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Citation for published version (APA):

Looijmans, S. F. S. P., Menyhard, A., Peters, G. W. M., Alfonso, G. C., & Cavallo, D. (2017). Anomalous temperature dependence of isotactic polypropylene α -on- β cross-nucleation kinetics. *Crystal Growth and Design*, 17(9), 4936-4943. <https://doi.org/10.1021/acs.cgd.7b00872>

DOI:

[10.1021/acs.cgd.7b00872](https://doi.org/10.1021/acs.cgd.7b00872)

Document status and date:

Published: 18/07/2017

Document Version:

Accepted manuscript including changes made at the peer-review stage

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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Anomalous temperature dependence of isotactic polypropylene α -on- β cross-nucleation kinetics.

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KEYWORDS *Cross-nucleation; polymorphism; isotactic polypropylene*

ABSTRACT: A particular kind of heterogeneous nucleation, i.e., cross-nucleation, is sometimes observed in polymorphic substances, when a new crystal structure nucleates on the surface of a crystal of a different modification. Here we show a unique and apparently incongruous nucleation behaviour in polymorphic isotactic polypropylene (i-PP). The rate of cross-nucleation of the monoclinic α -phase on the trigonal β -phase crystals increases with increasing temperature. This behaviour is contrary to that of the heterogeneous nucleation kinetics of the same crystal on various solid substrates, and also to the previously reported cases of cross-nucleation rate of other polymorphic systems, which exhibit the expected decrease with temperature. i-PP α -on- β cross-nucleation apparently eludes the nucleation theory. The results are explained as a manifestation of a kinetic competition between α -on- β cross-nucleation and growth of β -crystalline seeds, and finally reconciled with the theoretical understanding of nucleation. These new finding indicates that further theoretical efforts are needed to include the cross-nucleation phenomenon in the framework of a comprehensive understanding of polymorphic crystallization. Incidentally, this study highlights the intrinsic limits of the, industrially desirable, promotion of β -phase formation in polypropylene.

Introduction

Despite cross-nucleation has been the last to be recognized,¹ among the different possible crystallization pathways of polymorphic materials,^{2,3} it immediately attracted the attention of the scientific community.⁴⁻¹⁰ Cross-nucleation between polymorphs is observed whenever a given crystal modification nucleates on the surfaces of a different pre-existing crystalline structure of the same material. The two polymorphs are generally addressed as “parent” and “daughter” phases, to indicate the direction of cross-nucleation. However, this is effectively a nucleation phenomenon, and does not imply any phase transition between the two structures, as deduced by the occurrence of both stable-on-metastable and metastable-on-stable cross-nucleation events.^{4,7,11} The process seems not to be governed by thermodynamics, but rather by kinetics. Indeed, in order to observe cross-nucleation, a necessary (but not sufficient) condition is that the daughter polymorph grows faster than the parent one.^{7,11}

The understanding of cross-nucleation is certainly of importance to improve our knowledge of polymorphic crystallization, and of nucleation processes in a wider perspective, but it also has technological implications. In fact, cross-nucleation between polymorphs nullifies the efficiency of a common strategy adopted to control the structural outcome of polymorphic crystallization, i.e., the seeding of melt or solution with crystals of the desired polymorph. Notwithstanding several experimental studies on “small” organic molecules^{1,4,12-15} and macromolecules,¹⁶⁻²⁰ and despite the simulation works on spherical particles,^{8,10} clathrate hydrates²¹ and water,²² the description of cross-nucleation is still mainly phenomenological. From a mechanistic and kinetic point of view, the process has been naturally regarded as a particular case of heterogeneous nucleation. As such, simple or more detailed models have been applied to cross-nucleation rate data with good success.^{5,20,23}

However, due to the concomitant growth of the nucleating substrate, the process appears more complex than conventional heterogeneous nucleation. In principle, a competition between hetero-polymorphic cross-nucleation and homo-polymorphic secondary nucleation (i.e., growth of the parent seed) exists at the growth front of the parent crystal. The effect of parent polymorph growth rate on cross-nucleation kinetics was suggested by Yu et al.,¹² who noticed a higher nucleation rate of D-Mannitol α -form on the slow-growing faces of a β -phase crystalline seed. Since epitaxial matching between the two structures does not seem to play a major role in cross-nucleation,^{4,13,24} this result suggests a hindering effect of homo-polymorphic crystal growth on hetero-polymorphic nucleation. However, in the cases that have been quantitatively examined so far, there are few chances that the formed cross-nucleus gets hampered by the simultaneous growth of the other polymorph, because the daughter polymorph's growth rate is several times larger than the parent's one.

In this respect, an interesting case-study is the nucleation of monoclinic α -phase of isotactic polypropylene on the trigonal β -modification. The two structures crystallize concomitantly from the melt with very similar growth rates. The metastable β -phase grows slightly faster than the stable α -form at crystallization temperatures approximately between 100 and 140 °C.^{16,25-27} α -on- β cross-nucleation (known as "growth transition" in polymer literature) can therefore occur both at low or high undercooling.^{16,27} Earlier reports suggest that the frequency of nucleation events increases approaching the melting point.^{16,24}

This work investigates the inconsistency of these observations with the theory of heterogeneous nucleation, and relates it to the competition between cross-nucleation and the growth of the nucleating substrate. The kinetics of cross-nucleation of the stable isotactic polypropylene (i-PP) α -phase on the metastable β -form is quantitatively studied by means of polarized optical microscopy, adopting an in-situ seeding strategy. Eventually, a model for cross-nucleation accounting for both the contradictory normal and inverse temperature dependence of nucleation kinetics is proposed.

Experimental section

The material under investigation is an isotactic polypropylene Tipplon H305 (neat reactor powder, Melt Flow Rate 7-12 g/10 min), produced by MOL Petrochemicals in Hungary. Since the spontaneous nucleation of the β -phase is rare in pure i-PP samples, a small amount of selective nucleating agent (10 ppm of Calcium Suberate²⁸) is added by melt compounding. Homogenization was done in a Brabender W50EHT internal mixer at 210 °C and 50 min⁻¹ of rotation speed. Time of homogenization was 3 min after complete melting of the powder. Small pieces of the compounded material are manually compressed between two

glass slides, on a hot-stage at around 210 °C. Films with a final thickness of 20-40 μ m are obtained.

The crystallization and cross-nucleation behaviour of β -nucleated i-PP samples was investigated by means of polarized optical microscopy (POM), using a Leica DMLP transmission microscope, equipped with a plan (H.20x/0.40) lens and a Pixellink PL-A662 digital camera. The various thermal histories were applied by means of a calibrated Metler Toledo FP82HT hot stage, controlled via a FP90 Central Processor.

Prior to the cross-nucleation study, the growth rates of both α - and β -phase are accurately determined. Samples are heated to 214 °C and kept at that temperature for 5 minutes, to erase their previous thermo-mechanical history. After cooling to the chosen crystallization temperature T_C , the sample is kept isothermal for a sufficient period of time, while acquiring POM images with a suitable frequency. To avoid thermal degradation, all the samples are used for a limited number of measurements only (between 2 and 6 depending on the experiment temperature). The spherulitic growth rates were determined with the use of Matlab 2015b image processing toolbox, at first the POM images were converted in binary pictures and then the spherulite radius is obtained for each frame, by fitting a circle to the selected spherulite. In the case of hexagon-like hedrites (β -superstructures), the radius is that of the circle which circumscribes the hexagon, corresponding to the direction of fastest growth. A minimum increase of radius of 20-25 μ m is considered, in order to obtain accurate growth rate data. For each crystallization temperature, at least 4 measurements were performed, typically on different spherulites of two different samples.

The thermal protocol for cross-nucleation experiments is depicted in Figure S1 of the Supplementary Information. After having erased the previous thermal history of the sample as described above, the polymer is cooled to 139 °C, where large and isolated β -phase spherulites are grown (concomitantly with α -phase) for 2 hours. Finally, the sample is heated to the chosen cross-nucleation temperature ($T_{CN} > T^*$, see text), and kept there for an adequate time while acquiring the optical micrographs. Again, samples are used for 1-2 cross-nucleation experiments only, to avoid thermal degradation.

The acquired time-resolved optical micrographs are analysed to quantify the cross-nucleation rate, according to two methods previously adopted in the literature.^{5,20} The number of cross-nuclei developing in time is either counted directly, when the parent polymorph does not grow to a meaningful extent; or evaluated from the average number of nuclei as a function of the distance from the centre of the parent phase morphology, if the two polymorphs grow concurrently at the temperature of the experiment. The two procedures are described in details in the Supplementary Information, where examples of data analysis are also presented in Figure S2 and S3.

Results

At first, the growth rates of the two polymorphs are determined by isothermal crystallization experiments in the relevant temperature range. The results are shown in Figure 1, together with examples of typical morphologies. The two polymorphs can be easily distinguished by optical microscopy due to their different morphology and birefringence.²⁹ The α -phase forms spherulites composed of several radial fibrils of lamellar stacks, while β -crystals tend to crystallize as hedrites:³⁰ aggregates of predominantly flat-on lamellae, with roughly hexagonal habit.

The mean value of the growth rate at each temperature is reported, with the error bars indicating the standard deviation. The data have been fitted with an exponential function. We note that, in order to study the cross-nucleation kinetics, the growth rate of the β -spherulite at T_{CN} must be known. This value is derived from the fitting curve, since the growth of β -morphologies is not directly measurable at high temperatures, due to the occurrence of fast and extensive α -on- β cross-nucleation.

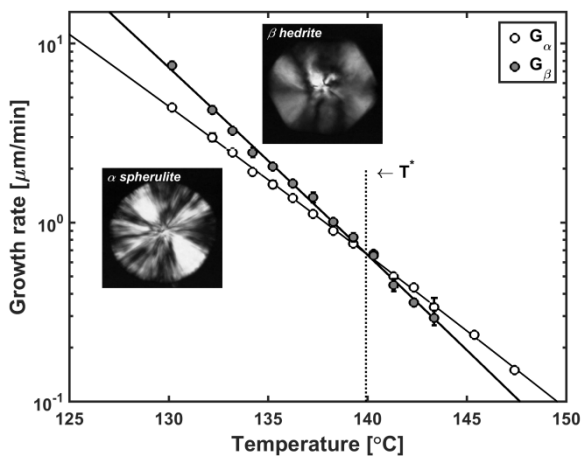


Figure 1. Temperature dependence of the linear growth rate of the two i-PP polymorphs. Open symbols: α -phase, filled symbols: β -phase. The cross-over temperature, T^* (see text), is indicated with a dotted line. Inset: examples of typical α - and β -phase morphologies.

In agreement with previous literature reports,^{16,25} α - and β -phases grow at very similar paces in the whole explored temperature range, and a crossover between the two rates exists at a temperature $T^* = 140$ °C. Above this crossover temperature α -crystals grow slightly faster than β -crystals, while the opposite is true below T^* . To fulfil the kinetic requirement,^{7,11} the α -on- β cross-nucleation experiments must be performed at temperatures above 140 °C.

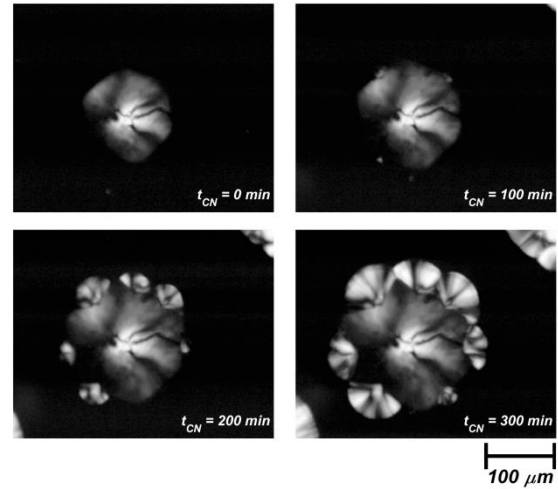


Figure 2. Optical micrographs taken at different times (t_{CN} , indicated) during a cross-nucleation experiment at 145 °C. The more birefringent α -phase spherulites nucleate at the advancing front of a β -hedrite initially grown at 139 °C.

As such, the in-situ seeding procedure includes a first partial isothermal crystallization slightly below T^* , to grow large and isolated β -phase hedrites (concomitantly with some α -phase spherulites). Secondly, the sample is heated at the chosen cross-nucleation temperature ($T_{CN} > T^*$), where the previously grown β -crystals serve as seeds for the nucleation of the α -phase (see Experimental details section and Figure S2 of the Supplementary Information).

Figure 2 shows an example of the time evolution of the morphology upon cross-nucleation at 145 °C. While the initial β -crystal still grows at a given rate, α -phase nucleates on the periphery of the original β -morphology, eventually overgrowing the β -phase. From the micrographs presented in Figure 1 it can be deduced that the number of α -phase cross-nuclei increases with time. The growth of these nuclei, faster than that of the β -hedrite, prevents β -crystals from growing along the same direction, eventually leading to a morphology consisting of "multi-pointed star-shaped" β -cores with slightly curved edges³¹ overgrown by α -spherulites. To confirm the identification of the phases and better disclose the exact points cross-nucleation, which is required for quantification of the process kinetics, the difference in melting temperatures between the two modifications^{29,32} can be exploited. The various parts of the initial composite morphology melt at distinct temperatures, as indicated in Figure 3.

As a consequence of the well-known crystallization temperature dependence of polymer crystal melting,³³ the melting of the β -phase core, crystallized at 139 °C during the nucleation step, is firstly observed. This is followed by the disappearance of the small amount of β -phase grown at T_{CN} . Finally, the α -phase cross-nucleated crystals melt at a temperature about 11 °C higher than that of the β -crystals formed at the same temperature (T_{CN}).

The temperature dependence of cross-nucleation rate can be qualitatively inferred from the examination of the morphologies after a given time at the different cross-nucleation temperatures (Figure 4). The number of α -phase spherulites cross-nucleated within three hours on the lateral surface of β -hedrites with similar sizes, steadily increases with increasing the experiment temperature. Only 2-3 cross-nuclei are present at 142 °C, while the surface of the β -crystals is completely covered by more than 10 α -phase spherulites if T_{CN} is increased by only 3 °C. These micrographs clearly indicate that the α -on- β cross-nucleation rate becomes distinctly faster with decreasing undercooling, i.e., the difference between (equilibrium) melting temperature and crystallization temperature, contrary to what can be expected from a conventional heterogeneous nucleation process, but in agreement with earlier reports on i-PP growth transition/cross-nucleation.^{16,24}

The anomalous trend of nucleation rate qualitatively assessed with Figure 4 deserves further quantitative investigation. Cross-nucleation kinetics between polymorphs can be determined from time-resolved optical micrographs using two different procedures, valid either when the two structures grow concomitantly,^{5,23} or when the growth of the parent phase is negligible.²⁰ Detailed descriptions of the methods and explanation of their derivation are given in the Supporting Information (Figure S2 and S3). Since at $T_{CN} > 145$ °C the fast nucleation of α -phase spherulites on β -phase surfaces prevents the parent phase from growing to a meaningful extent, both the quantification analyses are applied in order to cover the widest possible range of undercooling.

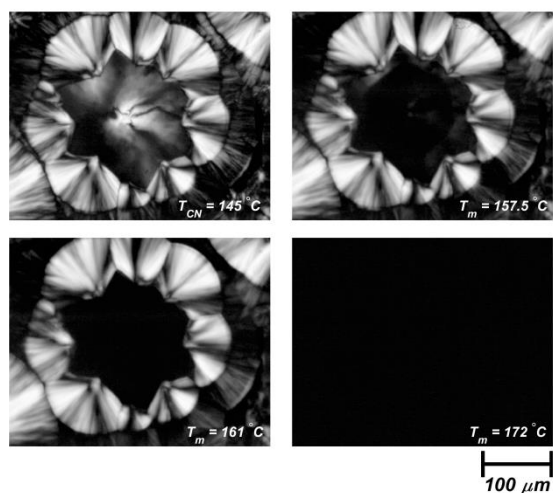


Figure 3. Example of temperature resolved optical micrographs during heating of the cross-nucleated sample from $T_{CN} = 145$ °C at 2.5 °C/min. The low-birefringent morphology at the periphery is α -phase crystallized during cooling of the partially crystallized sample to room temperature. The indicated temperatures are the observed melting points (T_m) of the different parts of the cross-nucleated composite morphology (see text).

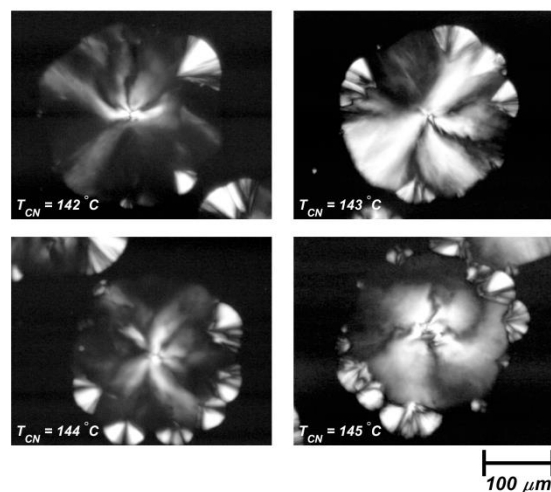


Figure 4. Optical micrographs taken after three hours at the indicated cross-nucleation temperature. The size of α -phase overgrowths at each temperature is related to the value of α -phase growth rate and to their time of nucleation.

The results obtained for the two quantification procedures are shown in Figure 5. The method proposed by Yu⁵ can be slightly adapted to seeded cross-nucleation experiments (see Supporting Information), and applied to analyse cross-nucleation in the T_{CN} range 141-145 °C, when β -phase grows at a measurable rate. Figure 5a shows the average number of cross-nuclei nucleated within a given distance from the β -hedrite centre, plotted versus $(R_{p,i}^2 - R_{o,i}^2)$ normalized to take into account the sample thickness (h_i) and the growth rate of the β -crystals, G_β (which is a function of temperature). In this way, the slope of the lines in Figure 5a is exactly equal to the cross-nucleation rate at T_{CN} . The displayed data represent 30 to 80 different cross-nucleation events, measured both on several hedrites in a single experiment, as well as by repeating multiple times (3-6) the same cross-nucleation experiment.

All the data taken at different temperatures show a good linearity in the $n_{avg} - \pi h_i(R_{p,i}^2 - R_{o,i}^2) / G_\beta$ plot, with a slope that decreases with increasing undercooling. It should be noted that the curves deviate from linearity at higher values of n_{avg} (not shown), due to the decrease of β -phase surface available for cross-nucleation because of α -phase overgrowth. A similar trend has been observed in the cross-nucleation of D-Mannitol and polypivalolactone.^{5,23}

At higher cross-nucleation temperatures, the growth of β -crystals before extensive α -phase nucleation at their periphery is negligible, thus preventing the use of this quantification method. However, in such case, the number of developing nuclei on the parent surface can be simply counted directly in time²⁰ (see Supporting Information, Equation s5).

The number density of cross-nuclei as function of time during cross-nucleation at different temperatures is shown

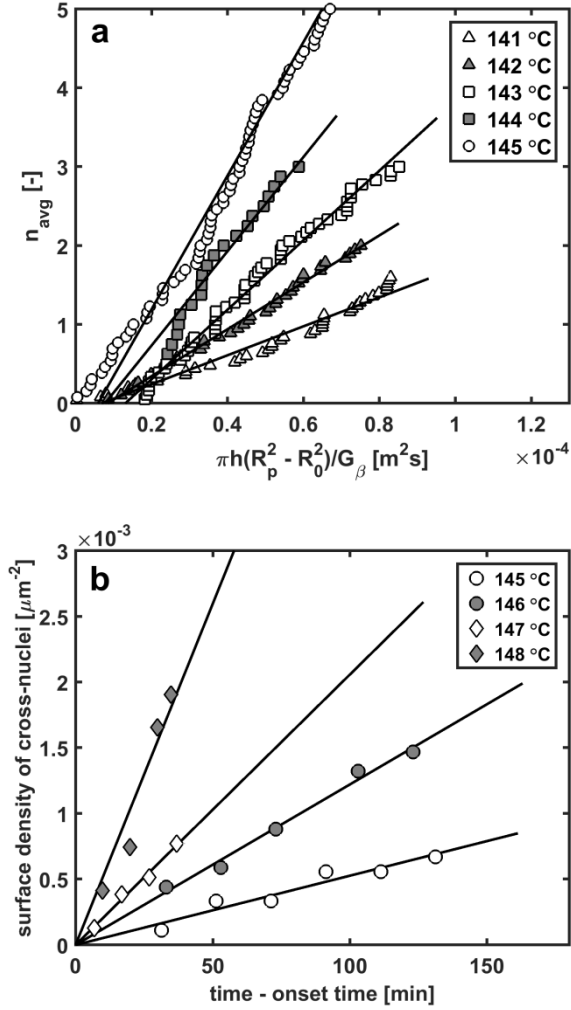


Figure 5. a) Average number of α -cross-nuclei as a function of the “normalized” $(R_{p,i}^2 - R_{o,i}^2)$ (according to Equation S2 and S3 of the Supporting Information). Results relative to different indicated cross-nucleation temperatures are shown; b) Number of α -phase cross-nuclei per unit area of β -hedrite lateral surface as a function of time, at the indicated cross-nucleation temperatures. In both plots, the slope of the fitted lines represents the cross-nucleation rate.

in Figure 5b. For the sake of clarity, the curves are horizontally shifted according to a specific “onset time” (intercept of the line with the time axis). It can be seen that the number of cross-nuclei increases linearly with time, thus allowing the quantification of the constant cross-nucleation rate as the slope of the fitting lines. Also in this temperature range, the rate of α -on- β nucleation increases with decreasing undercooling. Attempts of carrying out cross-nucleation experiments are also made at temperature exceeding 148 °C, however, at those high temperatures the number of

nuclei which develop practically at the same time is so large that a correct quantification is impossible.

The values of cross-nucleation rates determined by the direct counting method are the results of an average on 4-6 spherulites, observed in different experiments. For $T_{CN} = 145$ °C both quantification methods can be applied, since the β -hedrite area on which cross-nucleation occurs varies only slightly. In order to calculate the surface nucleation density, the average area of the β -phase growth front during the experiment is considered. The very good agreement between the two quantification method will be demonstrated in the following.

In compliance with the classical theory of nucleation and its application to polymer crystals,³⁴⁻³⁸ a simplified expression of the heterogeneous nucleation rate is:

$$J_{het} = J_0 \exp \left[\frac{-K_n}{T(\Delta T)^2} \right] \quad \text{Equation 1}$$

where J_{het} is given in nuclei per unit area and unit time, J_0 is a temperature independent frequency factor, ΔT represents the undercooling, and K_n is proportional to the free energy barrier for the creation of a nucleus of critical sizes. For the sake of simplicity, in Equation 1 we disregarded the diffusion-related term of nucleation rate,^{34,35,37,38} since it does not affect the following interpretation of the results in the considered temperature range.

Accordingly, the measured i-PP α -on- β cross-nucleation rates are reported as a function of the reciprocal of $T\Delta T^2$ in Figure 6. Literature data of cross-nucleation kinetics in other systems, and heterogeneous nucleation rates of i-PP α -phase on different solid substrates, are also shown for the sake of comparison. The increase in cross-nucleation rate with increasing crystallization temperature (Figure 4 and 5): is quantitatively confirmed α -on- β cross-nucleation rate increases by over an order of magnitude by decreasing the undercooling of 7 °C. This increase occurs both in the temperature region where the two polymorphs grow concomitantly and where the growth of β -phase is negligible ($T_{CN} > 145$ °C). Remarkably, the different quantification methods used in the two situations lead to a good agreement in the measured cross-nucleation rates.

The nucleation rate of a crystal on any substrate should be equal to zero at the crystal’s melting temperature. Therefore, a decrease in i-PP α -on- β -phase cross-nucleation rate with decreasing undercooling is expected at some point. On the other hand, cross-nucleation can only occur below the melting point of the parent phase. Consequently, the expected decrease is not experimentally detectable, because at higher crystallization temperatures the β -seeds melting range is entered.

By comparing the present data with the nucleation rates of the same i-PP α -phase on different heterogeneous substrates,^{39,40} and with other cases of cross-nucleation between polymorphs in small and macro-molecules,^{5,20,23} the incongruous behaviour is apparent. Although nucleation

rate is known to increase with decreasing undercooling at low temperatures, where diffusion and molecular mobility issues play a dominant role,³⁶⁻³⁸ this cannot be the case for the cross-nucleation of i-PP α -phase on β -seeds. In fact, the nucleation kinetics of the same crystal modification on diverse solid substrates exhibits negative temperature dependence, even at crystallization temperatures lower than those employed in this study.^{39,40} On the other hand it can be argued that if the work for the formation of a cross-nucleus is extremely small (i.e., low values of K_n in Equation 1), then the overall nucleation rate would still be dominated by the diffusion of the molecular stem across the melt-crystal interface, and thus an accelerating effect of temperature would be observed despite the relatively low undercooling.⁴¹ However this possibility can be safely ruled out, since cross-nucleation rate between polymorphs in other systems show the conventional decrease with increasing temperature, and the derived free energy barrier for cross-nucleation is not particularly low, but has values not dissimilar to those characterizing secondary nucleation-controlled crystal growth.²³

As such, we must conclude that the classical theory of heterogeneous nucleation fails to describe the temperature dependence of cross-nucleation rate between α - and β -phases of isotactic polypropylene. Our hypothesis is that this particular temperature dependence is linked to the intimate mechanism of cross-nucleation, and in particular to the competition between the heterogeneous nucleation of one polymorph on another and the growth of the same polymorph. In fact, we note that with respect to other cross-nucleating systems (D-Mannitol,⁵ isotactic poly(1-butene)²⁰ and polypivalolactone²³) which obey the general trend of heterogeneous nucleation kinetics with temperature, i-PP exhibits a much lower ratio between the growth rates of daughter and parent polymorphs: G_α/G_β is around 1.02-1.35 in the explored temperature range, as opposed to values between 2 and 100 for the other case-studies.

Discussion

At the molecular level, several different events take place concurrently on the surface of the growing β -crystals. Integrating cross-nucleation in the framework of the Hoffmann-Lauritzen's theory of polymer crystal growth,⁴²⁻⁴⁴ both phases first nucleate on the seed crystal, with characteristic rates $i_{\alpha/\beta}$ and $i_{\beta/\beta}$, and then grow laterally to cover the substrate at rates g_α and g_β . It should be underlined that cross-nucleation between polymorphs exhibits selectivity.⁴ In particular, although "kinetically" possible below T^* , the nucleation of i-PP β -phase on α -crystal is commonly not observed in isotropic samples,¹⁶ and we deduce it must be exceedingly slow with respect to α -on- α secondary nucleation, i.e., α -phase growth.

In view of the above described competition between the two polymorphs to cover the available seed's surface, the

measured α -on- β cross-nucleation rate might actually differ from the real ("molecular") one, $i_{\alpha/\beta}$. In fact, not all the formed cross-nuclei can develop a detectable morphology, since some of them are forbidden to grow by the impingement with the simultaneously growing β -phase secondary nuclei. If the area of β -substrate covered by the α -phase is much smaller than that covered by the β -polymorph, the growth of the α -phase will be halted by the parent phase overgrowth.

Intuitively, the probability that an α -cross-nucleus will be stopped in its growth by the β -phase, must depend on the individual values of secondary nucleation and lateral spread rates (i and g), which in turns determine the "macroscopic" growth rates of the two polymorphs.⁴³ The two extreme situations (schematized in Figure 7a and b) are encountered when the growth rate of one of the polymorph is much larger than the other one.

When the growth rate of α -phase (G_α) is much lower than the one of the β -form (G_β), the chances that a given cross-nucleus will grow and develop a detectable morphology, i.e., a spherulite, are negligible or extremely low (see Figure 7a). This consideration explains the well-known "kinetics constraint" of cross-nucleation: even if the nucleation events hypothetically occur with reasonable frequency, the cross-nucleated structure can become visible only when G_{daughter} overcomes G_{parent} . In the case of i-PP this is particularly clear, since it is unrealistic that α -on- β cross-nucleation rate would drop to zero below T^* , as the order of the polymorphs' growth rates inverts. On the other hand, if $G_\alpha \gg G_\beta$ the cross-nucleus will certainly grow to a detectable size (Figure 7b). In this case, the observed cross-nucleation rate is directly related to the "molecular" rate of formation of α -phase nuclei on the β -substrate, $i_{\alpha/\beta}$.

When G_α is only slightly larger than G_β , a more complex situation arises (Figure 7c). In fact, some of the formed α -phase cross-nuclei will be halted in their growth by the competition with the β -phase in covering the available β -substrate. Because of the previously mentioned selectivity in cross-nucleation, if the α -crystals manage to cover a sufficient area of the β -phase substrate (even after the completion of few monolayers), its growth can proceed unimpeded. Under these conditions, the observed number of cross-nuclei is just the fraction of successful nucleation events over the total ones.

On the basis of the mechanism illustrated in Figure 7, the measured cross-nucleation rate is just an "apparent" value. The "actual" cross-nucleation rate at the seed's growth front must decrease with increasing temperature, as expressed by the classical Equation 1. On the other hand, the anomalous temperature dependence of the observed cross-nucleation rate can be described by correcting Equation 1 with a probability function (P), which accounts for the chances of the cross-nucleus to reach an adequate coverage of the β -substrate and thus grow to a detectable morphology without being halted by the parent polymorph. In

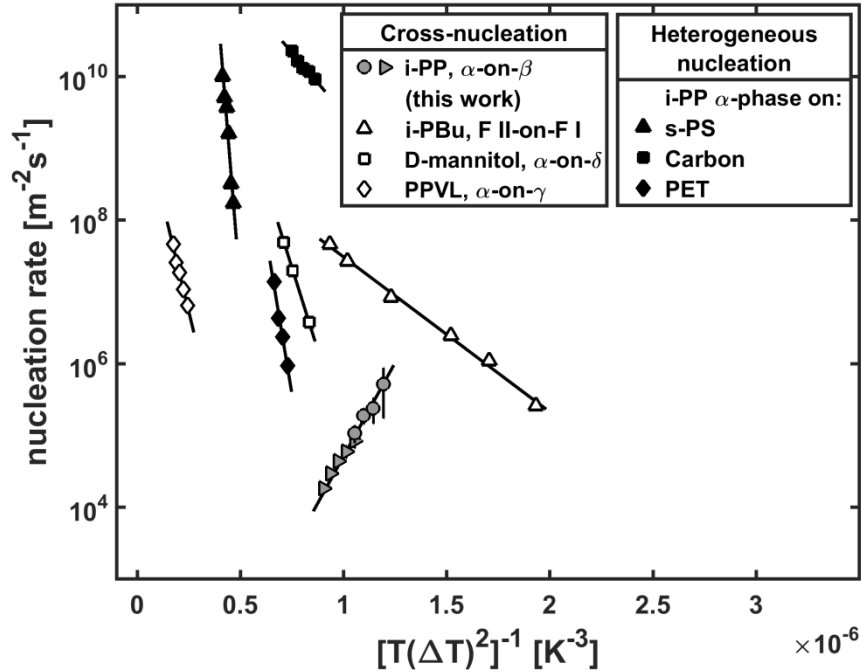


Figure 6. Measured α -on- β cross-nucleation rates of i-PP plotted as a function of $(T\Delta T)^{-1}$, according to the classical heterogeneous nucleation theory (gray filled symbols). The different symbols correspond to the values obtained with the two procedures described in the text and Supporting Information. Note that the error bar at low crystallization temperatures (lower values of $(T\Delta T)^{-1}$) is actually smaller than the marker size. The data are compared with cross-nucleation kinetics in other systems (open symbols: D-Mannitol,⁵ i-PBu = isotactic poly(1-butene)²⁰; PPVL = polypivalolactone²³) and to heterogeneous nucleation rate of α -phase i-PP on different substrates^{39,40} (black filled symbols: s-PS = syndiotactic polystyrene, carbon = carbon fibers and PET = poly(ethylene terephthalate)). The lines are exponential fit to the data.

turns, this probability should be a function of the temperature-dependent ratio of the polymorphs' growth rates:

$$J_{cross-nucl.} = J_0 P(G_{parent}, G_{daughter}) \exp\left(\frac{-K_n}{T\Delta T^2}\right)$$

(Equation 2)

Equation 2 can capture both the -apparently contradictory-normal and inverse temperature dependence of cross-nucleation rate between polymorphs (see Figure 6), depending on the exact variation of the nucleation and probability terms with crystallization temperature. In the previously studied cross-nucleating systems^{5,20,23} the growth rate of the daughter phase is always substantially higher than the one of the seed polymorph. Therefore, the probability of the cross-nucleus to rapidly cover the parent polymorph's substrate must be close to unity. Thus, the nucleation term of Equation 2 prevails, resulting in the normal decrease of the cross-nucleation rate with decreasing undercooling. Instead, $G_{daughter}/G_{parent}$ for isotactic polypropylene is only slightly higher than 1, and it increases with decreasing undercooling. In this latter case the probability term of Equation 2 has positive temperature dependence, and can eventually dominate the measured cross-nucleation rate.

The evaluation of the exact form of the hetero-polymorphic substrate coverage probability function is out of the scope of the present work. We believe that definite theoretical efforts and dedicated molecular dynamics simulations, capable of visualizing the processes at the level of the seed's growth front, would be required to this aim. However, in order to demonstrate the validity of the idea, the fitting of i-PP α -on- β cross-nucleation data according to Equation 2 is shown in Figure 8. The substrate coverage probability function is arbitrarily chosen as a logistic function of $G_\alpha/G_\beta(T)$, bounded between 0 and 1.

Noticeably, the experimental measurements are successfully described by Equation 2, using typical values of J_0 and K_n commonly observed for heterogeneous nucleation of α -i-PP on different substrates.^{39,40} On the other hand, the obtained P values are not necessarily realistic, due to the purely illustrative purposes of the chosen function. Nevertheless we recall that even with very low values of cross-nuclei development probability, the cross-nucleation process could be "observable" with a fair frequency, thanks to the magnitude of the frequency term J_0 .

The proposed semi-empirical description suggests that the inverse temperature dependence of cross-nucleation rate

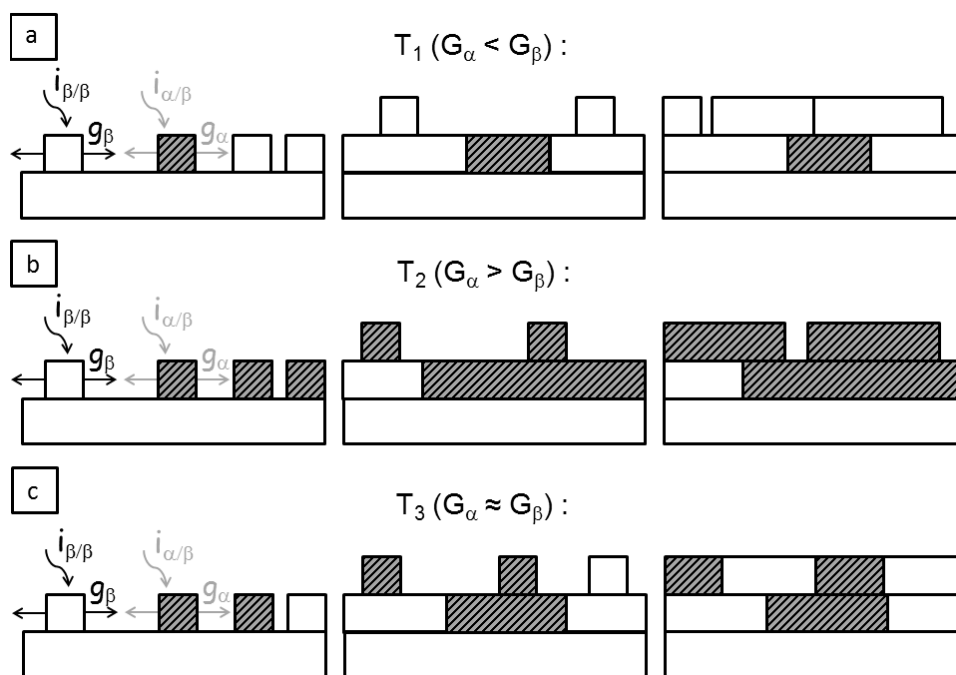


Figure 7. Schematic representation of the competition between α -on- β cross-nucleation and β -phase growth, occurring at the surface of a β -substrate during crystallization, time increases going from left to right. Different relative magnitude of the growth rates of the two polymorphs (G_α , G_β) are considered in part a, b and c.

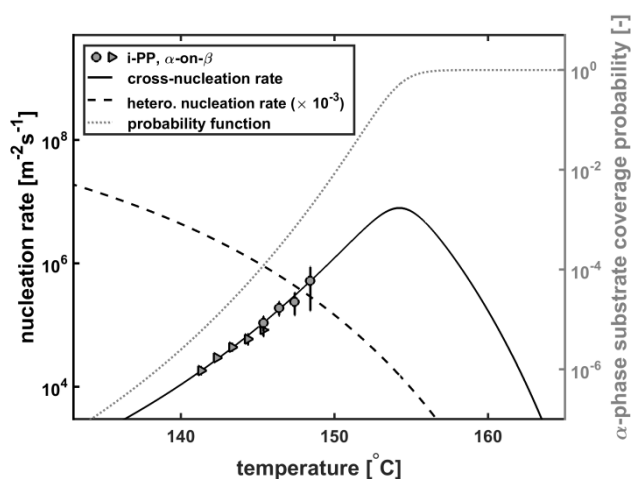


Figure 8. Apparent α -on- β cross-nucleation rates as a function of temperature, fitted with Equation 2. The temperature dependences of the α -phase substrate coverage probability function and of the nucleation term of Equation 2 (indicated as heterogeneous nucleation rate in the legend) are also shown. The different symbols correspond to the values obtained with the two methods described in the text and Supporting Information.

in the considered crystallization temperature range might result from an increase of about 2 orders of magnitude in P , while the overall number of nucleation events per unit time (nucleation term of Equation 2) decreases of 1 order of magnitude only. The same rationale can be used to describe the conventional temperature dependence of the cross-nucleation rate measured for other systems.^{5,20,23}

Conclusion

To summarize, we reported a case of cross-nucleation between polymorphs, which apparently does not comply with the theory of heterogeneous nucleation. We propose that this anomalous behaviour results from the competition between the two phases for the coverage of the parent polymorph's substrate. Although these results are obtained just for i-PP, we believe they are of general validity for cross-nucleation, whenever similar conditions are met. The richly polymorphic molecular crystals would surely provide other examples, and the idea could also be tested with molecular dynamics simulations. These new insights in the mechanism of cross-nucleation contribute to the general understanding of polymorphic crystallization, a fundamental step to achieve the selective control over the crystallizing structure. Eventually, we disclosed an inherent limit in the possibility of β -phase formation in bulk i-

PP products, an issue of great industrial interest.⁴⁵ β -selective nucleants practically lose their efficiency at high crystallization temperatures, due to extensive and rapid α -phase cross-nucleation on the β -crystals themselves. The same shortcoming is expected at low crystallization temperatures, due to the known cross-over between the growth rates of the two polymorphs.²⁵⁻²⁷

ASSOCIATED CONTENT

Supporting Information. Thermal protocol applied for the study of cross-nucleation, description of the quantification methods used to determine the kinetics of cross nucleation (PDF).

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REFERENCES

- (1) Yu, L. Nucleation of One Polymorph by Another. *Journal of the American Chemical Society* **2003**, *125*, 6380-6381.
- (2) Ostwald, W. The formation and changes of solids. *Z. Phys. Chem* **1897**, *22*, 289-330.
- (3) Bernstein, J.; Davey, R. J.; Henck, J.-O. Concomitant Polymorphs. *Angewandte Chemie International Edition* **1999**, *38*, 3440-3461.
- (4) Chen, S.; Xi, H.; Yu, L. Cross-Nucleation between ROY Polymorphs. *Journal of the American Chemical Society* **2005**, *127*, 17439-17444.
- (5) Tao, J.; Yu, L. Kinetics of Cross-Nucleation between Polymorphs. *The Journal of Physical Chemistry B* **2006**, *110*, 7098-7101.
- (6) Huang, J.; Chen, S.; Guzei, I. A.; Yu, L. Discovery of a Solid Solution of Enantiomers in a Racemate-Forming System by Seeding. *Journal of the American Chemical Society* **2006**, *128*, 11985-11992.
- (7) Yu, L. Survival of the fittest polymorph: how fast nucleator can lose to fast grower. *CrystEngComm* **2007**, *9*, 847-851.
- (8) Desgranges, C.; Delhommelle, J. Molecular Mechanism for the Cross-Nucleation between Polymorphs. *Journal of the American Chemical Society* **2006**, *128*, 10368-10369.
- (9) Desgranges, C.; Delhommelle, J. Insights into the Molecular Mechanism Underlying Polymorph Selection. *Journal of the American Chemical Society* **2006**, *128*, 15104-15105.
- (10) Desgranges, C.; Delhommelle, J. Molecular Simulation of Cross-Nucleation between Polymorphs. *The Journal of Physical Chemistry B* **2007**, *111*, 1465-1469.
- (11) Cavallo, D.; Alfonso, G. C.: Concomitant Crystallization and Cross-Nucleation in Polymorphic Polymers. In *Polymer Crystallization II: From Chain Microstructure to Processing*; Auriemma, F., Alfonso, G. C., de Rosa, C., Eds.; Springer International Publishing: Cham, 2017; pp 1-54.
- (12) Tao, J.; Jones, K. J.; Yu, L. Cross-Nucleation between d-Mannitol Polymorphs in Seeded Crystallization. *Crystal Growth & Design* **2007**, *7*, 2410-2414.
- (13) Stoica, C.; Tinnemans, P.; Meekes, H.; Vlieg, E.; van Hoof, P. J. C. M.; Kaspersen, F. M. Epitaxial 2D Nucleation of Metastable Polymorphs: A 2D Version of Ostwald's Rule of Stages. *Crystal Growth & Design* **2005**, *5*, 975-981.
- (14) Stoica, C.; Verwer, P.; Meekes, H.; Vlieg, E.; van Hoof, P. J. C. M.; Kaspersen, F. Heterogeneous 2D nucleation of the stable polymorphic form on the metastable form. *Journal of Crystal Growth* **2005**, *275*, e1727-e1731.
- (15) Park, Y.; Boerrigter, S. X. M.; Yeon, J.; Lee, S. H.; Kang, S. K.; Lee, E. H. New Metastable Packing Polymorph of Donepezil Grown on Stable Polymorph Substrates. *Crystal Growth & Design* **2016**, *16*, 2552-2560.
- (16) Varga, J.; Ille, A.; Fujiwara, Y. $\beta\alpha$ -BIFURCATION OF GROWTH DURING THE SPHERULITIC CRYSTALLIZATION OF POLYPROPYLENE. *Period. Polytech. Chem. Eng.* **1990**, *34*, 255-271.
- (17) Fraschini, C.; Jiménez, L.; Kalala, B.; Prud'homme, R. E. Polymorphism and cross-nucleation in poly(1,3-dioxolan). *Polymer* **2012**, *53*, 188-195.
- (18) Nozue, Y.; Seno, S.; Nagamatsu, T.; Hosoda, S.; Shinohara, Y.; Amemiya, Y.; Berda, E. B.; Rojas, G.; Wagener, K. B. Cross Nucleation in Polyethylene with Precisely Spaced Ethyl Branches. *ACS Macro Letters* **2012**, *1*, 772-775.
- (19) Cavallo, D.; Gardella, L.; Portale, G.; Müller, A. J.; Alfonso, G. C. On cross- and self-nucleation in seeded crystallization of isotactic poly(1-butene). *Polymer* **2013**, *54*, 4637-4644.
- (20) Cavallo, D.; Gardella, L.; Portale, G.; Müller, A. J.; Alfonso, G. C. Kinetics of Cross-Nucleation in Isotactic Poly(1-butene). *Macromolecules* **2014**, *47*, 870-873.
- (21) Nguyen, A. H.; Molinero, V. Cross-nucleation between clathrate hydrate polymorphs: Assessing the role of stability, growth rate, and structure matching. *The Journal of Chemical Physics* **2014**, *140*, 084506.
- (22) Hudait, A.; Qiu, S.; Lupi, L.; Molinero, V. Free energy contributions and structural characterization of stacking disordered ices. *Physical Chemistry Chemical Physics* **2016**, *18*, 9544-9553.
- (23) Cavallo, D.; Galli, F.; Yu, L.; Alfonso, G. C. Cross-Nucleation between Concomitantly Crystallizing α - and γ -Phases in Polypivalolactone: Secondary Nucleation of One Polymorph on Another. *Crystal Growth & Design* **2017**, *17*, 2639-2645.
- (24) Wang, J.; Ren, Z.; Sun, X.; Li, H.; Yan, S. The $\beta\alpha$ growth transition of isotactic polypropylene during stepwise crystallization at elevated temperature. *Colloid and Polymer Science* **2015**, *293*, 2823-2830.
- (25) Nakamura, K.; Shimizu, S.; Umamoto, S.; Thierry, A.; Lotz, B.; Okui, N. Temperature Dependence of Crystal Growth Rate for [alpha] and [beta] Forms of Isotactic Polypropylene. *Polym. J* **2008**, *40*, 915-922.
- (26) Lotz, B. α and β phases of isotactic polypropylene: a case of growth kinetics 'phase reentrancy' in polymer crystallization. *Polymer* **1998**, *39*, 4561-4567.
- (27) Lotz, B.; Fillon, B.; Thierry, A.; Wittmann, J.-C. Low Tc growth transitions in isotactic polypropylene: β to α and α to smectic phases. *Polymer Bulletin* **1991**, *25*, 101-105.
- (28) Varga, J.; Mudra, I.; Ehrenstein, G. W. Highly active thermally stable β -nucleating agents for isotactic polypropylene. *Journal of Applied Polymer Science* **1999**, *74*, 2357-2368.
- (29) Varga, J. Supermolecular structure of isotactic polypropylene. *Journal of Materials Science* **1992**, *27*, 2557-2579.
- (30) Varga, J.; Ehrenstein, G. W. High-temperature hedritic crystallization of the β -modification of isotactic polypropylene. *Colloid and Polymer Science* **1997**, *275*, 511-519.
- (31) Alfonso, G. C.; Moretti, P.; Pallenzona, P.; Yin, J. Growth rates of different polymorphs from interspherulitic boundary profiles. *Optical Engineering* **1995**, *34*, 3385-3392.
- (32) Varga, J. β -MODIFICATION OF ISOTACTIC POLYPROPYLENE: PREPARATION, STRUCTURE, PROCESSING, PROPERTIES, AND APPLICATION. *Journal of Macromolecular Science, Part B* **2002**, *41*, 1121-1171.
- (33) Wunderlich, B.: CHAPTER VIII - Equilibrium Melting. In *Macromolecular Physics*; Academic Press: San Diego, 1980; pp 1-127.
- (34) Turnbull, D. Kinetics of Heterogeneous Nucleation. *The Journal of Chemical Physics* **1950**, *18*, 198-203.
- (35) Turnbull, D.; Fisher, J. C. Rate of Nucleation in Condensed Systems. *The Journal of Chemical Physics* **1949**, *17*, 71-73.

- (36) Chatterjee, A. M.; Price, F. P.; Newman, S. Heterogeneous nucleation of crystallization of high polymers from the melt. III. Nucleation kinetics and interfacial energies. *Journal of Polymer Science: Polymer Physics Edition* **1975**, *13*, 2391-2400.
- (37) Price, F. P.: Nucleation in polymer crystallization. In *Nucleation*; Zettlemoyer, A. E., Ed.; Dekker: New York, 1969.
- (38) Wunderlich, B.: CHAPTER V - The Nucleation Step. In *Macromolecular Physics*; Academic Press, 1976; pp 1-114.
- (39) Wang, C.; Liu, F.-H.; Huang, W.-H. Electrospun-fiber induced transcrystallization of isotactic polypropylene matrix. *Polymer* **2011**, *52*, 1326-1336.
- (40) Wang, C.; Liu, C. R. Transcrystallization of polypropylene composites: nucleating ability of fibres. *Polymer* **1999**, *40*, 289-298.
- (41) Schmelzer, J. W. P.; Abyzov, A. S.; Fokin, V. M.; Schick, C.; Zanotto, E. D. Crystallization of glass-forming liquids: Maxima of nucleation, growth, and overall crystallization rates. *Journal of Non-Crystalline Solids* **2015**, *429*, 24-32.
- (42) Lauritzen, J. J. I.; Hoffman, J. D. Formation of Polymer Crystals with Folded Chains from Dilute Solution. *The Journal of Chemical Physics* **1959**, *31*, 1680-1681.
- (43) Lauritzen, J. J. I.; Hoffman, J. D. Extension of theory of growth of chain-folded polymer crystals to large undercoolings. *Journal of Applied Physics* **1973**, *44*, 4340-4352.
- (44) Hoffman, J. D.; Miller, R. L. Kinetic of crystallization from the melt and chain folding in polyethylene fractions revisited: theory and experiment. *Polymer* **1997**, *38*, 3151-3212.
- (45) Gahleitner, M.; Mileva, D.; Androsch, R.; Gloger, D.; Tranchida, D.; Sandholzer, M.; Doshev, P. Crystallinity-Based Product Design: Utilizing the Polymorphism of Isotactic PP Homo- and Copolymers. *International Polymer Processing* **2016**, *31*, 618-627.