

# Cross-nucleation between polymorphs: quantitative modeling of kinetics and morphology

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**Abstract:** Cross-nucleation is defined as the nucleation of one polymorph on the surface of another polymorph of the same substance. Although the description of this particular form of heterogeneous nucleation is mainly phenomenological, recently dedicated quantitative studies are performed on several systems. In this work we propose a model framework that captures the phenomenon of cross-nucleation for a spherulitic seed-surface geometry, as well as the kinetic competition between the seed growth and the cross-nucleus formation, by the introduction of a tangential growth rate of the daughter polymorph. Regardless of the growth rate of the parent spherulite, this model describes the experimental data up-to and including the final amount of cross-nuclei on its periphery, solely based on one parameter, the cross-nucleation rate. Furthermore, a strong temperature dependency of the kinetic competition between concomitantly growing  $\alpha$ - and  $\beta$ -phase isotactic polypropylene is observed and related to the previously reported anomalous behaviour of this cross-nucleating system.

KEYWORDS: cross-nucleation, polymorphism, polymer crystallization

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## Introduction

The phenomenon of cross-nucleation is a peculiar crystallization pathway, of interest for polymorphic substances.<sup>1-8</sup> In cross-nucleation a polymorph has the ability to nucleate on the periphery of another polymorph of the same material, contrary to classical heterogeneous nucleation, where the seed-substrate is an alien substance. Generally the direction of cross-nucleation is indicated by defining the two polymorphs as “parent” and “daughter”. Provided that the crystal growth rate of the nucleating

daughter is equal or larger than that of the parent, a nucleus can grow to a detectable size, despite the difference in thermal stability;<sup>5,9</sup> various examples of both stable-on-metastable and metastable-on-stable can be found in literature.<sup>2,5,9</sup> If the frequency of this special kind of heterogeneous nucleation is sufficiently high, the seed surface will eventually be overgrown by daughter-phase cross-nuclei.

Despite several experimental studies on organic systems<sup>1,2,10-13</sup> and macromolecules,<sup>14-18</sup> and numerical studies on spherical particles,<sup>6,8</sup> clathrate hydrates<sup>19</sup> and water,<sup>20</sup> the descrip-

tion of cross-nucleation is mainly phenomenological. In most cases, the cross-nucleation rate is experimentally determined by an oversimplification of the process, fitting a linear model to the data.<sup>3,18,21</sup> Commonly, the heterogeneous nucleation rate decreases with decreasing undercooling,<sup>22,23</sup> and most cross-nucleating systems tend to behave accordingly;  $\alpha$ -on- $\gamma$  polypivalolactone (PPVL),<sup>21</sup>  $\alpha$ -on- $\delta$  D-mannitol<sup>10</sup> and Form II-on-Form I isotactic polybutene (i-PBu)<sup>17,18</sup> all show a decreasing frequency of cross-nucleation when approaching the melting point. In our previous work,<sup>24</sup> we discussed the apparent contradictory case of isotactic polypropylene (i-PP), where the nucleation of the monoclinic  $\alpha$ -phase on the pseudo-hexagonal  $\beta$ -phase occurs with increasing frequency for temperatures exceeding 140 °C.<sup>14,24,25</sup>

It was argued by Yu et al.<sup>10</sup> that the growth rate of the parent polymorph affects the cross-nucleation kinetics. As epitaxial matching between cross-nucleating structures does not seem to be important for the phenomenon<sup>2,11,25</sup> a hindering effect of the homo-polymorphic secondary nucleation (i.e., growth of the parent phase) on the hetero-polymorphic nucleation is suggested. Based on the radial growth rates of parent ( $G_p$ ) and daughter ( $G_d$ ), this hypothesis seems probable; the ratio of  $G_d/G_p$  in the temperature window where cross-nucleation is observed is close to one for the case of i-PP,<sup>24</sup> while it ranges from two to one thousand in other systems where cross-nucleation data is available.<sup>10,26–28</sup>

In the present work, we propose a model framework which confirms that the competition between parent phase growth and daughter phase cross-nucleation is more pronounced in i-PP, as compared to other systems. Furthermore, by taking into account this growth competition, the observed cross-nucleation phenomenon is quantitatively described both from the morphological and kinetic point of view.

## Experimental

Our modelling is based on several quantitative experimental studies reported in the literature. The growth rate data of PPVL is taken from Alfonso et al.,<sup>26</sup> i-PBu from Yamashita,<sup>27,28</sup> D-mannitol from Yu et al.,<sup>3</sup> and i-PP from our previous work.<sup>24</sup> The cross-nucleation data is taken from Yu et al.<sup>3</sup> for D-mannitol and from our previous work<sup>24</sup> for i-PP.

On the morphological level, three ratios of  $G_d/G_p$  are considered, as indicated in Figure 1. If the growth of the parent is larger than that of the daughter, no cross-nucleation will be observed due to the necessary kinetic constraint.<sup>5,9</sup> Contrary, if the daughter polymorph grows considerably faster than the parent modification, hemi-spherical nuclei form on the periphery of the seed surface and are able to grow freely, since no hindering by the parent growth is present. The most complex yet interesting case is that where the growth rates are comparable; cross-nuclei grow in a “flower-like” shape on the growing crystal, see Figure 1.

In each of the three cases described above, a tangential growth rate of the daughter is defined as the rate at which the “intersection” of parent and daughter phase moves parallel to the parent’s surface, indicated with  $G_{d,tan}$  in Figure 1. From a modelling perspective this tangential growth rate is the key parameter for an accurate determination of the parent overgrowth.

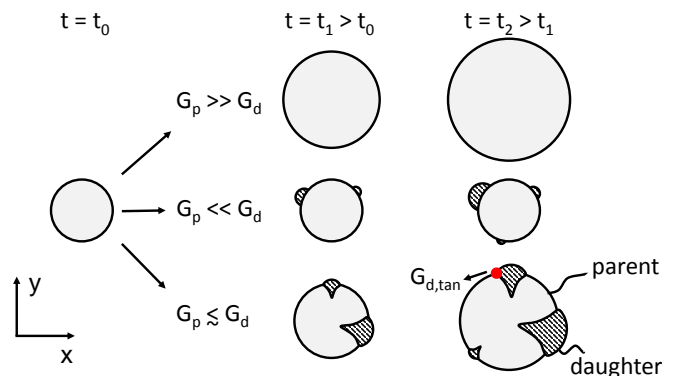


Figure 1: Schematic representation of the three regimes determined by the ratio of parent and daughter radial growth rates.

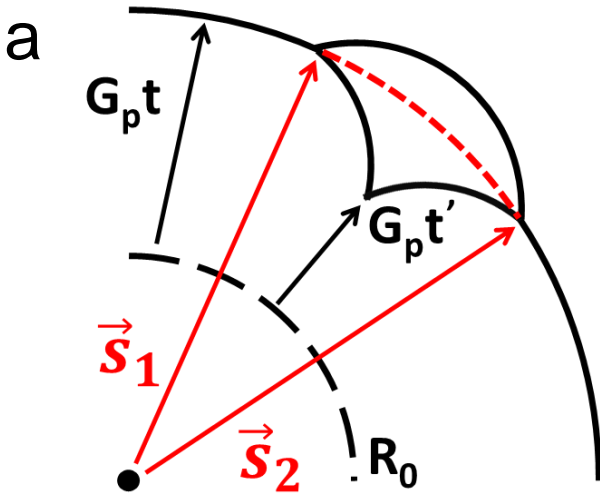
# Modelling

The starting point is the generic equation, Eq. (1), where the time derivative of specific, i.e. per unit area, number of nuclei,  $n$ , is defined as the cross-nucleation rate  $J$ . Being strongly dependent on the crystallization temperature, the cross-nucleation rate can decrease with decreasing undercooling, in agreement with classical nucleation theory,<sup>22,23</sup> or increase, as is observed for the case of i-PP.<sup>14,24,25</sup> The temperature dependence of the cross-nucleation rate  $J$  is elaborately discussed in our previous work.<sup>24</sup>

$$\dot{n} = J(T) \quad (1)$$

Experimentally the study of cross-nucleation is limited to disk-like parent superstructures to assure a proper detectability of every cross-nucleus. Hence, for a growing disk-like parent superstructure with initial seed surface area  $A_0$  the time evolution of the undisturbed surface is given by:

$$\begin{aligned} A_p &= A_0 + 2\pi h \int_{t_0}^t G_p(u) du \\ &= 2\pi h R_0 + 2\pi h \int_{t_0}^t G_p(u) du \end{aligned} \quad (2)$$



where  $R_0$  denotes the radius of the parent seed at time zero ( $t_0$ ) and  $h$  the sample thickness. The undisturbed area of the parent overgrown by the daughter phase depends on the momentary number of nuclei and the tangential growth rate ( $G_{d,tan}$ ) of the daughter according to:

$$A_d = \int_{t_0}^t \dot{n}(t') \left[ 2h \int_{t'}^t G_{d,tan}(u) du \right] dt' \quad (3)$$

The time evolution of the experimentally observed, i.e. real number of nuclei,  $\dot{n}_r$ , is given by:

$$\dot{n}_r = (A_p - A_d)\dot{n} = (A_p - A_d)J \quad (4)$$

This differential equation can be solved by calculating the macroscopic tangential growth rate as function of time. In this case  $G_{d,tan}$  is calculated from the two intersection points of two circular objects, one being the parent, and one representing the growing nucleus, nucleated at time  $t'$ , as indicated in Figure 2a. The growth rate parallel to the parent surface is then given by:

$$G_{d,tan} = \frac{d}{dt} \left[ \frac{1}{2} \arccos \left( \frac{\vec{S}_1 \cdot \vec{S}_2}{|\vec{S}_1| |\vec{S}_2|} \right) (R_0 + G_p t) \right] \quad (5)$$

where  $\vec{S}_1$  and  $\vec{S}_2$  denote the intersection points of parent and daughter polymorph. This tan-

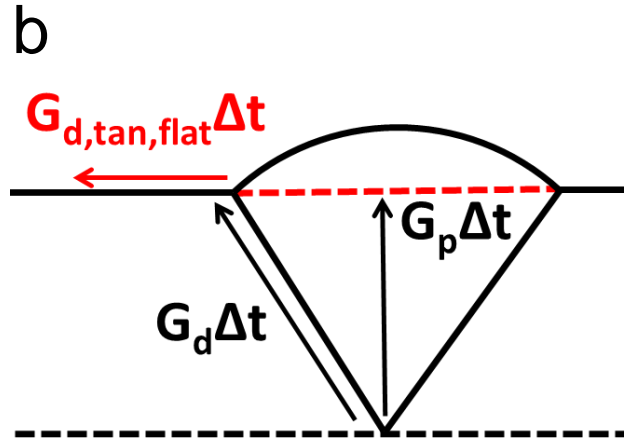


Figure 2: Schematic representation of a) the vectors  $\vec{S}_1$  and  $\vec{S}_2$  used in Eq. (5) to determine the overgrown area of parent spherulite, and b) a simplification the tangential growth rate in the case that a flat seed surface is assumed, Eq. (6).

gential growth rate is a complex function of the sizes of parent and daughter, and could be solved numerically. However, a simplified, time independent solution to Eq. (5) is given when the seed surface is considered flat, see Figure 2b:

$$G_{d,tan,flat} = \sqrt{G_d^2 - G_p^2} \quad (6)$$

The tangential growth rate of the daughter polymorph is in this case solely determined by the individual radial growth rates of the parent and daughter polymorph. This approximation is valid in the regime where the size of the cross-nucleating phase is small compared to the radius of the parent spherulite.

Numerical determination of the tangential growth rate as function of time shows, Eq. (5), for the systems considered, a nearly linear time-dependency, especially for the higher temperatures. In Figure 3 the tangential growth rate of the daughter polymorph of i-PP is shown as function of time. By the introduction of a mean tangential growth rate  $\bar{G}_{d,tan}$ , Eq. (3) can, to a good approximation, be rewritten as:

$$\begin{aligned} A_d &= 2h\bar{G}_{d,tan}t \int_{t_0}^t \dot{n}(t')dt' \\ &= 2h\bar{G}_{d,tan}n_r t \end{aligned} \quad (7)$$

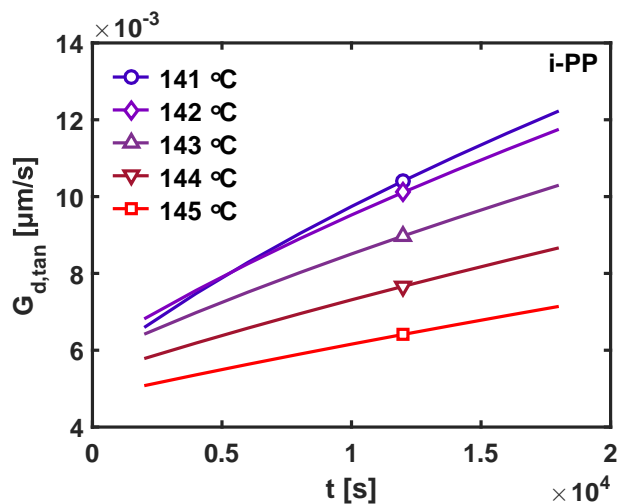


Figure 3: Numerical calculation of the tangential growth rate of the daughter polymorph, i.e.  $\alpha$ -phase i-PP, as function of time. To good approximation  $G_{d,tan}$  is linear in time.

Substitution of Eq. (2) and (7) into Eq. (4), makes that the phenomenon of cross-nucleation is defined by the differential equation:

$$\dot{n}_r + (an_r - b)t = c \quad (8)$$

with:

$$\begin{aligned} a &= J2h\bar{G}_{d,tan} \\ b &= J2\pi hG_p \\ c &= J2\pi hR_0 \end{aligned}$$

which can be solved analytically under the condition that  $\dot{n} \geq 0$ . The physical interpretation of this constraint implies the number of cross-nuclei can only grow for the time that there is area available; a situation where  $A_d > A_p$  is not possible. In the time where cross-nucleation occurs, the exact solution to Eq. (8) is given by:

$$\begin{aligned} n_r(t) &= \frac{b}{a} \left[ 1 - \exp\left(-\frac{at^2}{2}\right) \right] \\ &+ \frac{c\sqrt{\pi/2}}{\sqrt{a}} \exp\left(-\frac{at^2}{2}\right) \operatorname{erfi}\left(\frac{\sqrt{at}}{\sqrt{2}}\right) \end{aligned} \quad (9)$$

where the first term corresponds to the homogeneous solution that arises when the initial seed area equals zero. The second term, the particular solution, accounts for the consumption of seed surface by daughter overgrowth.

The key parameter in this model framework is  $G_{d,tan}$ , the tangential growth of the daughter. In the next section we show that by computing this parameter, we can quantitatively describe the number density of cross-nuclei in time for materials with widely different polymorphic growth and nucleation kinetics.

## Results and discussion

Experimental studies on cross-nucleation in different systems<sup>3,10,17,18,21,24</sup> revealed the concomitant growth of the two growing modifications on the macroscopic level. The angle of the phase boundary, i.e. the angle between parent and daughter polymorph at the intersection point, significantly changes with temperature in the case of i-PP, whereas for PPVL (and also for i-PBu<sup>17</sup> and D-mannitol<sup>3</sup>) this angle is

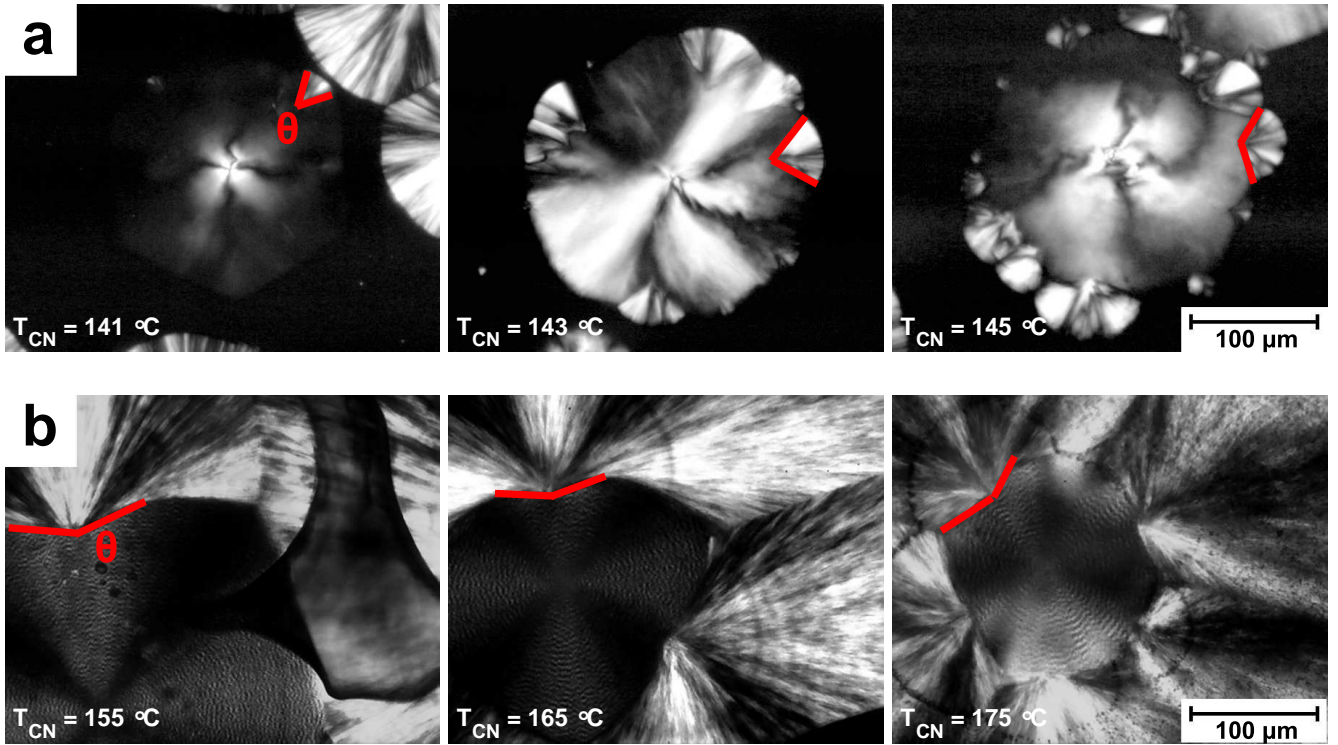


Figure 4: Angle ( $\theta$ ) of cross-nucleus growth at temperatures as indicated for a) isotactic polypropylene, and b) poly(pivalolactone).

almost temperature independent, as is shown in Figure 4. For i-PP, Figure 4a, only slightly above the cross-over temperature of the radial growth rates, the angle (defined as  $\theta$ ) is small, because the ratio of the growth rates is close to one. Upon a slight temperature increase, the difference in growth rate between the crystal phases increases and as a result  $\theta$  increases. In PPVL on the other hand, the angle remains constant over a temperature range of 20 °C, see Figure 4b. A nearly constant angle for PPVL indicates a temperature-independent ratio between the  $\alpha$  and  $\gamma$  modification growth rates, while in i-PP the angle increases with temperature because of the increasing ratio of the growth rates  $G_d/G_p$ .

By applying the flat surface approximation of a growing seed surface competing with a cross-nucleus, this morphological effect of the polymorph's growth rates is numerically calculated and shown in Figure 5. For each of the materials considered, the coordinates of one of the intersection points is plotted for a unit time in an Cartesian coordinate system for various temperatures. The origin of the axes is the

cross-nucleation point. The insets show the radial growth rates of the parent and daughter, together with the temperature range in which cross-nucleation is observed (gray area).

Contrary to other materials, i-PP displays cross-nucleation in a temperature window where the growth rates are very comparable. Reconsidering Eq. (6), it can be seen that when the divergence of the individual growth rates of the polymorphs is more important than their absolute decrease with temperature, the tangential growth rate of the daughter may increase with decreasing undercooling. This is the case for i-PP at temperatures just above the cross-over temperature of the radial growth rates (140 °C), see Figure 5a. Upon further increasing the temperature, the tangential growth rate of the  $\alpha$ -daughters goes through a maximum.

For i-PBu, where the growth rate of the parent is really negligible as compared to the daughter, the latter grows freely along the (flat) seed surface, at a rate of  $G_{\text{tetragonal,tan}} = G_{\text{tetragonal}}$ , see Figure 5b.

PPVL and D-mannitol show a comparable be-

behaviour, except for the temperature coefficient of the growth rates. From Figure 5c and 5d it can be deduced that the competition between the growth of seed and cross-nucleus, and thus the initial angle at which a cross-nucleus grows, is practically temperature independent, or at least far less temperature dependent as in  $\alpha$ -on- $\beta$  cross-nucleation in i-PP.

An effective way of describing this competition between the concomitantly growing polymorphs is the ratio of the tangential and radial growth rate of the daughter polymorph,  $G_{d,tan}/G_d$ . This ratio is shown in Figure 6 as function of temperature for the various systems. For i-PBu, PPVL and D-mannitol,  $G_{d,tan}/G_d$

is close to one, and more important, constant, implying a temperature-independent competition. On the other hand, i-PP displays a steep increase from zero to one in the temperature range where cross-nucleation is observed, as a result of the previously discussed maximum in the tangential growth rate of the  $\alpha$ -daughters, see Figure 5a.

Among the investigated systems, i-PP is the only one which displays an anomalous temperature dependence of cross-nucleation kinetics, i.e. the  $\alpha$ -on- $\beta$  nucleation rate increases with decreasing undercooling. In our previous work<sup>24</sup> we rationalized this observation by proposing a temperature-dependent prob-

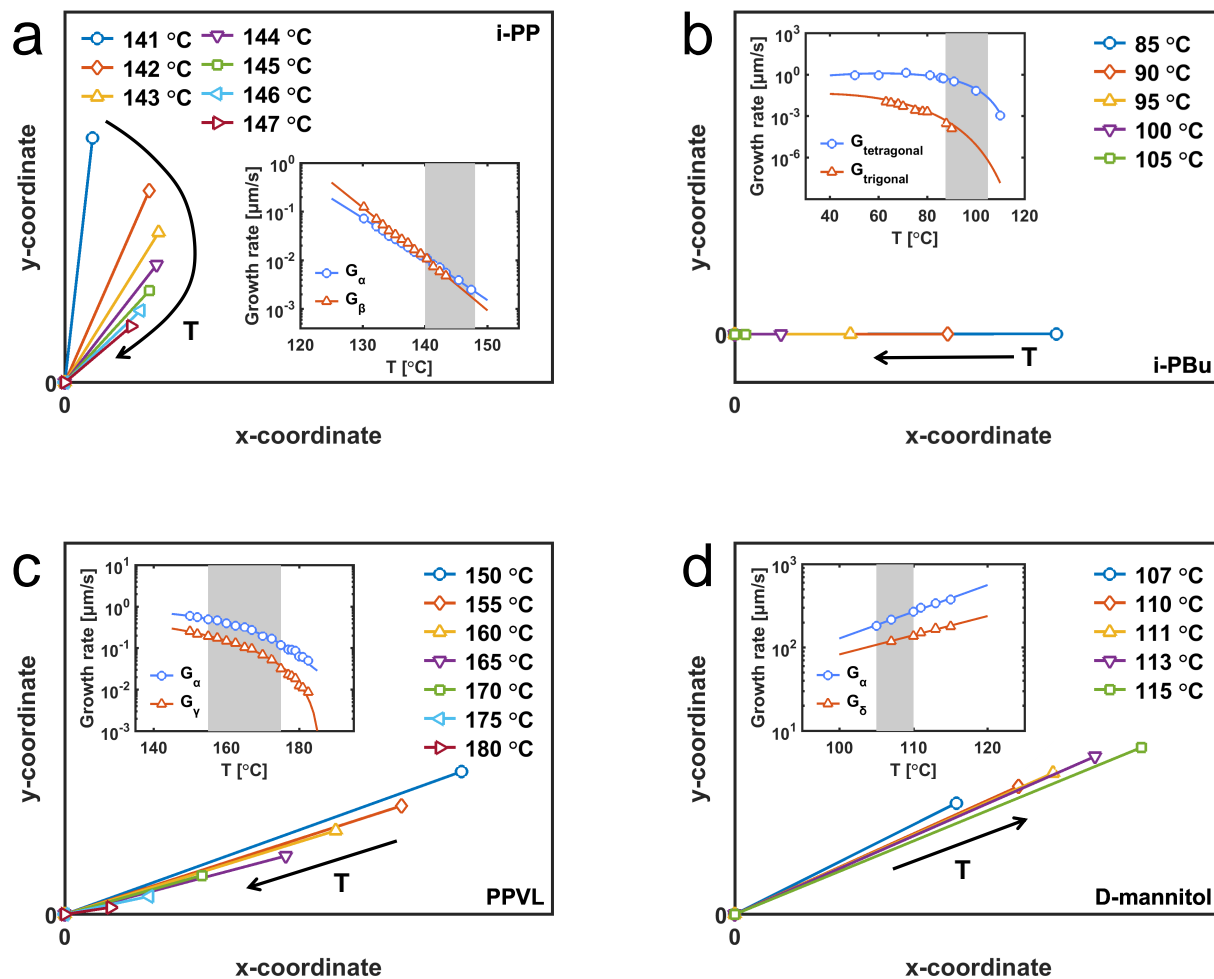


Figure 5: Location of the parent/daughter intersection point as indicated in Figure 1 in a unit time for a) isotactic polypropylene, b) isotactic polybutene, c) polypivalolactone and d) D-mannitol at different temperatures. The individual growth rates of parent and daughter are shown in the insets, together with the temperature range where cross-nucleation is observed (grey area).

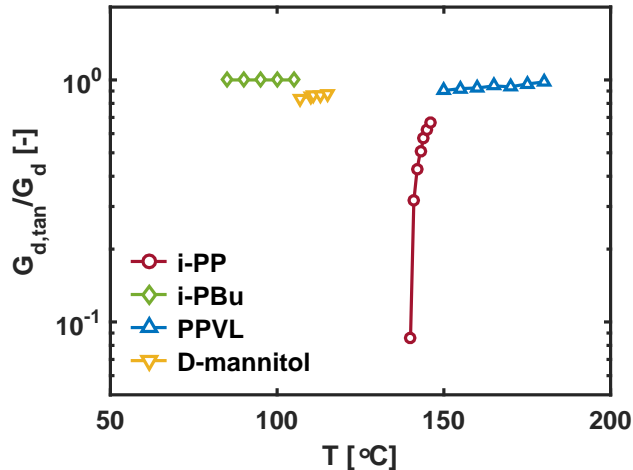


Figure 6: Ratio of the tangential growth rate and the radial growth rate as function of temperature.

ability of growing a cross-nucleus to a detectable size. This probability is lower when the competition between seed and daughter phase growth is more important. We note that, since  $G_{d,tan}/G_d$  quantifies this growth competition, it might reasonably be related to such probability. However, a direct link between this geometrically derived parameter ( $G_{d,tan}/G_d$ ) and the anomalous temperature dependence of cross-nucleation reported for i-PP, cannot be established at this stage. In fact, this would require detailed hypotheses on the molecular mechanism of nucleation between polymorphs, and is out of the scope of the present work.

The use of an average tangential growth rate to compute the consumption of seed surface, Eq. (7), is validated by comparing the exact solution given in Eq. (9) with the available experimental data on cross-nucleation.

In Figure 7 the average number of i-PP  $\alpha$ -phase cross-nuclei on a given  $\beta$ -phase seed ( $R_0 = 100 \mu\text{m}$  and  $h = 30 \mu\text{m}$ ) is shown as a function of time. Based on the cross-nucleation rates reported in our previous work,<sup>24</sup> a remarkable agreement between the model and experimental data is obtained, in the whole temperature range where the  $\alpha$ - and  $\beta$ -phase grow concomitantly. In particular, when the experimental data is collected for sufficiently long times, the saturation of the parent surface with cross-nuclei is accurately predicted on the

basis of the (bulk) radial growth rates of the individual phases.

A further demonstration of the applicability of the model is shown in Figure 8 for pure D-mannitol and a D-mannitol/polyvinylpyrrolidone mixture.<sup>3</sup> In both these systems the crystallization is not seeded and the cross-nucleation rate decreases with undercooling, contrary to the case of i-PP. Irrespective of the temperature dependence of the cross-nucleation rate, the parent overgrowth in the late stages of the process is accurately captured. The initial slope of the exact solution, being the cross-nucleation rate  $J_{d/p}$ , corresponds well with the values determined from the linearised approach used in the original experimental works.<sup>3,24</sup>

Since this model framework can accurately predict the saturation value of cross-nuclei on a parent polymorph of given dimensions, it can be applied to derive the kinetic of cross-nucleation indirectly from the final morphology: by measuring the saturation density of cross-nuclei on a seed surface, the cross-nucleation rate can be determined implicitly when the radial growth rates are known.

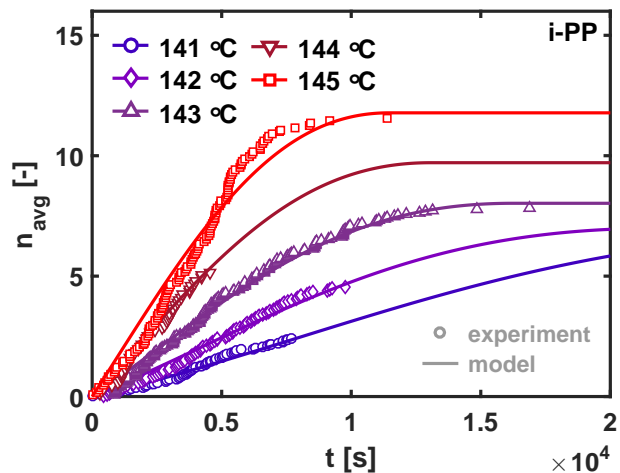


Figure 7: Comparison between the cross-nucleation model, based on the average tangential growth rate of  $\alpha$ -phase i-PP, and the literature data.

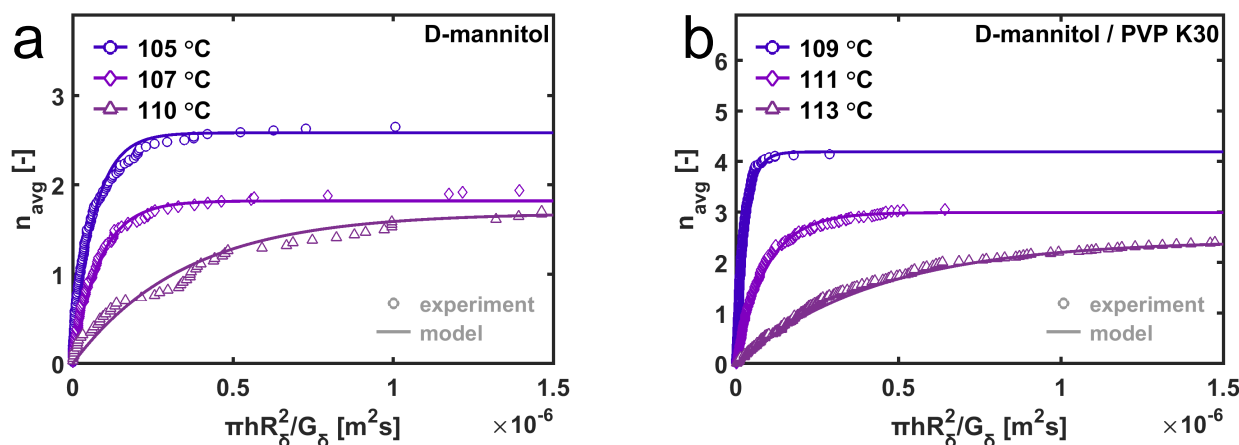


Figure 8: Comparison between the cross-nucleation model, and the experimentally measured cross-nucleation data of a) D-mannitol, and b) a mixture of D-mannitol and 10% w/w polyvinylpyrrolidone (PVP). The x-axis data is normalized for sample thickness  $h = 2.7 \mu\text{m}$  and parent growth rate  $G_\delta$ .

## Conclusion

For various systems the kinetic competition between two concomitantly growing polymorphs is modelled based on radial growth rates taken from literature. A combination of these growth rates and the seed geometry allows to calculate the time-evolution of daughter-overgrown area.

Irrespective of the temperature dependence of the cross-nucleation rate, the proposed model can be used to predict the final number of cross-nuclei on a parent spherulite of given dimensions. The implementation of this parent overgrowth allows for a quantitative description of the average number of nuclei in time, solely based on one independent parameter, i.e. the cross-nucleation rate. When this strategy is inverted, the cross-nucleation rate can be determined simply from the saturation density of daughter-phase nuclei on the parent seed.

Furthermore, the importance of growth competition between the polymorphs is quantified by the ratio of the daughter growth rates in the direction parallel and perpendicular to the seed surface. Contrary to the other systems, this ratio varies strongly with temperature for i-PP, for which an inverse temperature dependence of the cross-nucleation rate is also observed.

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### Notes

The authors declare no competing financial interest.

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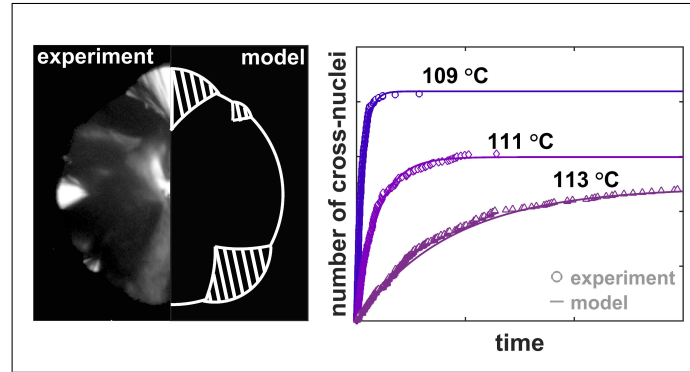


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# Graphical TOC Entry



## Synopsis:

A one parameter model for cross-nucleation, the nucleation of one polymorph on the surface of another polymorph, and the competition between seed growth and cross-nucleus formation, is presented. For three different substances a good agreement between experimental and model results is obtained in terms of cross-nuclei evolution. The strong temperature dependency of polypropylene is related to its anomalous cross-nucleating behavior.