grown from a one-component liquid typically increases and then decreases with undercooling since at small undercooling the growth rate is limited by the thermodynamic driving force for crystallization, while at large undercooling, it is limited by molecular diffusion in the liquid [8, 9]. The existence of diffusion-controlled crystal growth is evident from the proportionality of crystal growth rate and diffusivity for

crystallization solution and from the inverse proportionality between crystallization rate and viscosity for crystallization from melt, observed at large enough undercooling [9]. In conclusion, temperature changes are able to affect solidification from melt of homogeneous system when they cause an appreciable viscosity change of the liquid phase [10]. In other words, crystallization rate is also controlled by the mobility that atoms or molecules have in the liquid state. High mobility favors both nucleation and growth, since molecules may not only diffuse faster at the liquid–solid interface (small temperature changes, through diffusivity change of the crystallizing component, affect especially solidification from melt of heterogeneous system with composition gradients near the crystal–melt interface, and crystallization from solution [8], which are both beyond the purpose of this article) but may also change rapidly conformations thus allowing an easier nucleation and facilitating the subsequent incorporation of molecular segments in the lattice.

Both nucleation and growth rate have the same qualitative temperature dependence although the maximum in the nucleation rate curve is generally at a larger undercooling than that of the growth rate curve [3].

Because of the contrasting effects of a temperature change on the crystallization driving force and on molecular mobility, relatively to both processes of nucleation and growth, the rate of crystallization also shows a maximum between the glass transition and the melting temperature. To observe a maximum in the crystallization rate it is necessary to perform isothermal crystallizations in the whole temperature range between the glass transition and the melting temperature. Traditional measurements of the solidification rate are practically performed at temperatures much closer to the melting than to the glass transition temperature. The maximum crystallization rate is observed at the undercooling where a balance between the contrasting effects of the enhanced driving force for crystallization and of the mobility reduction is achieved. The trends of the nucleation and growth rates with temperature, confirmed by experimental observations on highly heterogeneous systems as magma since the nineteenth century [8], are, however, generally not completely observable for neat polymers since during undercooling procedures aiming to reach the liquidus as metastable phase, polymers rather transform, before the achievement of the desired low crystallization temperature, in glasses or solids [11]. Indeed, it is generally impossible by cooling a sample from melt with ordinary procedures and techniques to reach high undercooling without causing prior crystallization at temperatures where, notwithstanding the relatively poor driving force for crystallization, molecular mobility is high. If samples can avoid crystallization during cooling, they freeze into a glass state [11]. Crystallization under very

high undercooling has been recently achieved with very sophisticated procedures and often modified instruments that are not described here for the sake of simplicity and also because the conclusions here drawn for measurements performed with traditional DSC equipment are valid even for complex and not widely available procedures. Indeed, the object of the present study is the evolution of the shape of the original circular spherulites during coalescence and the relative effects on the crystallization rate, that is, ultimately the description of the crystallization rate as function of time, independently of temperature.

When solidification occurs at low undercooling, where viscosity is relatively low and diffusion is not the rate-limiting factor, the crystallization rate is connected to the need for heat removal from the growth front of the new phase [8, 12]. This is why crystallization is conducted industrially by continuous cooling (non-isothermal crystallization), whereas enquires on solidification are based on observations at a constant temperature (isothermal crystallization), which ensures accurate results. The mechanisms of the so-called non-isothermal and isothermal solidification are essentially the same, as proved by the shape of interfaces between the grains [13]. The only differences regarding the dynamics of the solidification mechanism result in a time dependence of nucleation and in a highly accelerated growth which lead to a much higher rate during crystallization at variable temperature.

During non-isothermal conditions the crystallization rates are appreciable only in a very narrow temperature range, because of the fast completion of solidification [14]. Therefore, the DSC curves describing the crystallization rates of a sample crystallized under non-isothermal conditions should not be confused with the bell-shaped curve obtained reporting, towards temperature, the average crystallization rates relative to isothermal measurements on a constant mass of a substance. Indeed, the "temperature range" involved in a non-isothermal crystallization is too small (depending on the cooling rate, only few temperature degrees or less) to effectively change viscosity or driving force for crystallization [14], but high enough to affect the heat transport rate because of the enhanced temperature gradients along the specimen [15]. In other words, as DSC crystallization peaks obtained isothermally, also DSC exothermal peaks obtained under continuous cooling do not represent the variation of the crystallization rate with temperature but, rather, with time. The additional increase of crystallization rates during non-isothermal procedures, relatively to isothermal processes carried out at average temperatures, is mainly due to the increase of the heat transport rate with increasing temperature gradients within samples. Low temperatures favor crystallization because, as stated by a Newton's law, high-temperature jumps between the

sample and the cooling device speed up the cooling of the growth front needed for crystal growth.

In conclusion, the increased cooling rate under non-isothermal conditions determines both an increase of the density of spherulites (i.e., the number of spherulites for space unit) and an accelerated growth because of the increase of the rate of heat transport from the beginning of crystallization. For these reasons and because of the negligible effect of the temperature change on both driving force for crystallization and viscosity during non-isothermal condition, we can assume that the crystallization rate is influenced merely by time not only during isothermal but also during non-isothermal crystallization.

The spherulitic morphology is typical, although not exclusive, of polymers crystallized from melt and has been ascribed to either diffusion- or heat flow-controlled crystallization rates [8]. An exhaustive description of spherulitic crystallization from melt is reported in several papers and books, which also describe the submicroscopic structure, the internal shape of spherulites and their boundary [13] also relatively to polymorphism [16]. Most recent publications deal with crystallization of isotactic polypropylene at high cooling rate and with applied pressure for a wide range of new processing conditions [17, 18] that would have not been allowed a few decades ago. Under these novel conditions, it has been also possible to determine the nucleation density from DSC curves [17, 19] and the linear growth rates of spherulites at different temperatures [19]. However, as said before, this paper does not directly focuses on the widely explored temperature dependence of the crystallization rate, but rather on the time dependence of the crystallization rate, especially during impingement. Indeed, no paper or book explains in detail the slowdown of crystallization occurring at advanced crystallization stage, i.e., soon after the start of spherulites coalescence. Namely, it is here reported a simple model to predict the time evolution of the spherulitic shape and the analytical time dependence of the crystallization rate for different numbers of coalescing spherulites at different positions and distances, both for thermal and athermal solidification. As all models, the present one is based on specific assumptions and boundary conditions whose choice, far from being too simple or unrealistic, have, however, been dictated by the need to make the article easier for students. For the same reasons, only the most readable conclusions of this work have been widely discussed and few legible comparisons with more recent work have been presented. For instance, the present model does not account for high cooling conditions since these could cause the formations of polymorphs growing with different linear rates and, in addition, solid–solid phase transitions during crystallization, leading to

considerable complications. Indeed, the extension of the present work to complex boundary conditions needs more advanced mathematical tools and would be a too weighty task for students. On the other hand, experts in the field can easily extend results of the proposed model even to asymmetric boundary conditions.

It is sufficient to say here that the variation of the crystallization rate found in a single experiment may be described, at constant or slightly variable non-isothermal conditions, as a bell-shaped function of time, which is referred to as crystallization peak. The apparently similar trend of the crystallization rate towards either temperature or time has very different roots. As said above, to observe a maximum towards temperature it is necessary to determine the isothermal crystallization rates at several temperatures in a temperature range from glass transition to melting (or, under non isothermal condition, the overall crystallization rate in dependence of the cooling rate). Actually no maximum, relatively to the variable temperature, in either the linear and true growth (or crystallization) rate of spherulites is observable in the ordinarily small ranges of explored isothermal temperatures, since only significant changes in mobility achievable at very low crystallization temperatures (close to the glass transition) are able to revert the monotonicity of the crystallization rate as a function of temperature. Practically, it is usually impossible to perform isothermal crystallization at relatively low temperatures without causing prior liquid–solid transformation during cooling. Sometimes, to estimate the rate of crystallization at low temperatures polymers are rapidly quenched below the glass transition to achieve a metastable amorphous state (the amorphous state is a false solid thermodynamically unstable at all temperatures, although kinetically inert) and then heated to allow crystallization. This procedure, as the traditional crystallization from melt, does not allow estimating the crystallization rate at temperatures next to and beyond the maximum, since prior amorphous-solid transitions occur. Moreover, the values of the crystallization rate obtained using experimental procedures entailing not only different starting states (liquid or amorphous, showing different thermal properties and mobility and, thus, different kinetic barriers or crystallization mechanisms) but also different thermal treatments (cooling or heating), are seldom comparable and cannot be combined since the two different sets of data are non-homoscedastic. Moreover, polymers often show polymorphism and this circumstance makes output of non-isothermal crystallization even more difficult to explain. Although polymorphs have their own temperature range of stability and crystallization rates, high cooling rate procedures can favor the formation of more than one solid phase and, furthermore, the compositional ratio between the different phases may change with the

cooling conditions. According to the theory, with traditional procedures and relatively low cooling rates, it is more reliable to observe only a decrease of the linear growth rate with increasing the temperature. Analogously, when a polymer is crystallized by heating from the amorphous phase, an increase of the linear growth rate will be observed with the temperature. A different trend provided by traditional DSC or optical measurements has to be carefully evaluated to disclose possible source of experimental or data processing inaccuracy [20].

The crystallization rate measured at constant temperature shows, relatively to time, the existence of a maximum neither due to the thermodynamic, kinetic or heat removal rate mentioned before, but mainly due to geometrical characteristics of the crystal growth before impingement and to spatial restrictions limiting the growth after impingement [21–25]. Indeed, it will be shown that the growth rate of bidimensional crystals has necessarily to increase until crystals grow separately. On the other hand, growing grains originated in more points of a melt must unavoidably impinge and the impossibility to grow in some directions after impingement slows down crystallization. In the next paragraph it will be shown that at a constant temperature the crystallization rate increases monotonically (namely linearly) up to impingement and, if crystals grew separate without coalescing at all, such a rising trend would continue for the whole crystallization. We will see hereafter that if solidification occurs simultaneously in the whole specimen, the crystallization peak is not symmetrically shaped relatively to the maximum. The major asymmetry arises from the fact that when the maximum is achieved, almost 90 % of solid has already been formed and, therefore, the time to complete the solidification is shorter (c.a. 30 %) than that required to reach the maximum. A time for crystallization completion shorter than the time needed to reach the maximum itself is not in contrast with the slowdown of crystallization caused by impingement, since at the start of impingement only a small amount of liquid phase (c.a. 20 % of the initial amount) remains to be transformed. Moreover, it will be shown that the first part of the crystallization curve, under certain conditions, should be fairly interpolated by a linear stretch. As the mechanism of isothermal and non-isothermal crystallization rate is essentially the same, with the only difference of a higher crystallization rate under non isothermal conditions, the same trend is expected, even more so, if solidification is performed non-isothermally at decreasing temperature. The discrepancy between the theoretical and the experimental crystallization rate usually found for polymers is here explained by taking into account the non-uniform nucleation along the thickness of the specimens because of the very low thermal conductivity of polymers relatively to metals [1].

Theoretical and experimental background

Crystallization mechanism

Crystallization of polycrystalline materials, such as metals and polymers, at temperatures below the melting point is successfully described by the theory of nucleation (referred to as primary nucleation) and growth (secondary nucleation). This theory, extended first to metals [21], is based on the evidence that solidification, as all exothermal processes, is accompanied by heat development and, therefore, the heat has to be removed in order to make advances in crystallization [12, 26]. The process starting solidification, i.e., nucleation, consists in the aggregation of a small number of atoms or molecules due to temperature fluctuations in the melt and, therefore, is generally described as a random process in space. However, the random description applies only when the heat flow rate does not depend on direction, that is, when heat propagation is isotropic [2, 15].

Under this circumstance, direct observations on polymers crystallizing from melt reveal the growth of circular crystalline units, thus called spherulite (see supplementary materials), usually made up of fibrillar crystals that originated in the center. The *linear growth rate* of spherulites, defined as the rate of change of the spherulite radius with time, is somehow connected with the illusory "movement" of the growth front. Actually, crystals grow by addition of material to their frozen boundaries without any real motion of the front. The solid phase seems to "advance" in the liquid but this apparent movement is generated by the progressive phase transformation of adjacent quiescent liquid layers. The peculiarity of spherulites, due to their circular shape, is the capability to extend bi-dimensionally as a result of mono-dimensional and uniform growth of all radial crystals within them. As two-dimensional crystals grow more quickly than separated rod-like crystals, admitting that no difference in the primary and secondary nucleation mechanisms for spherulites and rods exists, a bi-dimensional crystallization must be advanced relatively to a mono-dimensional growth (see Fig. 1). Moreover, circles have the lowest perimeter relatively to the area and, therefore, spherulites show the lowest surface energy compared with equivalent planar figures. Therefore, spherulites have the right shape to grow as fast as possible contemporaneously bearing the minimum surface energy.

As explained, the crystallization rate follows the increment of the mass of a solid in a time unit and depends on both nucleation and growth. It is important to repeat that the crystallization rate, often simply called "growth rate", is different from the linear growth rate of spherulites. Indeed, this latter gives indications on the rate of the secondary nucleation, that is, on the constant rate of the length
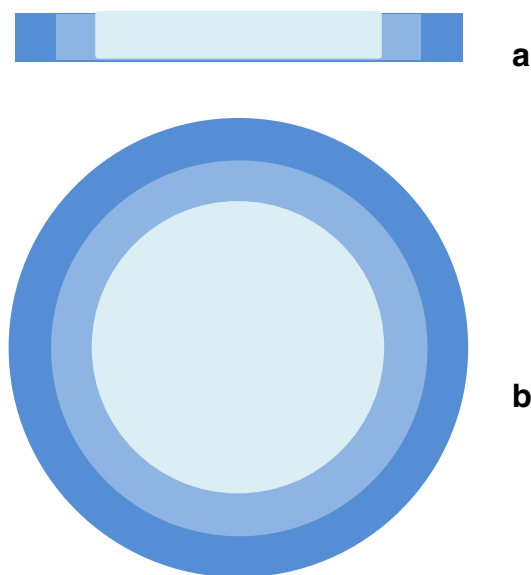
Fig. 1 a Development of a parallelepiped crystal according to constant linear and true growth rates. **b** Growth of a spherulite with constant linear growth rate. The *two circular coronas* represent the successive increments of the spherulite surface in two equal time intervals. The amount of solid material added to the growth front in a time unit (proportional to the area of the circular corona built in that unit), i.e., the true growth rate, is not constant but increases with time because of the size increment of the spherulite

advancement along each radial direction of a spherulite, whereas the growth of a circular spherulite occurs usually with an increasing rate. The true growth rate of spherulites would indeed be constant only if the linear growth rate and, consequently, the secondary nucleation rate decreased with time. When the growth occurs not from solution but from melt, molecules in the liquid phase surround the whole growth front and, since diffusion is not a limiting factor and compositional gradients do not occur, the linear growth rate of spherulites is usually found to be constant. This is not the case for the true growth rate of spherulites. Indeed, as illustrated in Fig. 1, crystals arranged radially within spherulites when growing at the external ends cause inherently also the growth of the perimeter of spherulites, maximizing the increment of area and, therefore, the crystallization rate. If the same number of the parallelepiped crystals forming a spherulite grew separately at two opposite flat faces, the whole growth rate could not increase but would remain constant as consequence of the null curvature of the growing faces. As shown in Fig. 1, due to geometrical characteristics of two-dimensional growth, even if each radial crystal within spherulites increases of the same length, the increase of the area of the spherulite is not constant but increases with the time.

Below it will be shown that the bi-dimensional growth of separate crystals such as spherulites (differently from mono-dimensional growth, which may occur with

constancy of the growth rate) entails always enhancements of the crystallization rate with time and, therefore, decreases in the rate during both isothermal and non-isothermal crystallization may only be caused by coalescence.

Growth rate dependence on time

Generally, nucleation at constant temperature in thin polymer films entails simultaneous appearance of all planar spherulites, whereas a time-dependent nucleation is detected, with spherulites of different sizes, when solidification is conducted by continuous cooling from melt (see Fig. 2; supplementary materials). Indeed, in agreement with the theory, the probability of nucleation is found to increase with decreasing temperature [16]. As also shown by Varga, coalescence of bi-dimensional spherulites generates a grain structure where each original spherulite is finally transformed in a geometric figure with linear and/or curved sides [16]. The shape of the interface between two spherulites may be predicted by considering the intersection of two families of concentric circumferences, representing the growth fronts of spherulites at different crystallization stages [13]. The linear growth rate of spherulites (i.e., the rate of change of the spherulite radius with time) is usually found to be constant at constant temperature [16]; therefore, it is the most measured and used parameter for rough comparison of crystallization rates. The assumption that spherulites grow circularly on their outer edges with equal linear rate, allows to deduce that spherulites with the same size must have been nucleated simultaneously and that they contribute, instant by instant, equally to the mass increment of the solid. Experimentally, the linear growth rate of spherulites may be determined by observing, through an optical microscope, the isothermal solidification of a molten specimen in a hot stage and measuring the radius of spherulites in micrographs taken at appropriate time intervals. Measurements of the radius of growing spherulites would require the exact identification of their centers; therefore, for accuracy reasons it is preferable to halve the length of diameters and to interpolate as many experimental points (couples radius-time) as possible with the mean squares method.

Even if it is found to be constant at constant temperature, the linear growth rate of spherulites cannot be used as a unique parameter for comparisons between different samples. Indeed, the crystallization rate of spherulites is related to their mass increment with time and depends not only on the growth rates, but also on the dynamics of nucleation (often improperly referred to as nucleation rate). The crystallization rate of all spherulites coincides with the crystallization rate of a sample, i.e., with the whole amount of solid produced in a time unit. Evidently, the higher the nucleation

Fig. 2 a Example of uniform distribution of spherulites originated by a time-dependent nucleation. Spherulites grow with two different sizes and rates, finally showing two opposite curved sides. Interfaces between spherulites with different size and growth rate are branches of hyperbolas, whereas interfaces between simultaneously originated spherulites are *lines*. For clarity, only the construction of hyperbolas between three aligned spherulites is shown in (**b**). If the distribution of spherulites is not uniform relatively to one of two orthogonal directions, late spherulites may completely be swallowed up by early spherulites and their final boundary consists of the intersection of two branches of hyperbolas, with the disappearance of flat sides
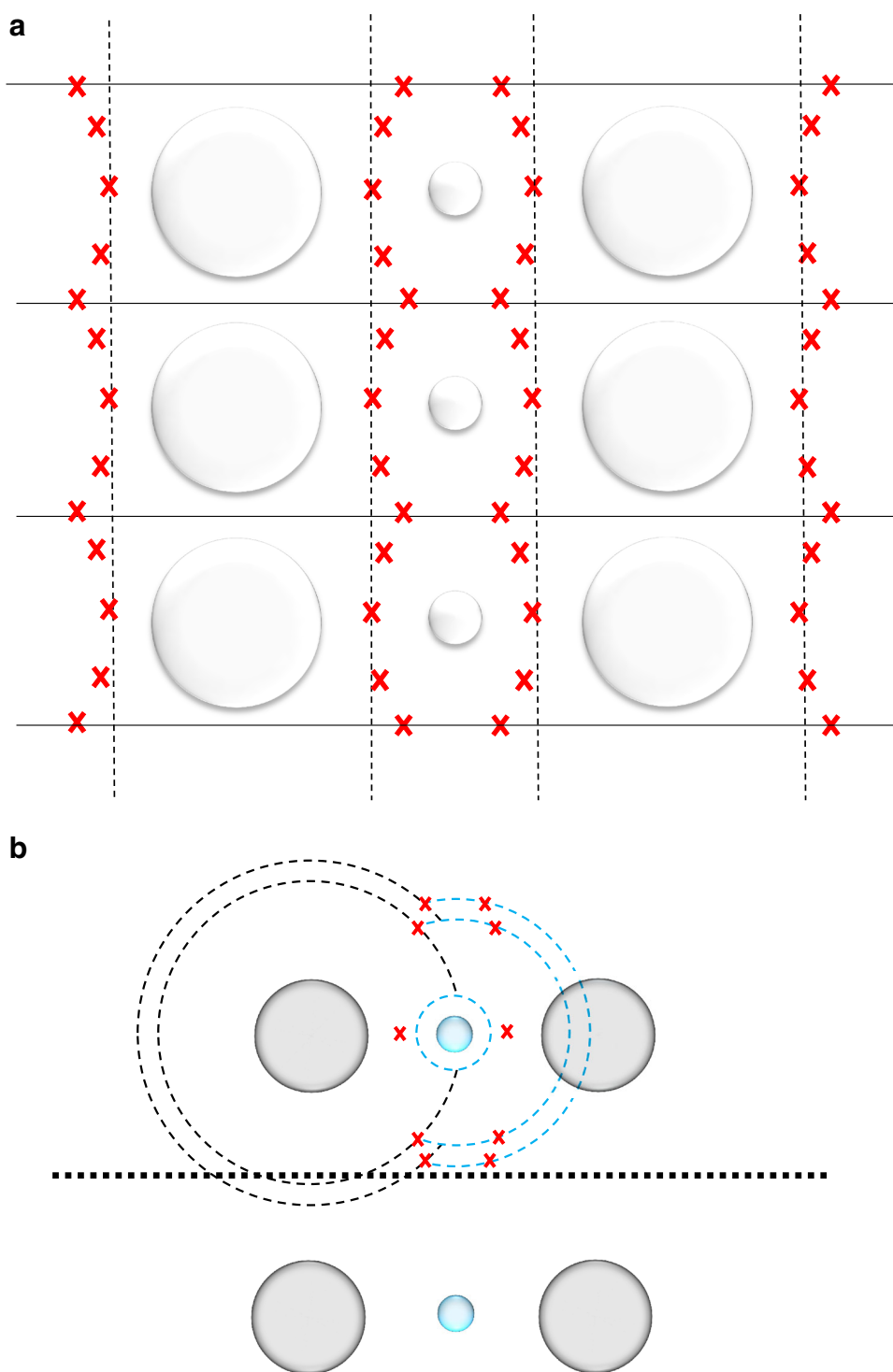
density and growth rate of spherulites, the higher the crystallization rate of samples. According to the crystallization theory, the actual crystallization rate of polymers cannot be constant with time, even if nucleation is instantaneous (which entails that all spherulites grow with the same size and that the nucleation density remains constant for the whole crystallization) and only growth is responsible for crystallization progress. Indeed, as shown in Fig. 1, the amount of solid added in a time interval to the growth front is not constant but depends on the spherulite size (hence on the time) since more and more material can be attached to a spherulite boundary as crystallization progresses. Since the

area of a spherulite is proportional to the mass, the derivative of the function describing the area of a spherulite is proportional to the growth rate. Considering a spherulite with a life time t growing separately with a linear growth rate g as a circle with area $A(t) = \pi r^2 = \pi g^2 t^2$, the rate of change of the spherulite area, i.e., the derivative of the area of the spherulite, is also function of time: $dA/dt = 2\pi g^2 t$. Using simpler geometrical notions, we can easily infer that the increment of the area of a spherulite (i.e., the area of a circular corona), divided by the time needed for that increment, gives the average growth rate of the spherulite in the considered time interval. This ratio changes not only with the wideness of the time interval but also, as shown in Fig. 1, according to time, since the area of circular coronae with the same thickness developed around a spherulite increases with the spherulite size. In conclusion, in case of constancy of the linear growth rate, the actual growth rate of an isolate bi-dimensional spherulite increases linearly with time in consequence of the enhancement of its incremental area with the growth.

As shown below, under the hypothesis of constancy of the linear growth rate of spherulites, deviations from linearity of the true growth rate of the whole solid can be due to time-dependent nucleation or impingement. Uniform random nucleation relatively to time (which means that the number of spherulites increases proportionally to the time) is likely to occur under slowly changing non-isothermal conditions and causes the transformation of the growth rate of all spherulites, up to the onset of impingement, in a piecewise linear function with ascending slopes. Under the hypotheses of uniform distribution of nuclei relatively to space and instantaneous nucleation, all spherulites will touch one another simultaneously and, soon after, the growth rate will decrease, with the appearance of a maximum in the crystallization rate. The resulting microstructure of a very thin specimen will consist of square tiles with equal size. If nucleation is not instantaneous and nuclei are distributed uniformly in space, earlier spherulites will touch each other before later spherulites, since these latter are smaller and their growth fronts, because of the higher distance, need more time to coalesce (see Fig. 2a). This circumstance will cause a shift of the maximum crystallization rate at a higher crystallization time, with a broadness of the crystallization peak. Non uniform random nucleation relatively to space also entails the contemporaneous presence of already coalesced spherulites meanwhile still separate spherulites are growing. Since the growth rate of spherulites within coalesced units begins to decrease, meanwhile the growth rate of isolated spherulites continues to increase unaffected, non uniform nucleation results in an anticipated deceleration and thus also in a slowdown of crystallization, with a lengthening of the overall crystallization time.

Although non-uniform nucleation in time and space has the same effect on the crystallization rate, these two retarding causes may be easily distinguished by visual inspection of relatively thick solids. If a solid shows a broad crystallization peak and uniform surface nucleation with linear interspherulitic interfaces [1, 4], it is likely that nucleation has occurred non simultaneously along the thickness even under external constant temperature because of the limited rate of heat propagation inside the sample. This is the usual reason for slow crystallization, since generally only very small and, hence, negligible deviations from uniform distribution in space are observed, especially at constant crystallization temperature, in thin polymer films.

DSC determination of the growth rate of solids

The curves of non-isothermal crystallization rates obtained by DSC are often expressed indifferently as function of temperature or time, with the assumption of a linear relationship between temperature and time. However, it is worth observing that under non-isothermal conditions crystallization is fast even if relatively low cooling rates are used and therefore only small temperature differences between the cooling device and the sample may arise during solidification. Moreover, these temperature differences are too low to generate appreciable differences in the molecular mobility of the liquid and, consequently, in the crystallization rate. Instead, during non-isothermal crystallization a time-dependent nucleation and increasing linear growth rates (with a further increase of the growth rate relatively to isothermal solidification) are expected only because of the increased rate of heat propagation. Indeed, if the external temperature is variable during solidification, also the density and the linear growth rate of spherulites are variable and, therefore, the growth of the solid material is strongly accelerated. Briefly, the high increase of the crystallization rate in non-isothermal procedures is mainly due to the increase of the rate of heat removal from the solid fronts because of the higher temperature differences between the specimen and the external temperature during solidification [15].

As already explained, the true crystallization rates of polycrystalline samples are attainable by determining the mass of solid formed, within the liquid medium, with time. The direct measure of the mass of a solid would require the preliminary separation of the two phases at several crystallization time and is, therefore, considered complicate and time wasting. More conveniently, the crystallization rate is estimated by monitoring during crystallization at constant temperature quantities proportional to the solid mass, as the heat flow rate is measured by a differential scanning calorimeter. The rate of heat evolution from a

crystallizing specimen in a DSC cell at a definite crystallization temperature is proportional to the solidification rate and reproduced in a DSC curve towards time by a bell-shaped curve, referred to as isothermal crystallization peak. Indeed, if $A(t)$ is the area of the solid, given by the contributes of all growing spherulites at any time t, and t_f is the time at which crystallization stops, the fraction of solid in a two-dimensional sample can be expressed by the ratio

$$\frac{\int_0^t (dA/dt)dt}{\int_0^{t_f} (dA/dt)dt} \qquad (1)$$

The crystallization rate of a three-dimensional sample results from the contribution along the thickness of each plane of bi-dimensional spherulites, whose nucleation occur according to a layer-by-layer crystallization [1]. If we imagine a polycrystalline sample constituted of equidistant and aligned spherulites simultaneously nucleated in each horizontal plane of the specimen, so that after complete impingement a tessellated structure composed of aligned squares in each layer arises, the fraction of solid at any time will be given by

$$\frac{\int_0^t (dA/dt)dt}{\int_0^{t_f} (dA/dt)dt} = \frac{\int_0^t (dA/dt)dt}{l^2}$$
$$= \frac{\int_0^{t_i} (dA/dt)dt + \int_{t_i}^t (dA/dt)dt}{l^2}, \qquad (2)$$

where l is the length of the sides of the final squares (l coincides with the distance between the centers of two adjacent spherulites) zero is the time of incipient crystallization and t_i the time at which spherulites begin to touch one another. The first addend at the numerator of formula (2) can be solved considering that for $t < t_i$ a primitive of dA/dt is $A(t) = \pi r^2$, and, therefore, the solid fraction before the impingement is described by the function

$$\frac{\int_0^t (dA/dt)dt}{\int_0^{t_f} (dA/dt)dt} = \frac{\pi r^2}{l^2} \qquad t < t_i \qquad (3)$$

At the start of impingement $r_i = b = l/2$; therefore, the solidification has already produced much more than 50 % of the achievable solid amount:

$$\frac{\int_0^{t_i} (dA/dt)dt}{\int_0^{t_f} (dA/dt)dt} = \frac{\pi}{4} = 0.78 \qquad (4)$$

After the appearance of interfaces between spherulites, the solid fraction increases accordingly to the following formula:

$$\frac{\int_0^t (dA/dt)dt}{\int_0^{t_f} (dA/dt)dt} = \frac{\pi}{4} + \frac{\int_{t_i}^t (dA/dt)dt}{l^2}, \qquad (5)$$

where the integral at the second member of (5) represents the difference between the area of the solid at a certain instant $t > t_i$ and at the onset of impingement, and the ratio $\int_{t_i}^t (dA/dt)dt/l^2$ must vary between 0 and 0.22. The mathematical expression of the area of a spherulite after coalescence will be determined in paragraph 4.

Since the heat from a crystallizing specimen in a DSC cell develops at a rate proportional to the rate of production of the solid phase, the values of the crystalline fraction may be experimentally obtained by replacing in formula (1) the function area $A(t)$ with the function $Q(t)$ expressing the heat developing during crystallization:

$$\frac{\int_0^t (dQ/dt)dt}{\int_0^{t_f} (dQ/dt)dt} \qquad (6)$$

To summarize, the heat flow rates measured by a DSC are proportional to the solidification rates. This implies that a DSC curve recorded during solidification should reproduce the shape of the crystallization rate function. Therefore, the ratio between the area of a portion of the crystallization peak (measured at definite time from the onset of crystallization) and the total area of the peak may be considered coincident with the solid fraction produced up to that time instant during solidification. The solid fraction produced during solidification can be then calculated as function of time. Hereafter the variation of the growth rate of spherulites owing to coalescence is considered to explain the experimental dependence on time of the overall crystallization rate and to elucidate the crystallization dynamics.

Growth rate variation after coalescence

Coalescence of only two spherulites

To determine the function describing the area of a spherulite after coalescence with an adjacent growing spherulite, let us place the center of a growing spherulite in the point $(0, -b)$ of a Cartesian reference [meaning that the center of the spherulite has a distance $b > 0$ from the origin (0,0) of the Cartesian axes]. The area of that spherulite may be described, up to impingement, by a simple function of the variable r: $A(r) = \pi r^2$ with $0 < r < b$. If another spherulite nucleated simultaneously and centered in the point $(0, b)$ is also growing with the same rate, the two spherulites will grow separately until their radius r is below b; then they start to coalesce in the origin $(0, 0)$ of the axes, and finally, for $r > b$ a linear interface (lying on the abscissa axis) will develop between the two spherulites (see Fig. 3). Even when two spherulites impinge with a progressive reduction of their growth fronts, we can still image the whole circular
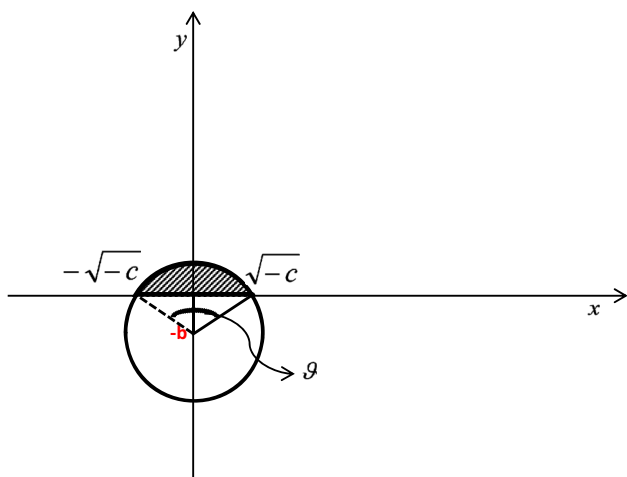
Fig. 3 Shape, at a general crystallization time, of one of two coalescing spherulites. It is supposed that the two growing spherulites maintain equal sizes during the whole crystallization. During coalescence the interface "advances" along the abscissa axis, hindering the growth of the spherulite in the two top quadrants of the Cartesian system. Each spherulite transforms into the greatest circular segment (*non-hatched area*) defined by the chord-interface with length $2\sqrt{-c}$. The surface lost by each spherulite at any time (*hatched area*) corresponds to the smallest circular segment defined by the interface
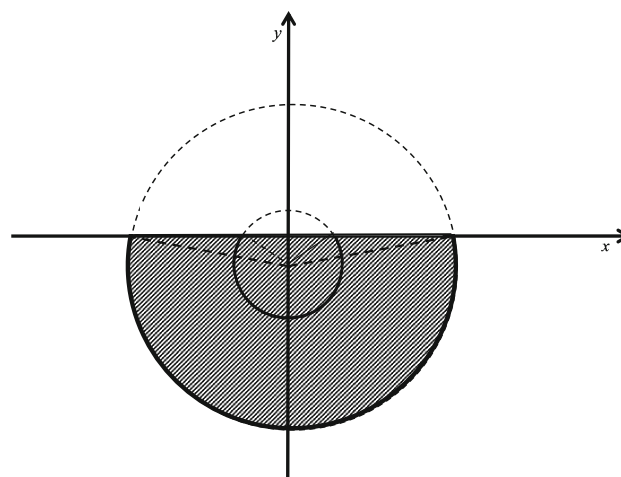
Fig. 4 Growth fronts of a spherulite coalescing with an adjacent spherulite (the second spherulite is not shown for the safe of clarity) at two different times. At any time, the length of the front still growing (*solid line*) is higher than that of the phantom arc (*dotted line*), whose growth is prevented by the interface. This entails that during coalescence the growth rate of both spherulites increases up to the end of crystallization, obviously at a rate lower than before impingement. Indeed, the length of the phantom arc of each spherulite increases with time, but remains shorter than the length of the still growing front, which, in turn, is reduced relatively to a whole circumference

boundaries (and, thus, also the whole area) that spherulites would have if they had continued to grow circularly without "collision". We can also divide, by means of the ends of the interspherulitic interface, each circular growth front in two arcs: a real still growing arc and a phantom arc, without real existence, inside the coalesced spherulites, as shown in Figs. 3 and 4. Focusing on one of two coalescing spherulite shown in Fig. 3, the instantaneous area of the spherulite will be equivalent to the area of the larger circular segment built on the chord-interface, which is given by (see "Appendix A")

$$A(\vartheta) = \pi r^2 - \left(\frac{1}{2}r^2\vartheta - \frac{1}{2}r^2\sin\vartheta\right), \qquad (7)$$

where ϑ is the angle between the two spherulite radii touching the ends of the interface, hereafter called "interfacial" angle.

Since $r^2 = b^2 + x^2$ and $\vartheta = 2\arcsin x/r$ for $r \geq b$, it results: $\cos(\arcsin x/r) = \left(1 - (x/r)^2\right)^{1/2} = b/r$. Considering also that the $\sin 2\alpha = 2\sin\alpha\cos\alpha$, with the appropriate substitutions (7) becomes:

$$
\begin{aligned}
A(x) &= \pi(b^2+x^2) - (b^2+x^2)\arcsin\frac{x}{\sqrt{b^2+x^2}} \\
&\quad + \frac{1}{2}(b^2+x^2)\left(2\sin\left(\arcsin\frac{x}{\sqrt{b^2+x^2}}\right)\cos\left(\arcsin\frac{x}{\sqrt{b^2+x^2}}\right)\right) \\
&= \pi(b^2+x^2) - (b^2+x^2)\arcsin\frac{x}{\sqrt{b^2+x^2}} \\
&\quad + (b^2+x^2)\left(\frac{x}{\sqrt{b^2+x^2}}\sqrt{1-\frac{x^2}{b^2+x^2}}\right) \\
&= (b^2+x^2)\left(\pi - \arcsin\frac{x}{\sqrt{b^2+x^2}} + \frac{bx}{b^2+x^2}\right)
\end{aligned}
$$

The function area can be hence expressed as function of x:

$$A(x) = (b^2 + x^2)\left(\pi - \arcsin\frac{x}{\sqrt{b^2+x^2}} + \frac{bx}{b^2+x^2}\right) \qquad (8)$$

or as function of x and r:

$$A(x, r(x)) = r^2\left(\pi - \arcsin\frac{x}{r} + \frac{bx}{r^2}\right) \qquad (9)$$

Since the function arcsine has values in the interval $[-\pi/2, \pi/2]$ and the function cosine has values in the interval $[-1, 1]$, the function $A(x, r(x))$ is expected to be

always positive and to increase with x (and, thus, with r) for $x > 0$. It is worth observing that the negative quantity $c = -x^2$, instead, decreases with increasing x and r.

During impingement, two opposite effects on the spherulite growth may be considered: the enhancement of the growth rate due to the size increment of each spherulite, and the decrease in the growth rate because of the loss of a portion of growth front with coalescence. Since πr^2 increases more than the phantom area $(r^2 \arcsin \frac{x}{r} - bx)$ with increasing r, at any time the remaining area $A(x, r(x))$ of each coalescing spherulite is larger than the lost area and, moreover, the difference between two successive areas of a coalescing spherulite is larger than the corresponding difference between two successive phantom areas. This means that the growth rate reduction due to the interface formation is less than the growth rate enhancement due to the increase of the spherulite boundary with r, and, therefore, the growth rate of two spherulites will continue to increase after coalescence, even if the rate of increase is slower. The slower increase of the growth rate of a coalescing spherulite as a consequence of the growth of the phantom area with time is shown in Fig. 4. Briefly, the increase of the growth rate of a coalescing spherulite prevails on the rate of the decay, since the lost growth front is shorter than the length gained because of the size progress and, therefore, the spherulite growth rate will continue to increase. It is intuitive that the phantom area of a spherulite with variable radius r cannot exceed the area $\pi r^2/2$ of half spherulite, which represents the area approached by each coalescing spherulite at infinite crystallization time. In other words, being always $\vartheta < \pi$ even for high crystallization time, the radial directions where growth can progress overcome those where growth is hindered and, therefore, during coalescence there is still a net increase of the growth rate of the two spherulites, although the increase is less pronounced than that occurring before coalescence. This means that a hypothetical sample consisting of only one or two growing spherulites will show a crystallization rate increasing with time for the whole

phase transformation duration. For a mathematical demonstration of the formulas used in this paragraph refer to "Appendix B".

Coalescence of more than two spherulites

If more than two spherulites begin to coalesce, a growing interface is generated between each couple of adjacent spherulites. Simple considerations allow to deduce that the growth rate of spherulites will not start to decrease at the onset of impingement, but only at a little more advanced crystallization time, when the phantom growth directions interrupted from interfaces prevail on the still real growth directions. Mathematically, it can be stated that if coalescence occurs the graph of the growth rate of a spherulite towards time is usually no more a line but transforms into a curve. The maximum point of the curve is achieved when "acceleration" reduces to zero and is very close to the onset of coalescence.

Let us consider a sample constituted of only three aligned spherulites, assumed to be nucleated simultaneously. During impingement, the middle spherulite contributes to the growth rate enhancement less than the two ending spherulites (see Fig. 5). When the ϑ angle is $\pi/2$, the length of each interfaces reaches the value $2b$ and the radius attains the value $2\sqrt{b}$. At this point, the contribute to the growth rate of the middle spherulite is half of that of each ending spherulite. Under these conditions, a square with side $2b$ may be inscribed within each spherulite and the growth rate of the central spherulite reaches its final constant value. The crystallization time corresponding to growth rate increases of the middle spherulite is $\sqrt{2}b/g$, whereas the average linear growth rate of the interfaces along one x direction is given by

$$\frac{b}{(\sqrt{2}b/g - t_i)} = \frac{b}{(\sqrt{2}b/g - b/g)} = \frac{g}{\sqrt{2} - 1} \cong 2.41g,$$

where t_i is the time needed for coalescence to start.

The growth rate of three aligned spherulites results from the contribution of each spherulite. When ϑ overcomes

Fig. 5 Sketch of the instantaneous shape of three coalesced spherulites, taken when the growth rate of the central spherulite is still growing
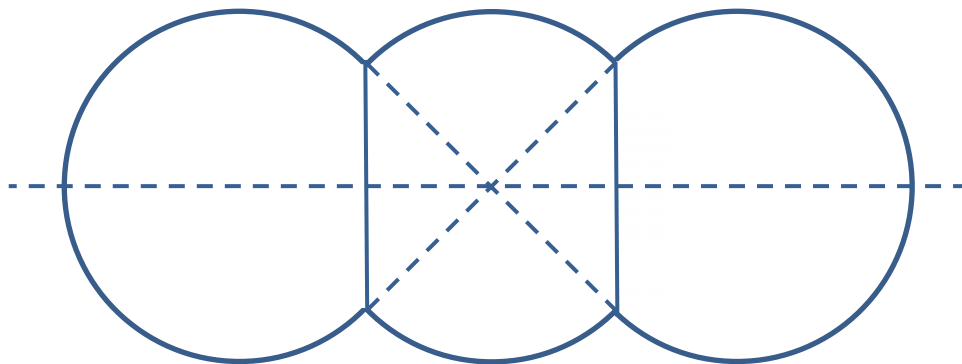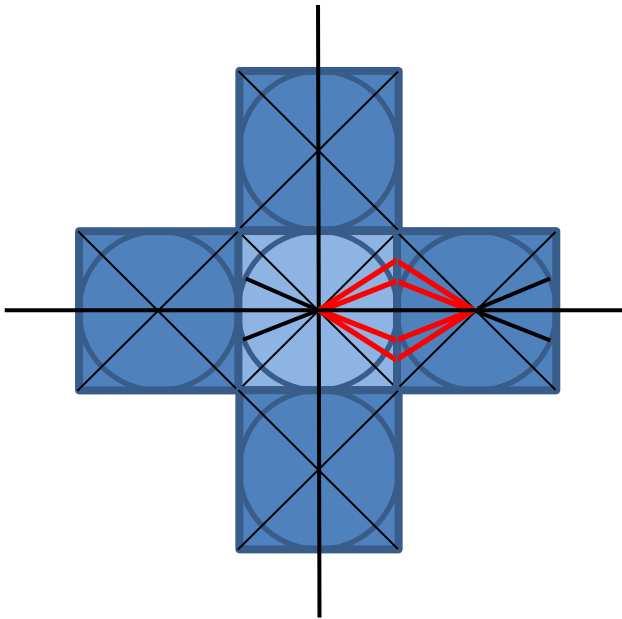
Fig. 6 Growth of a spherulite surrounded by four equidistant spherulites. The contribute to the solid fraction of each spherulite at any time is given by $4r^2/l^2$, where r is the radius at that time. When the radius of spherulites reach the length corresponding to $\vartheta = \pi/4$, the acceleration becomes zero and the solid fraction shows an inflection point
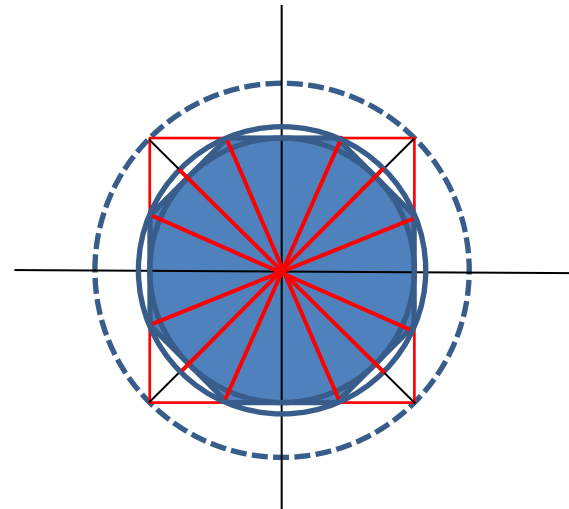

Fig. 7 Schematic growth of a spherulite surrounded by four equidistant spherulites (*not drawn*), under the hypothesis of instantaneous nucleation. After the onset of coalescence, the growth rate still increases for a short time, reaching the maximum when the curved spherulite boundaries overlap the circle (*red* radii) circumscribing the octagon with apothem b. The growth rate of the almost octagonal-shaped spherulite begins to decrease; meanwhile the ϑ angles change from 45° to 90°. Simultaneously, the growth acceleration becomes negative and the spherulite converts finally into a *square*

$\pi/2$, the growth rate of the middle spherulite remains constant and this spherulite cannot cause any increase of the growth rate of the sample.

However, since the growth rate of the two ending spherulites continues to increase (even if more slowly than before impingement) up to the end of crystallization, also the growth rate of the whole specimen will continue to increase.

Assuming that the nucleation in a polycrystalline sample occurs instantaneously with uniform random events in space and that all adjacent spherulites are centered at a unique distance $l = 2b$, after crystallization completion the spherulites will become regular squares with side l. As illustrated in Figs. 6 and 7, the growth rate of a spherulite surrounded by other four equidistant spherulites will be maximum when each of the four ϑ angles achieves the value $\pi/4$, that is, when the interfaces and the radii reach the length of $2b\sqrt{2-\sqrt{2}}\big/\sqrt{2+\sqrt{2}}$ and $2b\big/\sqrt{2+\sqrt{2}}$,

respectively. These values can be obtained by means of the well-known relationship between the side length L and the apothem b of an octagon and the radius of the circumcircle ($L = r\sqrt{2-\sqrt{2}}$, $b = r\sqrt{2+\sqrt{2}}/2$). Indeed, from the relationship between the apothem of an octagon and the radius of the circumcircle, for $\vartheta = \pi/4$ it follows that $r_{\max} = r_{\pi/4} = 2b\big/\sqrt{2+\sqrt{2}}$. Substituting this expression in that of the side L of the inscribed octagon, it is observed that $L = 2b\sqrt{2-\sqrt{2}}\big/\sqrt{2+\sqrt{2}}$. Therefore, the crystallization time corresponding to the maximum growth rate of the middle spherulite is

$$t_{\max} = r_{\max}/g = 2b\Big/\left(g\sqrt{2+\sqrt{2}}\right),$$

whereas in the time interval

$$t_{\max} - t_i = \left(2b\Big/\left(g\sqrt{2+\sqrt{2}}\right)\right) - b\Big/g = (b/g)\left(\left(2\Big/\left(\sqrt{2+\sqrt{2}}\right)\right) - 1\right)$$
$$= (b/g)\left(2 - \sqrt{2+\sqrt{2}}\right)\Big/\sqrt{2+\sqrt{2}} = 0.082b/g \cong 0.082t_i$$

the average linear growth rate of the interfaces along one of the growth directions results:

$$\left(b\sqrt{2-\sqrt{2}} \Big/ \sqrt{2+\sqrt{2}} \right) \Big/ (t_{\max} - t_i)$$
$$= \left(g\sqrt{2-\sqrt{2}} \right) \Big/ \left(0.082\sqrt{2+\sqrt{2}} \right) \cong 5.0\,g$$

In general, the growth rate of a spherulite will begin to decrease when the sum of the interfacial angles with neighbor spherulites reaches the value π, that is, when the lost area is higher than the actual area gained during coalescence. To observe a decrease of the crystallization rate of the whole sample, it is necessary, however, that the size of coalesced groups of spherulites be rather

Theoretical determination of the growth rate function of coalescing spherulites

As the area of a spherulite coalescing with four equidistant spherulites (see also "Appendix B") is given by

$$A(x) = (b^2 + x^2)\left(\pi - 4\left(\arcsin\frac{x}{\sqrt{b^2+x^2}} - \frac{bx}{(b^2+x^2)} \right) \right)$$
$$= (b^2 + x^2)\left(\pi - 4\arcsin\frac{x}{\sqrt{b^2+x^2}} + 4\frac{bx}{(b^2+x^2)} \right)$$
$$= r^2\left(\pi - 4\arcsin\frac{x}{r} + 4\frac{bx}{r^2} \right), \tag{10}$$

where the first, second and third derivatives of the function area are

$$\frac{dA(x)}{dx} = 2x\left(\pi - 4\arcsin\frac{x}{\sqrt{b^2+x^2}} + 4\frac{bx}{(b^2+x^2)} \right) + (b^2+x^2)\left(-4\left(\frac{1}{\sqrt{1-\frac{x^2}{b^2+x^2}}} \right)\left(\frac{\sqrt{b^2+x^2} - \frac{2x^2}{2\sqrt{b^2+x^2}}}{b^2+x^2} \right) + 4\frac{b(b^2+x^2) - 2bx^2}{(b^2+x^2)^2} \right)$$
$$= 2x\left(\pi - 4\arcsin\frac{x}{\sqrt{b^2+x^2}} + 4\frac{bx}{(b^2+x^2)} \right) - 4(b^2+x^2)\left(\frac{b}{b^2+x^2} - \frac{b^3 - bx^2}{(b^2+x^2)^2} \right)$$
$$= 2x\left(\pi - 4\arcsin\frac{x}{\sqrt{b^2+x^2}} + \frac{4bx}{(b^2+x^2)} \right) - 4(b^2+x^2)\left(\frac{2bx^2}{(b^2+x^2)^2} \right)$$
$$= 2x\left(\pi - 4\arcsin\frac{x}{r} + \frac{4bx}{r^2} \right) - \frac{8bx^2}{r^2} = 2x\pi - 8x\arcsin\frac{x}{r} = 2x\left(\pi - 4\arcsin\frac{x}{r} \right) \tag{11}$$

high, since as long as coalescence involves only a restricted number of spherulites it can lead to further increase of the overall growth rate even if the number of isolated groups of spherulites is high. Indeed, the true growth rate of polycrystalline films depends not only on the number of spherulites and on time dependence of nucleation but also on the exact distribution of the distances between crystalline nuclei, since this latter affects the start of impingement of each couple of adjacent spherulites.

It is worth noting that, although the subject of the present work is new relatively to the analytical description of the spherulite growth rate during coalescence, it shares with earlier articles and theories assumptions and results on the morphology of originated microstructures and spherulitic interfaces [16]. Moreover, also quantitative results are consistent with previous observations. For instance, Fig. 8e of the present article and Fig. 7 of reference 16 show that when more than 50 % of the solid phase has already been produced, there are still growing crystallites which can contribute to further increases in the crystallization rate.

$$\frac{d^2A(x)}{dx^2} = 2\pi - 8\arcsin\frac{x}{\sqrt{b^2+x^2}}$$
$$- 8x\left(\frac{1}{\sqrt{1-\frac{x^2}{b^2+x^2}}} \right)\left(\frac{\sqrt{b^2+x^2} - \frac{2x^2}{2\sqrt{b^2+x^2}}}{b^2+x^2} \right)$$
$$= 2\pi - 8\arcsin\frac{x}{\sqrt{b^2+x^2}} - 8x\frac{b}{b^2+x^2}$$
$$= 2\pi - 8\arcsin\frac{x}{r} - \frac{8bx}{r^2} \tag{12}$$

$$\frac{d^3A(x)}{dx^3} = -8\left(\frac{1}{\sqrt{1-\frac{x^2}{b^2+x^2}}} \right)\left(\frac{\sqrt{b^2+x^2} - \frac{2x^2}{2\sqrt{b^2+x^2}}}{b^2+x^2} \right)$$
$$- 8\left(\frac{b(b^2+x^2) - 2bx}{(b^2+x^2)^2} \right)$$
$$= -8\frac{b}{b^2+x^2} - 8\frac{b}{b^2+x^2} + \frac{16bx}{(b^2+x^2)^2}$$
$$= -\frac{16b}{r^2} + \frac{16bx}{r^4} = -\frac{16b}{r^2} + \frac{16}{r^2}\cos\frac{\vartheta}{2}\sin\frac{\vartheta}{2}$$
$$= -\frac{16b}{r^2} + 8\frac{\sin\vartheta}{r^2} = -\frac{8}{r^2}(2b - \sin\vartheta) \tag{13}$$
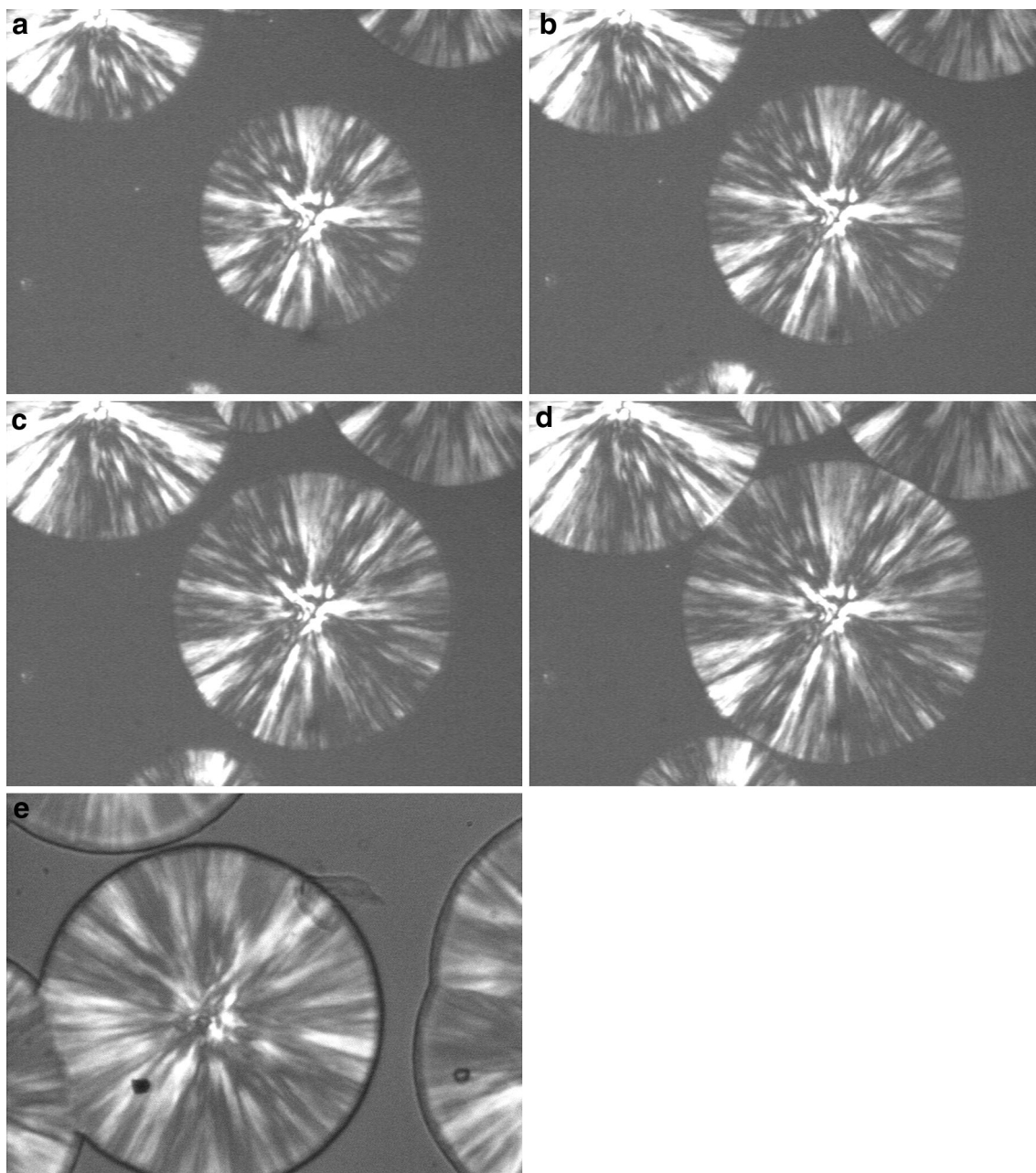
Fig. 8 a–d Optical micrographs of isotactic polypropylene taken during isothermal crystallization (130 °C) at different times. It is shown that, even during coalescence, a spherulite can continue to grow along radial directions far from the developing interfaces. If spherulites are almost uniformly distributed in space so that their distances are not too different (as idealized in Fig. 7), it is evident that, irrespective of the nucleation dynamics, the contact amongst spherulites starts when most of the sample is already solid: the hindered growth directions overcome the still growing directions only in the latest stage and crystallization slows down shortly just before the end. **e** This micrograph shows that, even if the amount of liquid amongst spherulites is very limited, a few spherulites may be still able to grow in most of the directions with an increasing growth rate

The second derivative (12) is zero (and, therefore, the crystallization rate expressed by the first derivative (11) is maximum) when the interfacial angle is $\vartheta = \pi/4$. To obtain the zero points of the second derivative (12), let us to write the product $r^2 \frac{\mathrm{d}^2 A(x)}{\mathrm{d}x^2}$ as

$$
\begin{aligned}
r^2 \frac{\mathrm{d}^2 A(x)}{\mathrm{d}x^2} &= 2\pi r^2 - 8r^2 \arcsin\frac{x}{r} - 8bx \\
&= 2\left(\pi r^2 - 4r^2 \arcsin\frac{x}{r} - 4bx\right) \\
&= 2\left(\pi r^2 - 4\left(r^2 \arcsin\frac{x}{r} - bx\right) - 8bx\right) \\
&= 2(A(x) - 8bx)
\end{aligned}
$$

It follows that

$$\frac{\mathrm{d}^2 A(x)}{\mathrm{d}x^2} = \frac{2(A(x) - 8bx)}{r^2}$$

It is easy to verify that the equation $\frac{\mathrm{d}^2 A(x)}{\mathrm{d}x^2} = \frac{2(A(x) - 8bx)}{r^2} = 0$ is verified when $A(x) = 8bx + \text{const} = 16\frac{bx}{2} + \text{const}$, that is, when the difference between the area of an hypothetical central spherulite growing isolate and the actual area of the coalesced "spherulite" is equivalent to the difference between the actual area of the coalesced "spherulite" and the area $8bx$ of the regular octagon with apothem b and side $L = 2x = b/1.207$, with $x > 0$. This condition is verified for $\vartheta = \pi/4$, when both the differences equals four times the area of the smaller circular segment built on a chord of length L of the central spherulite (see Fig. 7).

Moreover, since the second derivative (12) of the monotonically crescent function area (10) has a zero point, the function $A(x)$ must have an inflection point for $\vartheta = \pi/4$. The function (10), determined by the analysis of DSC crystallization peaks explained in paragraph 3, is indeed almost universally found to have a typical "sigmoidal" shape (the adjective sigmoidal is here used to indicate a monotonically crescent function with an inflection point).

The sign of the third derivative (13) can give information about the crystallization rate (11). Equaling (13) to zero and multiplying per $-r/8$ results in $\frac{2b}{r} - \frac{\sin\vartheta}{r} = 0$, which may be re-written as

$$2\cos\frac{\vartheta}{2} - 2\frac{\sin\frac{\vartheta}{2}\cos\frac{\vartheta}{2}}{r} = 2\cos\frac{\vartheta}{2} - 2\frac{\sin\frac{\vartheta}{2}}{r}\cos\frac{\vartheta}{2}$$
$$= 2\cos\frac{\vartheta}{2} - 2\frac{x}{r^2}\cos\frac{\vartheta}{2} = 0$$

To be verified, this equation requires that $x = r^2$, a condition that cannot be satisfied, whatever the value of ϑ be. For $\vartheta = \pi/4$, it is $2b = 2r_{\pi/4}\cos(\pi/8)$ and, therefore, $2b/r_{\pi/4} = 2\cos(\pi/8) = \sqrt{2 + \sqrt{2}} \cong 1.85$. Moreover, $\sin(\pi/4)/r_{\pi/4} = \frac{\sqrt{2}}{2}\frac{\sqrt{2+\sqrt{2}}}{2b} \cong 0.65/b$; hence $2b/r_{\pi/4} > \sin(\pi/4)/r_{\pi/4}$. Analogously, it must also result $2b/r_{\pi/2} > \sin(\pi/2)/r_{\pi/2}$, since $2b/r_{\pi/2} = 2\cos(\pi/4) = 2/\sqrt{2} \cong 1.41$ and $\sin(\pi/2)/r_{\pi/2} = \frac{1}{\sqrt{2}b} \cong 0.71/b$. This entails that the third derivative (13) is always negative and, consequently, the first derivative is a convex curve with a maximum in correspondence of $\vartheta = \pi/4$ (where the second derivative is null). Therefore, the crystallization rate increases from $\vartheta = 0$ to $\vartheta = \pi/4$ and then begins to decrease. Finally, when $\vartheta \geq \pi/2$ the area cannot increase further and the crystallization rate becomes zero because the liquid phase is finished.

Observing Fig. 7, it can be deduced that for $\vartheta = \pi/4$ the area that the central "spherulite" has more than a regular octagon with apothem b is exactly half of the area that a separate spherulite would have more than the same octagon, i.e., $A_{\pi/4} - A_o = 1/2\left(\pi r_{\pi/4}^2 - A_o\right)$, that is, $A_{\pi/4} = 1/2\left(\pi r_{\pi/4}^2\right) + A_o/2$. Since the area of an octagon can be expressed as function of the radius of the circumcircle: $A_o = 4(\sin\pi/4)r_{\pi/4}^2 = 2\sqrt{2}r_{\pi/4}^2$, it follows that, for $\vartheta = \pi/4$, the area of a coalescing spherulite is $A_{\pi/4} = 1/2\left(\pi r_{\pi/4}^2\right) + \sqrt{2}r_{\pi/4}^2$. Since $A_{\pi/4}\big/\pi r_{\pi/4}^2 = 1/2 + \sqrt{2}/\pi = 0.95$, for $\vartheta = \pi/4$ the area of a coalescing spherulite is almost 95 % of the area of a hypothetical still separate spherulite, whereas at the end of crystallization (i.e., for $\vartheta = \pi/2$), the area of a spherulite is 64 % of the area of a still separately growing spherulite (this value can be obtained by the ratio $2/\pi$ between the area of a square and the area of the circumcircle). Briefly, we can say that the crystallization rate increases with a constant acceleration up to the start of coalescence t_i; then the acceleration starts to decrease with a simultaneous reduction of the crystallization rate of coalesced spherulites relatively to the crystallization rate that isolated spherulites with the same radius would have, although for $0 < \vartheta < \pi/4$ the crystallization rate will continue to increase. For $\vartheta = \pi/4$, the crystallization rate of a coalescing spherulite reaches its maximum value and the acceleration becomes zero. After, the crystallization rate decreases meanwhile the acceleration becomes negative.

Since it has been assumed that the linear growth rate of spherulites is constant, indicating with $t_{\max}$ the time corresponding to the maximum of the crystallization rate, it comes out that

$$t_f - t_{\max} = \frac{r_f - r_{\max}}{g} = \left(\sqrt{2}b - 2b\big/\sqrt{2+\sqrt{2}}\right)\big/g$$
$$= (1.41b - 1.08b)/g = 0.33b/g = 0.33t_i$$

This means that the time $t_f - t_{\max}$ needed to complete crystallization, meanwhile growth rates are decreasing, is even shorter than the time needed to achieve the maximum growth rate. Indeed, crystallization peaks may result asymmetric, with a frontal part even prominent relatively to the final part. This apparent paradox of high crystallization time at high crystallization rates and shorter time at low growth rates is due to the fact that spherulites grow mostly when they are separate, whereas only a small fraction of liquid has to be still transformed in solid during impingement.

At the end of crystallization, the radius reaches half of the length of square's diagonal $\sqrt{2}(l/2)$ and $x = b = l/2$; therefore, formula (10) gives

$$A(t_f) - A(t_i) = \frac{\pi}{4}l^2 - 2l^2 \arcsin\frac{1}{\sqrt{2}} + l^2 = \left(1 - \frac{\pi}{4}\right)l^2$$
$$= 0.22l^2$$

Therefore, only 22 % c.a. of the whole area of the system remains to be crystallized in the time interval $t_f - t_i$. Assuming a constant linear growth rate of spherulites for the whole crystallization, the time $t_f - t_i$ needed to complete crystallization from the start of impingement can be calculated from the following proportion: $(t_f - t_i) : t_i = (r_f - r_i) : r_i$, with $r_f = \sqrt{2}b$ and $r_i = b$. This leads to the result: $t_f - t_i = (\sqrt{2} - 1)t_i = 0.41t_i$. Therefore, the crystallization time after impingement is almost 41 % of the time before impingement. As already shown in paragraph 4.2, after coalescence the growth rate continues to increase for the short time $t_{max} - t_i = 0.082t_i$ (meanwhile almost 9 % of the solid is being formed since, as shown in the next paragraph, the solid fraction changes from 78 to 87 % in the interval $t_{max} - t_i$), before decreasing. Totally, the time elapsed from the onset of crystallization up to the maximum growth rate is $1.082t_i$, whereas the time from the maximum growth rate to the end of crystallization is almost $0.33t_i$. Since the time remaining for crystallization is shorter (almost 1/3) than the elapsed time by onset of crystallization up to the maximum, the peak describing the solidification process should appear asymmetric.

Shape and symmetry of the crystallization rate curves

Let us consider a polycrystalline sample constituted of equidistant spherulites nucleated simultaneously, so that after complete impingement a tessellated structure composed of all aligned squares arises; the fraction of solid for $\vartheta = \pi/4$ is given by the formula

$$\left(A_O + \frac{A_C - A_O}{2}\right)\Big/A_Q,$$

where $A_C = \pi r_{\pi/4}^2$ is the area of the circumcircle, $A_O = 2\sqrt{2}r_{\pi/4}^2$ is the area of the inscribed octagon and $A_Q = l^2 = 4b^2$ the area of the final square with side l (see also Fig. 7). With the appropriate substitutions and considering that $b = \left(r_{\pi/4}\sqrt{2 + \sqrt{2}}\right)\Big/2$, it comes out that for $\vartheta = \pi/4$ the solid fraction is $(\pi + 2\sqrt{2})/(4 + 2\sqrt{2}) = 0.87$. Therefore, meanwhile the solid fraction increases up to 0.87 in the time $t_{max} = 2b\Big/\left(g\sqrt{2 + \sqrt{2}}\right)$, the growth rate increases up to the maximum and then starts to decrease. As shown in paragraph 5, the further time needed to complete solidification, measured from the time

corresponding to the maximum growth rate, is $t_f - t_{max} = 0.33t_i$. As the typical sigmoid curve describing the solid fraction versus time in case of instantaneous nucleation is not symmetric with respect to the inflection point, the growth rate curve is usually not symmetric relatively to the maximum. Irregularities in the shape of DSC crystallization peaks of relatively small masses of high thermal conductivity samples are, therefore, no exception, since solidification can be considered instantaneous in the whole volume because of the high rate of heat conduction. As stated in paragraph 3, the area of each original spherulite at the end of the crystallization will be l^2, whereas the area at the onset of impingement, when $\vartheta = 0$, is $l^2\pi/4$. This means that at the start of impingement, corresponding to the time $t_i = l/(2g) = b/g = t_f r_i/r_f = t_f/\sqrt{2} \cong 0.71t_f$, the fraction of solid material is $\pi/4 \cong 0.78$. Therefore, at the starting time of impingement crystallization is already completed for 78 % and progresses towards the end in a time $t_f - t_i \cong 0.29t_f$ with a brief further increase of the rate (the time $t_{max} - t_i \cong 0.082t_i$ needed to reach the maximum growth rate and a solid fraction of 87 % is indeed very short) followed by a final continuous decrease. However, samples with a very low thermal conductivity as polymers, unless in the form of very thin films, cannot reach immediate equilibrium with cooling or heating devices. Therefore, in a transitory regime before the onset of crystallization, a polymer film will host a temperature gradient along the thickness, which, according to the crystallization theory, will in turn generate a time-dependent nucleation. Non instantaneous nucleation in the whole volume of the sample, together to small irregularity of tessellation, retards full crystallization and causes the appearance of symmetric crystallization peak. For instance, in Fig. 9 the crystallization peak of indium (In) and that of a polymer are shown for a comparison.

The above conclusion may be extended to the crystallization rate of samples with any spatial distribution of spherulites.

For instance, a spherulite nucleated in the center of a circumference on which other three equidistant spherulites have been simultaneously nucleated (see Fig. 10), will show a decrease of the growth rate when the ϑ angles reaches the value $\vartheta = \pi/3$, and the growth rate will fall to zero when $\vartheta = 2\pi/3$. If we focus only on the growth of the central spherulite, finally transformed in an equilateral triangle with height $3d/2$ and side $\sqrt{3}d$, we will observe that the time elapsed from nucleation to onset of coalescence is equal to the remaining time of crystallization of that spherulite. The central spherulite will achieve the maximum growth rate when the length of the radius is $r_{max} = d/(2\cos(\pi/6)) = d/\sqrt{3} \cong 0.58d$ and the crystallization time $t_{max} = r_{max}/g = 0.58t_f$, being t_f the usual

Fig. 9 a DSC crystallization peaks obtained by cooling c.a. 40 mg of In from melt at a scan rate of −5 °C/min. The *peak* in the *top curve* reproduces exactly the crystallization rate predicted for simultaneous and uniform nucleation: a linear fast increase followed by an abrupt in the heat flow. The crystallization peak of In shown in the bottom DSC curve has been obtained in the presence of an inert low conductivity layer of a high melting point polymer. In such a case, the crystallization peak of In becomes broader and shorter since the heat removal from the growth front of In grains is delayed by the underlying solid and crystallization of In is consequently retarded.
b Crystallization peak of polyoxymethylene (POM) obtained by continuous cooling at −5 °C/min. While crystallization of 40 mg of In is completed in c.a. 1 min, complete crystallization of c.a. 17 mg of POM takes more than 7 min. Because of the very slow heat removal from internal regions of polymers, nucleation is not instantaneous along the thickness and growth is also slow. Indeed, polymer crystallization results slower than crystallization of metals. The slowdown of polymer crystallization is even more evident during the final stage of impingement
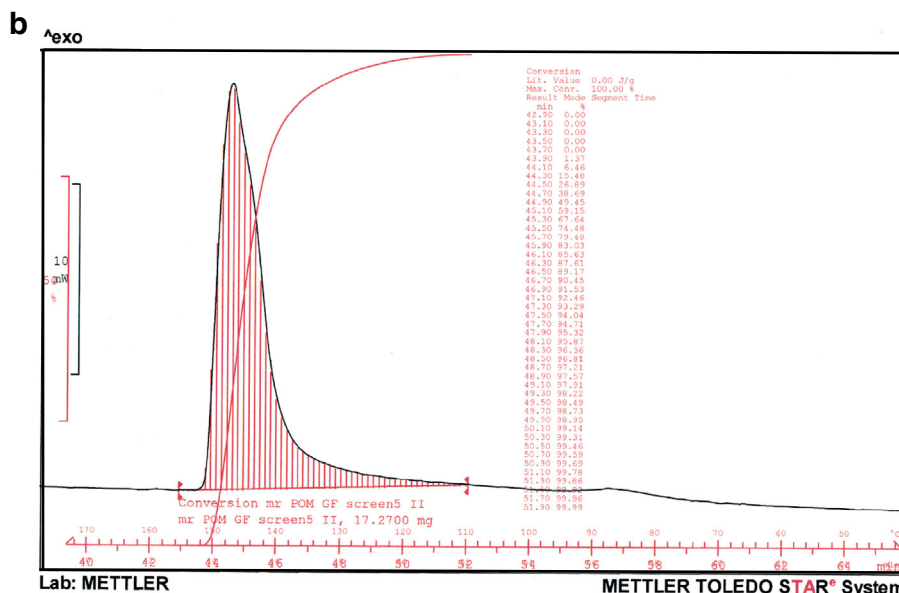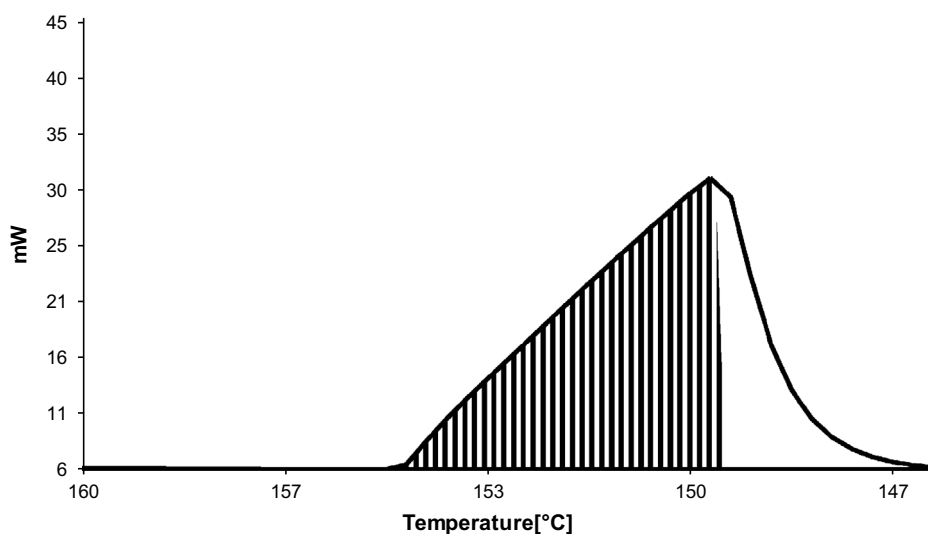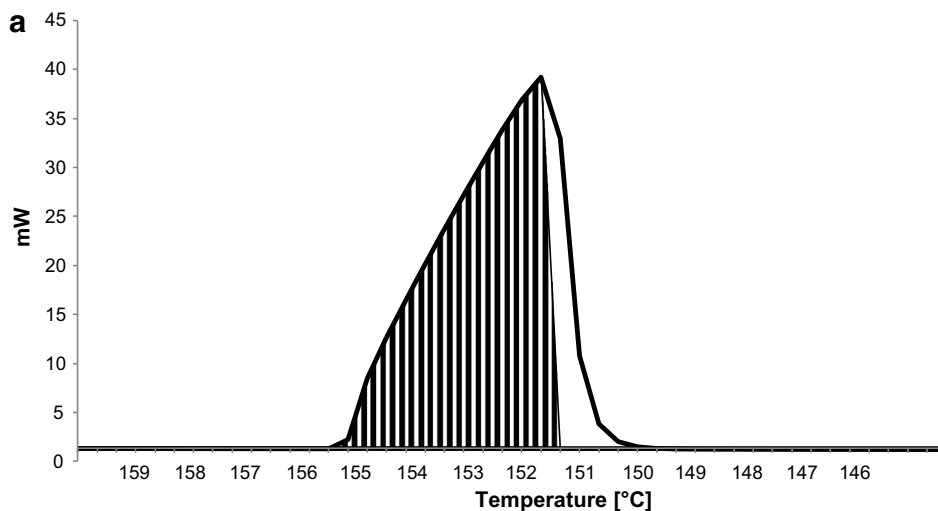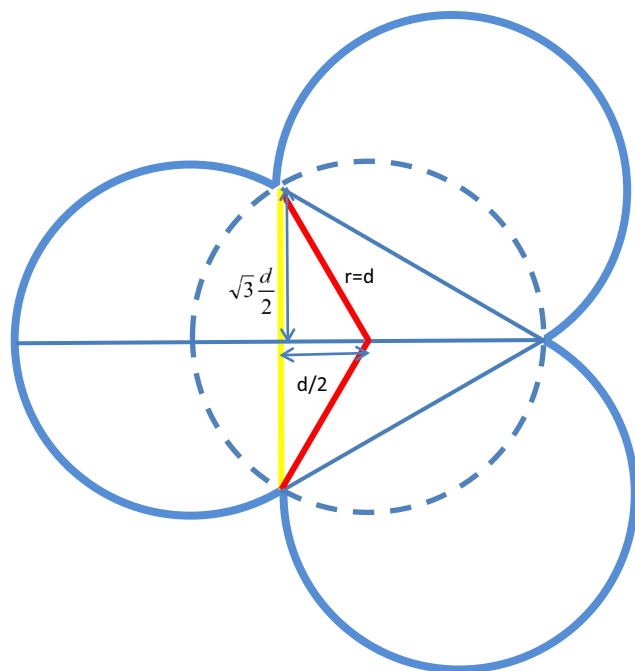
Fig. 10 *Triangular shape* of a spherulite after coalescence with three surrounding spherulites. The distance between the centers of adjacent spherulites is d

time needed for the whole crystallization. At the start of impingement, the solid fraction is already 60 %, as the ratio between the areas of the inscribed circle and the triangle is $\frac{\pi r_i^2}{3\sqrt{3}r_i^2} = \frac{\pi}{3\sqrt{3}} = 0.60$. Therefore, even when the time t_i needed to touch neighbors equals the remaining crystallization time $t_f - t_i$, the time corresponding to the maximum growth rate of a spherulite is higher than the half-time of crystallization (this latter is defined as the time needed to have 50 % of the final solid mass). However, in an ideal solid where each spherulite is surrounded by three equidistant spherulites, the crystallization peak results more symmetrical than in other discussed cases and the time needed for the impingement of all adjacent spherulites (not coinciding with the maximum point) can be approximatively obtained from the DSC curve as half of the overall crystallization time since $t_i = d/2g = t_f/2$, i.e., $t_f - t_i = d/2g = t_i$.

Conclusions

In this article an overview on the solidification mechanism and its consequence on the shape of the DSC crystallization peak, both at constant and decreasing temperature, have been provided. It has been highlighted that the true crystallization rate of a material is usually not constant with time, even if crystallization is performed at constant

temperature and crystallites develop with a constant linear growth rate. At constant external temperature, the rate of heat removal from the growth front is also constant and the crystallization rate increases up to a maximum, finally decreasing because of coalescence of spherulites. Continuous cooling instead causes a variable temperature difference between the DSC platform and the growth front that, in turn, accelerates the rate of heat removal and, hence, the crystallization rate. Moreover, it has been shown that the shape of the crystallization rate function is reproduced experimentally by the DSC crystallization peak and that a theoretical prediction of such a shape can also be made by means of simple mathematical tools. The crystallization rate reduction observed during a single solidification experiment of a polycrystalline material, performed at constant or slightly variable temperature, is only ascribable to impingement. To appreciate the influence of other factors such as molecular mobility and undercooling on the crystallization rate it is necessary to perform several experiments under very different temperatures or cooling conditions.

Appendix A: Area of a coalescing spherulite

The function which describes the area of a spherulite during coalescence with an adjacent spherulite may be obtained by starting from the equation of a circumference with radius $r = \sqrt{b^2 - c}$ (assuming $b > 0$ and $c < 0$) and center, of coordinates $(0, -b)$, distant from the x axis of a length $b = l/2$:

$$x^2 + y^2 + 2by + c = 0 \tag{14}$$

being l the distance between the centers of the two coalescing spherulites.

When the value of b is prefixed (in real crystallization, it generally depends on the temperature), with varying c the Eq. (14) represents all the circumferences of the plane xy centered in $(0, -b)$. The circumferences with radius $r > b$, considered in the real field, have the coefficient $c = b^2 - r^2$ negative and intersect the x axis in the two points $(-\sqrt{-c}, 0)$ and $(\sqrt{-c}, 0)$. Moreover, for each circumference the length of the chord laying on the x axis is given by $2\sqrt{-c} = 2\sqrt{r^2 - b^2}$.

Rewriting (14)

$$y^2 + 2by = -x^2 - c$$

Adding b^2 to both the members

$$y^2 + 2by + b^2 = -x^2 - c + b^2$$

and considering the first member as the square of a binomial

$$(y + b)^2 = -x^2 - c + b^2$$

finally results in

$$y = \left(-x^2 + b^2 - c\right)^{1/2} - b$$

$$
\begin{aligned}
|F(x)|_{-\sqrt{-c}}^{\sqrt{-c}} &= +\frac{1}{2}r^2 \arcsin\frac{\sqrt{-c}}{r} - \frac{1}{2}\sqrt{-c}\left(\sqrt{r^2 - \left(\sqrt{-c}\right)^2}\right) - \frac{1}{2}r^2 \arcsin\left(-\frac{\sqrt{-c}}{r}\right) + \frac{1}{2}\left(-\sqrt{-c}\right)\left(\sqrt{r^2 - \left(-\sqrt{-c}\right)^2}\right) \\
&\quad + \frac{1}{2}r^2 \arcsin\frac{\sqrt{-c}}{r} - \frac{1}{2}\sqrt{-c}\left(\sqrt{r^2 - \left(\sqrt{-c}\right)^2}\right) + \frac{1}{2}r^2 \arcsin\left(\frac{\sqrt{-c}}{r}\right) - \frac{1}{2}\left(\sqrt{-c}\right)\left(\sqrt{r^2 - \left(\sqrt{-c}\right)^2}\right) \\
&= r^2 \arcsin\frac{\sqrt{-c}}{r} - \sqrt{-c}\left(\sqrt{r^2 - \left(\sqrt{-c}\right)^2}\right) = r^2 \arcsin\left(\sin\frac{\vartheta}{2}\right) - b\sqrt{-c} = r^2\frac{\vartheta}{2} - b\left(b\tan\frac{\vartheta}{2}\right) \\
&= \frac{1}{2}r^2\vartheta - b\left(b\frac{r\sin\frac{\vartheta}{2}}{r\cos\frac{\vartheta}{2}}\right) = \frac{1}{2}r^2\vartheta - br\sin\frac{\vartheta}{2} = \frac{1}{2}r^2\vartheta - \frac{1}{2}br\frac{\sin\vartheta}{\cos\frac{\vartheta}{2}} = \frac{1}{2}r^2\vartheta - \frac{1}{2}r^2\sin\vartheta
\end{aligned}
$$

Therefore, the area between the x axis and a circumference with $r > b$ and $c < 0$ will be given by the definite integral:

$$\int_{-\sqrt{-c}}^{\sqrt{-c}} \left[\left(\left(-x^2 + b^2 - c\right)^{1/2} - b\right)\right] dx$$

To solve the above integral, it is sufficient to observe that $b^2 - c = r^2$ and to rewrite $\left(-x^2 + b^2 - c\right)^{1/2}$ as $\left(r^2 - x^2\right)^{1/2}$. The indefinite integral

$$\int \left(\left(r^2 - x^2\right)^{1/2} - b\right) dx = \int \left(r^2 - x^2\right)^{1/2} dx - bx \qquad (15)$$

has primitive functions of types $F(x) + \text{Const}$, and $F(x)$ can be obtained integrating by substitution or by part. Indeed, solving (15) with one of the two mentioned techniques

$$
\begin{aligned}
F(x) &= \int \left(\left(r^2 - x^2\right)^{1/2} - b\right) dx \\
&= +\frac{1}{2}r^2 \arcsin\frac{x}{r} + \frac{1}{2}x\left(\sqrt{r^2 - x^2}\right) - bx
\end{aligned}
$$

and substituting $\sqrt{r^2 - x^2}$ to b:

$$
\begin{aligned}
F(x) &= +\frac{1}{2}r^2 \arcsin\frac{x}{r} + \frac{1}{2}x\left(\sqrt{r^2 - x^2}\right) - x\left(\sqrt{r^2 - x^2}\right) \\
&= +\frac{1}{2}r^2 \arcsin\frac{x}{r} - \frac{1}{2}x\left(\sqrt{r^2 - x^2}\right)
\end{aligned}
$$

Defining θ $(0 < \theta < \pi)$ as the central angle as the central angle relative to the circular segment that, by varying r,

identifies the portion of area lost by each spherulite because of coalescence (hatched area in Fig. 3); this latter can be obtained as function of θ:

Expressing the area of the circular segment as function of ϑ and of $-c = r^2 - b^2$, it results also in

$$F(\sqrt{-c}) - F(-\sqrt{-c}) = +\frac{1}{2}r^2\vartheta - b\sqrt{-c}$$

Such formulas represent the area of the smaller circular segment sectionized by the x axis on each circumference with center $(0, -b)$ and radius $r > b$. Hence, the area of a spherulite coalescing with and adjacent spherulite is given by the area of the corresponding larger circular segment (see Fig. 3), i.e., by the difference between the area of the whole circle and the area of the smaller circular segment:

$$
\begin{aligned}
A &= \pi r^2 - \left(\frac{1}{2}r^2\vartheta - b\sqrt{r^2 - b^2}\right) \\
&= \pi(b^2 - c) - \left(\frac{1}{2}ra - b\sqrt{-c}\right),
\end{aligned}
$$

where $a = r\vartheta$ is the length of the arc with central angle ϑ. The function A assumes the first value $\pi r^2 = \pi b^2$ when $r = b$ and $c = 0$, i.e., when the impingement starts. The function A increases with increasing $x = -c$, but with a rate lower than the function πr^2.

Appendix B: Growth rate of two coalescing spherulites

Assuming b constant and relatively to the case of coalescence of only two original spherulites, the crystallization rate during impingement is proportional to the

derivative of the solid area with respect to x, which is given by

$$
\begin{aligned}
\frac{dA(x)}{dx} &= \frac{d}{dx}\left(\left(b^2 + x^2\right)\left(\pi - \arcsin\frac{x}{\sqrt{b^2 + x^2}} + \frac{bx}{(b^2 + x^2)}\right)\right) = 2x\left(\pi - \arcsin\frac{x}{\sqrt{b^2 + x^2}} + \frac{bx}{b^2 + x^2}\right) \\
&\quad + \left(b^2 + x^2\right)\left(-\left(\frac{1}{\sqrt{1 - \frac{x^2}{b^2 + x^2}}}\right)\left(\frac{\sqrt{b^2 + x^2} - \frac{2x^2}{2\sqrt{b^2 + x^2}}}{b^2 + x^2}\right) + \frac{b(b^2 + x^2) - 2bx^2}{(b^2 + x^2)^2}\right) \\
&= 2\pi x - 2x\arcsin\frac{x}{\sqrt{b^2 + x^2}} + \frac{2bx^2}{b^2 + x^2} + \left(b^2 + x^2\right)\left(-\frac{b}{b^2 + x^2} + \frac{b^3 - bx^2}{(b^2 + x^2)^2}\right) \\
&= 2\pi x - 2x\arcsin\frac{x}{\sqrt{b^2 + x^2}} + \frac{2bx^2}{b^2 + x^2} - b + \frac{b^3 - bx^2}{b^2 + x^2} = 2\pi x - 2x\arcsin\frac{x}{\sqrt{b^2 + x^2}} + \frac{2bx^2}{b^2 + x^2} - \frac{2bx^2}{b^2 + x^2} \\
&= 2\pi x - 2x\arcsin\frac{x}{\sqrt{b^2 + x^2}} = 2x\left(\pi - \arcsin\frac{x}{\sqrt{b^2 + x^2}}\right) = 2x\left(\pi - \arcsin\frac{x}{r}\right)
\end{aligned}
$$

Information on the trend of "the rate of the change of the solid area", i.e., of the crystallization rate, may be obtained from the sign of second derivative of $A(x)$:

$$
\begin{aligned}
\frac{d^2 A(x)}{dx^2} &= 2\left(\pi - \arcsin\frac{x}{r}\right) \\
&\quad + 2x\left(-\frac{1}{\sqrt{1 - \frac{x^2}{b^2 + x^2}}}\right)\left(\frac{\sqrt{b^2 + x^2} - \frac{2x^2}{2\sqrt{b^2 + x^2}}}{b^2 + x^2}\right) \\
&= 2\left(\pi - \arcsin\frac{x}{r}\right) - 2\frac{bx}{r^2}
\end{aligned}
$$

The above derivatives are both always positive which means that not only the function area $A(x)$ but also the function growth rate dA/dt continues to increase during the coalescence. The only difference from the case of separate growth consists in the progressively smaller enhancement of the growth rate during impingement, indicated by the monotonic decrease of the second derivative of the function area. Paraphrasing the well-known laws of kinematics, but reminding that actually no physical motion occurs, we can say that until a spherulite grows isolate its area increases with constant acceleration ($d^2A/dt^2 = 2\pi g^2$), that is, with a rate ($dA/dt = 2\pi g^2 t$) increasing linearly with time, whereas after coalescence the growth of two spherulites increases with a descending (but still positive) acceleration. Indeed, after coalescence the graphic of the growth rate towards time is not more a line but a rising convex curve. It is worth observing that if it was possible to have only two spherulites in a sample with infinite size, the growth rate would increase ad infinitum, whereas in a real sample the growth of two

spherulites ends suddenly soon after the whole liquid has been transformed into solid.

References

1. Raimo M (2008) Analysis of layer-by-layer phase transformation of a polyoxymethylene copolymer film. Acta Mater 56:4217–4225
2. Raimo M (2015) On the origin of transcrystalline morphology in polymers and their composites: re-evaluation of different views. Mater Today Commun 3:137–140
3. Kirkpatrick RJ (1976) Towards a kinetic model for the crystallization of magma bodies. J Geophys Res 81:2565–2571
4. Raimo M (2011) Estimation of polymer nucleation and growth rates by overall DSC crystallization rates. Polym J 43:78–83
5. Lauritzen J, Hoffman JD (1959) Formation of Polymer Crystals with Folded Chains from Dilute Solution. J Chem Phys 31:1680–1681
6. Fredriksson H, Akerlind U (2012) Solidification and Crystallization Processing in Metals and Alloys. Wiley, New York
7. Dubrovskii VG (2014) Nucleation Theory and Growth of Nanostructures, Chapter 1. Fundamentals of nucleation theory. NanoScience and Technology. Springer, Berlin, Heidelberg
8. Kirkpatrick RJ (1975) Crystal growth from the melt: a review. Am Mineral 60:614–798
9. Sun Y, Xi H, Chen S, Ediger MD, Yu L (2008) Crystallization near glass transition: transition from diffusion-controlled to diffusionless crystal growth studied with seven polymorphs. J. Phys. Chem. B 112:5594–5601
10. Salinga M, Carria E, Kaldenbach A, Bornhofft M, Benke J, Mayer J, Wuttig M (2013) Measurement of crystal growth velocity in a melt-quenched phase-change material. Nat Commun 4:1–8
11. Larini L, Ottochian A, De Michele C, Leporini D (2008) Universal scaling between structural relaxation and vibrational

dynamics in glass-forming liquids and polymers. Nat Phys 4:42–45

12. Gibbs JW (1961) The Scientific Papers of Willard Gibbs, Thermodynamics. Dover, New York

13. Raimo M (2007) "Kinematic" analysis of growth and coalescence of spherulites for predictions on spherulitic morphology and on the crystallization mechanism. Progr Polym Sci 32:597–622

14. Greco A, Maffezzoli A (2008) Correction of melting peaks of different PE grades accounting for heat transfer in DSC samples. Polym Test. 27:61–74

15. Hurle DTJ (1963) Mechanism of growth of metal single crystals from the melt. Prog Mat Sci 10:81–147

16. Varga J (1992) Supermolecular structure of isotactic polypropylene. J Mat Sci 27:2557–2579

17. van Drongelen M, van Erp TB, Peters GWM (2012) Quantification of non-isothermal, multi-phase crystallization of isotactic polypropylene: the influence of cooling rate and pressure. Polymer 53:4758–4769

18. Boyer SAE, Robinson P, Ganet P, Melis J-P, Haudin J-M (2012) Crystallization of polypropylene at high cooling rates: microscopic and calorimetric studies. J Appl Polym Sci 125:4219–4232

19. Menyhárd A, Bredács M, Simon G, Zsuzsanna Horváth Z (2015) Determination of nucleus density in semicrystalline polymers from nonisothermal crystallization curves. Macromolecules 48:2561–2569

20. Raimo M (2011) An overview on the processing of polymers growth rate data and on the methods to verify the accuracy of the input parameters in crystallization regime analysis. Prog Cryst Growth Charact Mater 57:65–92

21. Kolmogorov AN (1937) On the statistical theory of crystallization of metals. Bull Acad Sci USSR Math Ser 1:355–359

22. Avrami M (1939) Kinetics of phase change I. J Chem Phys 7:1103–1112

23. Avrami M (1940) Kinetics of phase change II. J Chem Phys 8:212–224

24. Avrami M (1941) Kinetics of phase change III. J Chem Phys 9:177–184

25. Evans VR (1945) The laws of expanding circles and spheres in relation to the lateral growth rate of surface films and the grain-size of metals. Trans Faraday Soc 41:365–374

26. Stefan J (1891) On the theory of formation of ice, in particular in the polar see. Annalen der Physik Chemie (Wiedemann) 42:269–286