

Selective Dissolution as a Tool for Detecting Spatial Variations in the Metastability within Lamellar Polymer Crystals

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This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

Described in this paper is how a narrow low-molecular-weight fraction of PEO was spin-coated into a thin film, then melt-crystallized and finally how the dissolution of the thus obtained dendritic crystals was monitored by AFM. The idea of the experiment is sound and the execution apparently well performed. The problem is the interpretation and the authors' patchy background knowledge that did not allow them to put their results in a proper perspective. There are also some inconsistencies in interpretation of the results, parts of the discussion contradicting other parts.

1. Starting with references, those pre-2010 to basics of polymer crystallization and morphology in the introduction are conspicuously missing. This 70-year-old field did not start in 2018, as a casual glance at the reference list might suggest. Already the 1st sentence on chain folding gives 3 references – all 2018. Also that thermal stability of lamellar crystals depends on lamellar thickness was not discovered in 2014 (ref 4), and that lamellar thickness is smaller than chain length and lateral lamellar size wasn't discovered in 2018 (refs 5,6).

2. But a more serious problem is the authors' apparent unawareness of the seminal works on crystallization and morphology of melt-grown single crystals of the very same system, i.e. narrow low-molecular fractions of PEO, by Andre Kovacs in the 1970s. E.g. J. Polym. Sci., Polym.

Symp. 1975, 50, 283; or Prog. Colloid Polym. Sci. 1975, 58,

44. No reference even to single crystal morphologies of the same system by Stephen Cheng, whom they otherwise cite in a different context. Had they studied those works, particularly the intriguing changes of crystal habits on annealing by Kovacs, they could have achieved a better understanding of their own observations.

3. The other major problem, hampering appropriate interpretation of results, is the lack of realization by the authors that the (140) faces of PEO crystals are not crystallographic planes but are, instead, rough (120) faces of variable tilt resulting from high secondary nucleation rate and unequal spreading rates of layers in opposite directions due to the asymmetry of the (120) crystallographic planes – see Shcherbina et al. Macromolecules, 2007, 40, 402. (see also below).

4. Regarding holes in the annealed crystals, on L 161, when mentioning holes observed in annealed single crystals, it says "This morphology (in particular the holes) were attributed to heterogeneities within such crystals, expressed as variations in the degree of metastability.[6, 11]" Holes are holes, not heterogeneities. Of course, they are likely to be nucleated on defects. Incidentally, as far as I am aware, those holes go back to Statton, published in the 1960s. And were found to be due to the material adhering to the substrate, hence unable to move toward thickened areas. When deposited on "slippery" gel, crystals were shown to thicken without the creation of holes. In fact when crystals were annealed in solution, not only did they not develop holes, but it was clear from their electron micrographs along which crystallographic planes the material had been slipping toward the thickening areas and feeding them. (Organ et al. J. Polym. Sci., Pt. B: Polym. Phys. Ed. 1990, 28, 2365).

5. L 254 and Figures 2 and S4e,f: As mentioned above, the seemingly "140" facet is a product of unequal layer spreading rates on (120) planes during crystal growth. The "140" face is thus not regular as drawn in Figure S4f, but has irregularly distributed steps reflecting random growth. It would have been interesting to consider the kinetics of asymmetric dissolution,

or “unzipping”, of layers of stems on the (120) face, causing the tilt of the crystal edge to appear like (130) or (140) facets. Of course taking into account, at the same time, that the edge is affected by the dynamic near-equilibrium between stem dissolution and deposition. Instead, while describing Fig 2, the authors keep stating that “different crystallographic planes exhibited different dissolution rates.” What they mean here is that (140) dissolves faster than (120). It is not unexpected that a plane with more steps on it, i.e. the “140”, would dissolve faster than a plane with no steps (i.e. a smooth 120). Instead, the authors offer a rather vague and uncommitting view of the observations in Fig 2 (L 198-): “In analogy to crystallization, the rate-limiting step of dissolution is associated with the detachment probability of crystalline stems or whole chains from the various crystal faces. The corresponding energy barriers for dissolution is related to the surface free energy of crystalline stems or whole chains on the dissolution front. These energy barriers may depend on the orientation of the crystal surface and may vary with the local degree of metastability, which includes the degree of chain folding.” Just like crystallization does not depend just on attachment rate and attachment barrier, but also on thermodynamic driving force, i.e. free energy difference between the phases and hence the lifetime of the depositions, so dissolution equally depends on its driving force, which is undoubtedly larger for a rough face than for a smooth one.

6. In the paragraph starting on L 228 the difference between dissolution rates of two dendrite branches is attributed to their different orientations relative to the concentration gradient in the solution. “The latter dissolved away in toluene at 20.5 °C within 300 s, but the former remained until 780 s.” What concentration gradient would persist in a toluene solution for 13 minutes and why? And which way was the gradient directed anyway? Decreasing concentration with decreasing distance from the crystal? Evidence from experiments on polymer crystals in solution is in fact opposite – higher local concentration near the crystal surface. By the way, I find the stated analogy with the direction of temperature gradient in quenching metal melts rather irrelevant and unhelpful.

7. Much of the subsequent text and figures concern the slowing down of dissolution with time. As seen in Fig 3a the main reason for the slowdown is the fact that “140” faces dissolve faster than the 120 faces, and as the former also approach the regularity of the 120 faces, i.e. as the faces become less rough and more resistant to dissolution, the whole dissolution process slows down, as shown in Fig 3b. The fact that the rough high-energy “140” faces dissolve faster than the smoother low-energy 120 faces is hardly surprising. The intriguing thing is that, by page 15, the authors seem to have forgotten about Figure 3b and the cause of the retardation of cumulative (overall) dissolution. Instead, they now attribute the slowdown to the crystal lamellae being thicker in the center of crystal than at the periphery. Incidentally, for the latter the authors provide no experimental evidence, even though they measure the crystal thickness by AFM. Then, by the time we reach the Conclusions, the authors change their minds again, and say (L 439): “This decay in dissolution velocity reflects that, due to reorganization in the course of their growth, the centre parts of the crystal were more stable than the peripheral ones.” Not clear what is now meant by “reorganization”, but this line is also repeated in the Abstract. But no mention at all any more about the early depletion of the fast-dissolving “140” faces.

8. Next the temperature dependence of the dissolution rate is considered. In Fig 5 a parameter related to the reciprocal of the speed of dissolution (denominator in the exponent in exponential decay of crystal with time) is plotted as log against $1000/T$ in an Arrhenius-type fashion. From the slope of the linear fit the authors obtain an activation energy E for dissolution, which is very high indeed. However, one has to be sceptical about the E -value derived in this way. At best, it is an estimate of the upper limit. The rate of dissolution does not depend only on the rate of detachment, but also on the rate of re-attachment. The net rate is the difference between the two. The authors' method would only be valid if the back-reaction could be neglected, i.e. at infinite or very high dilution. Importantly with polymers, what matters is local, not global concentration, and that is rarely low. We should really know the polymer-solvent phase diagram, i.e. its liquidus curve. For polymers that curve is almost horizontal for most of the concentration range, so that one even talks about equilibrium dissolution temperature of a polymer in a solvent, as if it did not depend on concentration. In other words, the concentration should be really low indeed, and the solution should be vigorously stirred, for the re-attachment rate to be ignored. Satisfying neither of these requirements were mentioned in the text. It is therefore clear that the re-attachment rate and the lifetime of the unstable re-attachments may be strongly dependent on temperature and thus influence the determination of E via Arrhenius. A vivid illustration of the simultaneous dissolution and recrystallization for polymer crystals held in solution are the well-documented “picture-frame” crystals, which should also be mentioned in the paper.

Less important but needing attention:

9. L 52: “Generally speaking, heterogeneity within a polymer lamellar crystal is reflecting differences in packing of molecules, varying somewhere between perfectly arranged crystalline structures and fully amorphous chain segments.[8]” This statement is dubious and contradicts the well-accepted 2-phase model of semicrystalline polymers. It reminds one of the very early days of studies of semicrystalline polymers, where a view existed that those polymer adopt a state between crystal and amorphous, denying the 2-phase structure.

10. It is unfortunate that the authors use symbol a^* for $a \sin(\beta)$ in describing the real space unit cell. a^* is normally used for a reciprocal lattice parameter, in $1/\text{nm}$ or $1/\text{\AA}$ units. $a \sin(\beta)$ should be used instead.

11. There are superfluous sentences like, when describing crystal dissolution, the authors say (L 187) “Most obviously, the size of crystal became smaller as the cumulative dissolution time increased.”

12. More on superfluous text and inappropriate references: L 147: “This indicated that annealing at an elevated temperature (e.g., at 51 °C), which is still below the melting point, resulted in a thickening of the metastable crystal, causing an increase of its stability.[27]” Everyone vaguely familiar with semicrystalline polymers would be aware that increasing lamellar thickness lowers the free energy. So why do we have to be reminded, and are even given a reference (27) to a 2005 article? And just a little further (L 153): “The lamellar thickness is widely accepted to be the characteristic feature that determines

crystal stability.” And the rather overused and not very meaningful phrase “degree of metastability”, used 21 times in this paper.

Recommendation: resubmit after major revision.

Reviewer #2

(Remarks to the Author)

In this manuscript the authors introduce time dependent dissolution measurements as a method to investigate the local (meta)stability of polymer crystals in thin films. Polymers crystallize as thin lamellar crystals, in which the chains take on a folded conformation. It is well known that these crystals are a non-equilibrium structures, their stability depends on their thickness, which is typically lying in the nanometer range. Isolated crystals form in thin films, and if the films are very thin, the crystals are dendritic. The stability of these crystals can vary depending on the distance to the growth front due to reorganization going on in parallel to crystal growth. The reorganization is typically related to the existence of intracrystalline mobility, which is high for PEO, used as a model substance here. Reorganization becomes faster during heating, it is therefore difficult to use heating as a measure of stability, unless it takes place very fast. At this point the idea introduced here sets in: dissolution in a solvent at ambient temperatures takes place without reorganization and dissolution speed therefore reflects the local stability of the crystals. The crystals are mostly dissolved in the lateral direction, inverse to the path crystal growth has taken place before with a few exceptions, in which holes form in the middle of the crystals. In this paper the authors demonstrate the application this approach on a model system consisting of dendritic crystals grown in thin films of PEO of relatively low molecular weight using AFM and optical microscopy as experimental methods.

The paper is based on previous work of the authors, in which polymer crystals grown in thin films have already been studied and also washing has been introduced as a technique for partial dissolution. To use this approach for a systematic investigation of the dissolution kinetics is to my knowledge novel and provides an interesting illustration of the spatially varying stability of the crystals. Furthermore, the measured temperature dependence (activation energy) of the dissolution speed gives insights about the molecular process of dissolution, provided the corresponding questions below can be answered. In general, the paper is well written, the experimental design is convincing, and the experiments seem carefully performed. I can mostly follow the arguments and interpretation of the results that the authors put forward with a few but important exceptions that need further clarification. These points are listed below.

- In line 191 and Fig. S4 the authors identify some surfaces of the crystals as specific crystallographic planes. It is not clear, how this assignment is done. I assume it rests on previous work, which should then either be cited or explained again here.

- In the paragraph starting at line 228 the authors claim that the observed higher dissolution tendency of some crystals is due to a competition between preferred crystal orientation and the concentration gradient direction. A few lines above they (line 200) they state that the barrier for dissolution is related to the surface free energy (of crystalline stems or whole chains on the dissolution front). First, it seems to me that surface energy is a concept, which applies to a larger region of the surface than a single chain. Furthermore, it seems obvious to me that a crystal surface with a certain inclination to a crystal plane will in general always be less stable than a surface which is parallel to a crystal plane due to the microscopic roughness caused by the inclination. I would think that this fact explains the faster dissolution. I am not sure if the authors mean just this fact or something else, I find the text not very clear at this point. This issue should be addressed.

- In the further part of the manuscript, the authors analyze in detail the observation that the dissolution becomes slower during the process with the advent of time. It is probably caused by an increasing stability with distance from the outer lateral surface of the crystal. The time dependent dissolution speed can be modeled with an exponential decay. The authors interpret the temperature dependence in terms of an activation energy for the transport of a molecule from the crystal to the solvent. I am not sure if I can follow this argument. It seems to me that something is wrong with the equation in line 327. τ_d describes the spatial variation of stability of the crystal. Should the temperature dependence of the dissolution velocity, if it is caused by the barrier for the transport to the solvent, not show up in the temperature dependent prefactor $v_d(T_d)$ instead of in τ_d ? A temperature dependence of τ_d means that the spatial variation of stability changes with temperature. Why should this be related to the activation energy of dissolution? The authors should please check and clarify this issue and provide a more detailed explanation in their text.

Reviewer #3

(Remarks to the Author)

The authors report on experiments to sequentially dissolve a single lamellar crystal grown on a solid substrate. By analyzing the patterns after each step of dissolution they can calculate the speed of dissolution. The authors argue that the experiments indicate a spatial variation of “metastability” of the crystalline polymer which is not reflected by the height of the crystal. Although the experiments are certainly of interest for the polymer community the conclusions are speculative, and to some extent the work is premature for presentation to a larger audience. Key concepts used by the authors like “metastability” remain vague and it is difficult for me to take a clear message home after reading. Therefore, I do not recommend publication. Below, I address some issues in more detail which may help the authors to improve the manuscript for submission in a more specialized journal.

1) I do not understand the argument “From the constant lamellar thickness revealed by time-resolved in situ AFM measurements in Figure S3, we can safely assume that, in contrast to thermal annealing, selective dissolution does not change the degree of metastability of the crystal.”

Obviously, the author made a difference between height (thickness) of the crystal and “metastability”. If so, how can the authors conclude from the missing height difference during dissolution that the metastability has not changed?

2) In order to explain the different speed of dissolution of two side-branches they write: “I may suggest that it was preferentially grown at a smaller angle with respect to the direction of the concentration gradient. Thus, although they have a similar thickness, these two side branches possessed different thermal stabilities as demonstrated by their selective dissolution, allowing classifying them as “favourably oriented” and “unfavourably oriented” “

First of all, why the side branch should not grow in the direction of the (local) concentration gradient? I note that the speed of growth is very low in the thin film where the growth is taken place in 2D and is diffusion-controlled. But the key question is: What should be the molecular origin in the different stability given that both branches have the same height?

3) The authors speculate about the observed decrease of dissolution velocity: “Therefore, we believe that the exponential decay of V_d , total with t_d revealed an exponential decrease of the degree of metastability from the initial edge to the centre of the lamellar crystal.”

What means “exponential decrease of the degree of metastability from the initial edge to the centre of the lamellar crystal.”? Exponential with respect to what? I can only speculate that the authors assume with respect to the distance within the crystal? Since V_d is exponentially decreasing in time this cannot be mapped to an exponential decrease of “metastability” (a term which was never defined exactly) as a function of the distance.

4) In the analysis of the characteristic time for the decay of dissolution velocity the authors observe an Arrhenius-like relation with respect to temperature which they associate with the energy barrier to dissolve a chain or a stem. I cannot see how this can be concluded if the process of dissolution is more complex and involves dissolution of whole clusters of chains, or maybe only parts of chains. The argument of considering the barrier as given by the heat of fusion seems not striking. This would indicate that the solvent does not have any impact on the state of the chains exposed to the surface. It also means that different solvents should have the same barrier. In order to substantiate the claim, experiments with shorter and longer chains should be performed, and also with different solvents.

How does the predicted constant energy barrier (heat of fusion per chain) relate with the original observation that the speed of dissolution is higher at the border of the crystal?

5) The term “metastability” as imposed by the authors (as an orthogonal property to the crystal thickness) is indeed very difficult to understand. The authors argue that this might have to do with unfavorable growth direction, or with the effective time of transport of the chains through the depletion zone. But this should lead to crystalline structure which also should display different energy barriers (and heat of fusion). Could the decrease of dissolution velocity be related to the more stable attachment to the substrate of the “earlier” crystalline parts?

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

I have checked the extensive and detailed response to my comments by the authors and am satisfied that they have responded satisfactorily in full, and made the appropriate changes. There is just one minor detail which I would like them to correct. On page 17, line 341-, there is the sentence

“There, at any given dissolution temperature in an almost infinitely dilute solution, the free energy difference (i.e., the gain) upon dissolving a polymer from a rough face is higher than from a smooth one.”

Upon dissolution above the dissolution temperature the free energy drops rather than gains, otherwise the process would not go ahead. The drop is caused by the increase in entropy of the system.

Otherwise, I do not have any further objections and am recommending publication of this fine paper.

[Note from the Editor: Reviewer #1 also assessed the response given to reviewer #2 who was not able to look over the revision again:]

I have checked the authors' answers to the comments of Reviewer 2. Some of the answers and changes made to the manuscript are already given in response to comments by reviewers 1 and 3. Regarding comment 3 by reviewer 2, the answer given clarifies the situation, at least clarifies the method used. Taking the average dissolution velocity when the velocity varies significantly with time may not be an ideal technique when it comes to Arrhenius fitting. However, I suppose there is some justification for it, given the dissolution kinetics in this system. Why the velocity drops so drastically with time is still something of a puzzle to me. Separating the contributions from rough and smooth surfaces makes a lot of sense, as rough faces dissolve earlier than smooth ones. Yet even after separation, the individual components $V(R)$ and $V(S)$ still decay with time. By the way I cannot see the shapes of separate $V_R(t)$ and $V_S(t)$ – am I missing something? So what is the reason these separate rates should slow down as dissolution front approaches the center of the crystal? During the growth of the crystal, has the center perfected while the periphery was still growing? But on the timescale of the experiment, all parts of the crystal would have had time to perfect before the dissolution experiment. And also, in their rebuttal the authors say: “Furthermore, given that the samples were kept at maximum (after multiple steps) only up to ca. 1000 s in pure solvent, we do not anticipate any significant reorganization processes to occur.” So what causes the increased resistance of the crystal center? I suggest that serious consideration should be given to fractionation during growth of the crystal. It is true that, on the scale of commercial polymers, PDI of 1.14 is a rather narrow fraction. Nevertheless, the polymers used are not monodisperse, and the higher MW fraction is expected to crystallize first forming the crystal center, while the lower MW fraction would have been left at the periphery. The consequences for dissolution process are obvious. One comment about the “degree of metastability”, which has been discussed at some length in the correspondence between the author and the reviewers. Like the other reviewers, I also do not like this fuzzy term. But if it has to be used, I see no problem in defining it. Surely it must be the excess free energy of phase 1 above the most stable phase, phase 2. So if phase 1 is an imperfect or a small crystal and phase 2 the perfect infinite crystal then the excess free enthalpy can be expressed, to a good approximation, as $\Delta G = \Delta T \cdot \Delta S$, where ΔT is melting point depression and ΔS is melting entropy. Similar for dissolution. I advise the authors to consider these comments. If they feel they are helpful and making changes to the paper in response to them would improve the paper, please make those changes at your discretion.

Reviewer #4

(Remarks to the Author)

[Note from the Editor: Reviewer #4 assessed the response given to reviewer #3.]

A method based on the selective dissolution at constant temperature in a pure solvent of isothermally grown poly(ethylene oxide) (PEO) dendritic single crystals is described. The method allows to probe differences in the metastability of PEO crystals, while providing information on the relationships between growth kinetics and the “degree of metastability” of different single crystal regions.

The revised manuscript correctly accommodated the changes proposed by the initial reviewers, resulting in an excellent work that highlights unsolved problems in polymer physics. In my opinion it should be published unchanged.

I think it would be nice to complement the approach, using selected area electron diffraction (SAED) of the single crystals dissolved for different times, coupled with dark field imaging, in order to map the coherent contribution to ED reflections from the different stem layers and to visualize the defects

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Detailed response on the comments (*written in blue*) by Reviewer #1

Described in this paper is how a narrow low-molecular-weight fraction of PEO was spin-coated into a thin film, then melt-crystallized and finally how the dissolution of the thus obtained dendritic crystals was monitored by AFM. The idea of the experiment is sound and the execution apparently well performed. The problem is the interpretation and the authors' patchy background knowledge that did not allow them to put their results in a proper perspective. There are also some inconsistencies in interpretation of the results, parts of the discussion contradicting other parts.

We are deeply grateful for the attention reviewer #1 has paid to our work and her/his very useful comments. The referee is right that our inadequate discussion of the literature impedes the understanding of the results as well as a smooth reading. Also, we thank the referee for the professional suggestions/comments that helped us to recognize some important issues with respect to our conclusions. We believe that the revised manuscript has been improved in clarity and quality thanks to the referee's constructive comments. In the following, we provide responses to the comments and suggestions in a point-by-point fashion. **Again, we are very much indebted to you for your highly valuable advice!**

1. Starting with references, those pre-2010 to basics of polymer crystallization and morphology in the introduction are conspicuously missing. This 70-year-old field did not start in 2018, as a casual glance at the reference list might suggest. Already the 1st sentence on chain folding gives 3 references – all 2018. Also that thermal stability of lamellar crystals depends on lamellar thickness was not discovered in 2014 (ref 4), and that lamellar thickness is smaller than chain length and lateral lamellar size wasn't discovered in 2018 (refs 5,6).

We fully agree with the referee that the pioneering works on the basic knowledge of polymer crystallization and morphology in the multitude of pre-2010 publications are of great significance. As the referee pointed out, polymer crystallization has drawn much attention and there has been extensive research over the past at least seventy years.

Firstly, the concept of chain folding at least dates back to Storks in 1938 while investigating thin films of gutta-percha.^[R1] Later, in the 1950s, Jaccodine^[R1], Keller^[R2], Fischer^[R3] and Till^[R4] have made experiments which allowed to characterize and analyze chain-folded polymer single crystals. In particular, Keller had the major merit to popularize and to transfer the concept of chain folding to bulk materials. Since then, chain-folding was recognized as a conformational motif in crystalline structures of all

chain-like molecules. Furthermore, the chain-folding model has become a prevailing concept for the investigation of polymer crystallization. Thus, the discovery of chain-folded states has triggered countless investigations on the crystallization process of polymers.^[R5-9]

Experimental observations enabled by an isochronous decoration method^[R10] showed that switching between two crystallization temperatures resulted in sharp boundaries between regions differing in well-defined lamellar thickness. This observations proved that the lamellar thickness reflects the kinetic stability at the lateral growth front.^[R11, 12] Armitstead et al.^[R13] have proposed that the growth rate is the consequence of a driving force and a barrier term. The thickness corresponding to the maximum growth rate is slightly above the minimum thickness which is required for thermodynamic stability. This minimum thickness has been experimentally shown to be inversely proportional to the degree of supercooling.

The lamellar thickness of chain-folded polymer crystals is usually in the range of ten to some tens of nanometers, which is much less than the chain contour length and the lateral size of the crystal.^[R2, 14] Such a limited thickness has consequences (i.e., reduces) their thermal stability.^[R15] The corresponding melting temperature depression associated with the finite crystal thickness can be expressed quantitatively through the Gibbs–Thomson relation^[R16], as applied to polymer crystals in the Hoffman–Weeks formulation^[R17, 18].

Accordingly, we have improved the manuscript and added these classic studies in the modified version.

The sentences “Polymer crystals usually grow at conditions far away from thermodynamic equilibrium, giving rise to metastable lamellar crystals, often consisting of highly folded chains. It is generally believed that fast kinetic pathways determine the degree of metastability (lamellar thickness) of a folded-chain lamella. Mostly, thermal stability of lamellar polymer crystal is related to their lamellar thickness, which is typically much less than the chain contour length and the lateral size of the crystal.” ***have been modified as*** “As already revealed by observations in the pioneering works by Keller¹, Till² and Fischer³, polymer crystals usually grow at conditions far away from thermodynamic equilibrium, giving rise to metastable lamellar crystals, often consisting of highly folded chains.^{4, 5} It is generally believed that (fast) kinetic pathways determine the (small) thickness of a folded-chain lamellar crystal.⁶⁻⁹ Commonly, the thermal stability of polymer crystal is related to their lamellar thickness^{10, 11}, which is typically much less than the chain contour length and the lateral size of the crystal^{1, 12}.” (Page 3 line 42-48)

The following references have been added. (Page 24 line 482-509)

1. Keller, A. A note on single crystals in polymers: Evidence for a folded chain configuration. *Philosophical Magazine* **1957**, 2 (21), 1171-1175.
2. Till Jr, P. H. The growth of single crystals of linear polyethylene. *Journal of Polymer Science* **1957**, 24 (106), 301-306.
3. Fischer, E. Stufen-und spiralförmiges Kristallwachstum bei Hochpolymeren. *Zeitschrift Naturforschung Teil A* **1957**, 12a, 753-754.
4. Ungar, G.; Stejny, J.; Keller, A.; Bidd, I.; Whiting, M. C. The Crystallization of Ultralong Normal Paraffins: The Onset of Chain Folding. *Science* **1985**, 229 (4711), 386-389.
5. Keller, A.; Cheng, S. Z. D. The role of metastability in polymer phase transitions. *Polymer* **1998**, 39 (19), 4461-4487.
6. Bassett, D. C.; Keller, A. On the habits of polyethylene crystals. *Philosophical Magazine* **1962**, 7 (81), 1553-1584.
7. Dosiere, M.; Colet, M. C.; Point, J. An isochronous decoration method for measuring linear growth rates in polymer crystals. *Journal of Polymer Science Part B: Polymer Physics* **1986**, 24 (2), 345-356.
8. Tian, M.; Dosiere, M.; Hocquet, S.; Lemstra, P. J.; Loos, J. Novel aspects related to nucleation and growth of solution grown polyethylene single crystals. *Macromolecules* **2004**, 37 (4), 1333-1341.
9. Armitstead, K.; Goldbeck-Wood, G., Polymer crystallization theories. In *Macromolecules: Synthesis, Order and Advanced Properties*, Springer Berlin Heidelberg: Berlin, Heidelberg, 1992; pp 219-312.
10. Hoffman, J. D.; Weeks, J. J. Melting Process and the Equilibrium Melting Temperature of Polychlorotrifluoroethylene. *Journal of Research of the National Bureau of Standards. Section A, Physics and Chemistry* **1962**, 66A, 13-28.
11. Wunderlich, B., *Macromolecular Physics, Crystal Melting*. First Edition ed.; Academic Press: New York, 1980; Vol. 3, p 363.
12. Keller, A. Polymer crystals. *Reports on Progress in Physics* **1968**, 31 (2), 623.

2. But a more serious problem is the authors' apparent unawareness of the seminal works on crystallization and morphology of melt-grown single crystals of the very same system, i.e. narrow low-molecular fractions of PEO, by Andre Kovacs in the 1970s. E.g. J. Polym. Sci., Polym. Symp. 1975, 50, 283; or Prog. Colloid Polym. Sci. 1975, 58, 44. No reference even to single crystal morphologies of the same system by Stephen Cheng, whom they otherwise cite in a different context. Had they studied those works, particularly the intriguing changes of crystal habits on annealing by Kovacs, they could have achieved a better understanding of their own observations.

We thank the referee for this highly valuable advice. As the referee notes, the

crystallization behavior of low-molecular-weight (LMW) PEO fractions has been extensively studied by André Kovacs et al.^[R19-23] and Cheng et al.^[R24-35] Both groups found that the shape of PEO single crystals, when grown from the melt, changes from a faceted to a rounded and back to a faceted habit in a temperature range near the equilibrium melting temperature.^[R19, 20, 22, 23, 27] Kovacs et al.^[R19-23] demonstrated the relationship between linear growth rate, single crystal morphology, and the integral folding (IF) structure. Cheng et al.^[R27, 36] suggested that the growth rate difference along different crystallographic planes of LMW PEO single crystals indicates the different dependencies on supercooling for nucleation barriers of the (120) and (100) planes. Thus, specific values of the nucleation barriers exist for the various crystallographic planes.

In particular, Kovacs et al.^[R20] systematically studied the thickening and melting behaviors of LMW PEO crystals. Their experiments **for crystals of once-folded chains** resulted in several observations. (1) Chain folded crystals do not superheat since they start to shrink without any appreciable time lag. (2) The decrease of their dimensions along the two symmetry axes is proportional to the melting time. (3) Along these directions, **the rates of shrinkage, or rates of melting, are constant** and depend on the degree of superheating. However, the shrinkage is initially more rapid at the corners of the crystals. Their growth faces, thus, become rounded and the overall habit ellipsoidal, reminiscent of the Wulff construction of equilibrium crystal shapes (https://en.wikipedia.org/wiki/Wulff_construction). (4) During melting, the interior of a folded chain crystal thickens around the central seed or other extended chain nuclei.

On the other hand, **for extended chain crystals**, when the temperature is higher than their melting point, Kovacs et al. have found that they do not thicken and **their initial rate of melting gradually decreased with time before reaching a constant value**. These observations are similar to the temporal variation of dissolution rate observed in our experiments, which also showed an initial decrease and then remained unchanged.

Accordingly, we have modified and improved our manuscript.

The sentence “In accordance with previous studies^{33, 34} on the molecular model of chain packing in a lamellar PEO single crystal, the coordinate system in lower left corner of panel (d) indicates the orientation of the $a \cdot \sin\beta$ - and b -axis of the monoclinic crystal unit cell (see also Figure S3). The two black arrows labelled $a \cdot \sin\beta$ and b indicate the (100) and (010) planes, respectively.” *has been added.* (Page 8 line 148-151)

The sentence “Kovacs et al.^{35, 36} and Cheng et al.³⁴ found that the habit of low molecular weight PEO single crystals, which were grown from the melt, changed from faceted to circular and back to faceted within a narrow range of supercooling.” *has*

been added. (Page 8 line 154-156)

The following references have been added. (Page 25 line 565-576)

33. Kovacs, A.; Straupe, C.; Gonthier, A. Isothermal growth, thickening, and melting of poly(ethylene oxide) single crystals in the bulk. II. *Journal of Polymer Science: Polymer Symposia* **1977**, 59 (1), 31-54.

34. Cheng, S. Z. D.; Chen, J. Nonintegral and integral folding crystal growth in low-molecular mass poly (ethylene oxide) fractions. III. Linear crystal growth rates and crystal morphology. *Journal of Polymer Science Part B: Polymer Physics* **1991**, 29 (3), 311-327.

35. Kovacs, A. J.; Gonthier, A. Crystallization and fusion of self-seeded polymers. *Kolloid-Zeitschrift und Zeitschrift für Polymere* **1972**, 250 (5), 530-552.

36. Kovacs, A. J.; Gonthier, A.; Straupe, C. Isothermal growth, thickening, and melting of poly(ethylene oxide) single crystals in the bulk. *Journal of Polymer Science: Polymer Symposia* **1975**, 50 (1), 283-325.

*3. The other major problem, hampering appropriate interpretation of results, is the lack of realization by the authors that the (140) faces of PEO crystals are not crystallographic planes but are, instead, rough (120) faces of variable tilt resulting from high secondary nucleation rate and unequal spreading rates of layers in opposite directions due to the asymmetry of the (120) crystallographic planes – see Shcherbina et al. *Macromolecules*, 2007, 40, 402. (see also below).*

We sincerely appreciate this highly valuable comment. The referee is fully right that the apparent (140) facets are in fact rough (120) growth faces.

As we mentioned above, Kovacs et al.^[R19, 20] and Cheng et al.^[R27] found that the shape (habit) of PEO single crystals, which were grown from the melt, changed from faceted to circular and back to faceted within a narrow range of supercooling. In view of the observed habit, which involves two (100) and four (140) growth faces,^[R19, 20] Kovacs et al.^[R21] have proposed a molecular model for chain packing in a PEO single lamellar crystal. In this model, the folds are supposedly parallel to the (120) planes as in solution-grown crystals.^[R37] Though (100) folds may also be conceived in the (100) sectors, Cheng et al.^[R27] have proved later that the (100) folds are less favorable. Folds parallel to (140) are, however, unrealistic, since they would involve a fold packing which is too dense in the corresponding sectors. In addition, on a molecular scale, the growth faces of the PEO single crystals are highly serrated rather than smooth.^[R21] Cheng et al.^[R27] have suggested that the (120) growth faces are molecularly smooth, in contrast to other faces. Additionally, the apparent (140) facets are not densely packed planes. By contrast, single crystals of PEO grown from a dilute solution are clearly

bounded by (100) and (120) facets, both densely packed.^[R37] Further, for high molecular weight PEO lamellar single crystals grown from solution, Cheng et al.^[R38] showed that chain folding is mostly along the (120) growth planes.

To explain these morphological features, Ungar et al.^[R39, 40] computed the growth habit of PEO crystals using the Frank-Seto model. They proposed that the apparent (140) facets are in fact (120) growth faces with steps traveling toward the outlying (100) faces 4 times faster than away from them. This causes a pileup of growing layers toward the borders with (100) faces, causing the (120) faces to tilt. By contrast, crystals that grow from a dilute solution tend to have a low initiation-to-propagation ratio and thus display crystallographic facets. Therefore, Ungar et al.^[R39, 40] have suggested that the actual fold planes in PEO crystals are (100) and (120). Specifically, these planes have the highest lateral surface energy and the lowest growth rate. Moreover, they calculated that PEO single crystals are constructed from two symmetric (100) planes and four asymmetric (120) planes.

Consequently, we fully agree with the referee that the apparent (140) facets in our case are in fact rough (120) faces. Thus, we have modified and improved the manuscript (both, text and corresponding figures) accordingly.

The sentences “Figures 2b-d show the morphological changes of the crystal within $t_d = 300$ s. It is visible that the crystal started to dissolve along the contour line. Later on, it shrank along particular crystallographic planes, i.e., the (120) and (140) planes (see Figure 2b and 2c).” ***have been modified as*** “Figures 2b-f and S5a-c show that the morphological changes of the crystal at different dissolution stages. In the early stage of dissolution (i.e., within $t_d = 300$ s), two distinct pathways were clearly observed in the dissolution of dendritic crystal. It is visible that the branches grown along the (120) normal directions started to dissolve along the contour lines. Later on, they shrank along particular crystallographic planes (see Figure 2b).” (Page 12 line 220-225)

The sentences “Figure 2 revealed that the dissolution of dendritic PEO crystals occurs along specific crystallographic planes. Computing the growth habit of PEO crystals with the help of the Frank-Seto model, Ungar et al.^{48, 49} concluded that the fold planes in PEO crystals are (100) and (120). They also proposed that the apparent (140) facets of PEO crystals grown from the melt are in fact rough (120) faces of variable tilt, which resulted from a high secondary nucleation rate and unequal spreading rates of layers in opposite directions due to the asymmetry of the (120) crystallographic planes. Therefore, we suggest that during early stages the dissolution of PEO dendritic crystals is mainly along the rough and smooth (120) planes, designated as R(120) and S(120), respectively.” ***have been added.*** (Page 13 line 242-250)

Figure 2 has been modified as: (Page 11 line 200-215)

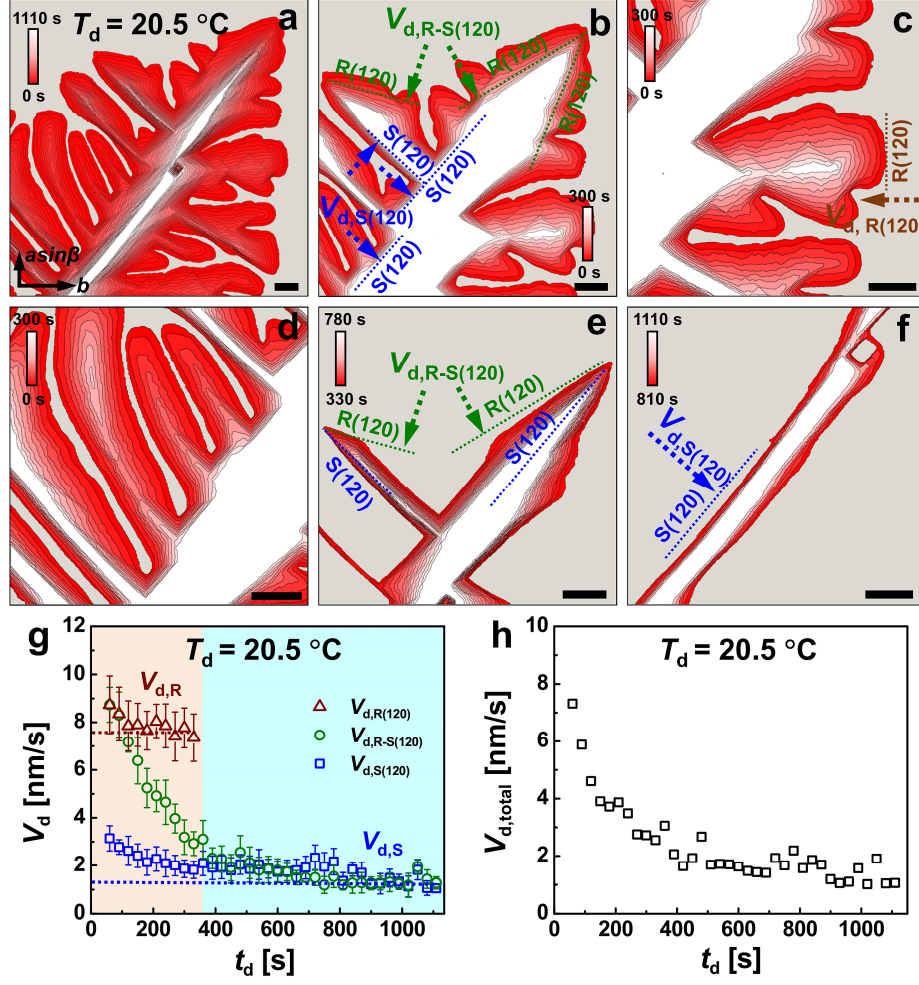


Figure 2. Temporal evolution of morphology in PEO lamellar crystals induced by selective dissolution and the dissolution kinetics of PEO lamellar crystals. (a) A false-colour overlay of AFM images showing the contour of a PEO crystal taken at different times (t_d) in the course of selective dissolution in toluene at $T_d = 20.5\text{ °C}$. The bare substrate is represented in a grey colour. The initial PEO crystal was grown at $(T_c, t_c) = (49\text{ °C}, 120\text{ s})$. Overlays of AFM images for the t_d -range of: (a) 0 ~ 1110 s, (b-d) 0 ~ 300 s; (e) 330 ~ 780 s and (f) 810 ~ 1110 s, respectively. The time intervals (Δt) between two successive layers for (a-e) and (f) are 30 s and 60 s, respectively. The scale bars represent 2 μm . (g) Time dependence of the dissolution velocity (V_d) along individual rough (120) and smooth (120) faces, respectively. The error bars indicate standard deviation. The brown and blue dashed lines correspond to the constant values, reached after a certain time, of the dissolution velocity along the R(120) and S(120) faces, respectively, which are designated as $V_{d,R}$ and $V_{d,S}$. The dissolution velocity of the branches grown along directions normal to (120) planes is denoted as $V_{d,R-S(120)}$, representing the transition from the dissolution of R(120) planes to the dissolution of S(120) planes. (h) Plot of the overall dissolution velocity ($V_{d,total}$) versus time during dissolution at $T_d = 20.5\text{ °C}$.

The following references have been added. (Page 26 line 606-610)

48. Shcherbina, M. A.; Ungar, G. Asymmetric Curvature of Growth Faces of Polymer Crystals. *Macromolecules* **2007**, 40 (3), 402-405.

49. Shcherbina, M. A.; Chvalun, S. N.; Ungar, G. Effect of crystallization conditions on the shape of polymer single crystals: Experimental and theoretical approaches. *Crystallography Reports* **2007**, 52 (4), 707-720.

4. Regarding holes in the annealed crystals, on L 161, when mentioning holes observed in annealed single crystals, it says “This morphology (in particular the holes) were attributed to heterogeneities within such crystals, expressed as variations in the degree of metastability. [6, 11]” Holes are holes, not heterogeneities. Of course, they are likely to be nucleated on defects. Incidentally, as far as I am aware, those holes go back to Statton, published in the 1960s. And were found to be due to the material adhering to the substrate, hence unable to move toward thickened areas. When deposited on “slippery” gel, crystals were shown to thicken without the creation of holes. In fact when crystals were annealed in solution, not only did they not develop holes, but it was clear from their electron micrographs along which crystallographic planes the material had been slipping toward the thickening areas and feeding them. (Organ et al. J. Polym. Sci., Pt. B: Polym. Phys. Ed. 1990, 28, 2365).

We thank the referee for this highly valuable advice. The referee is right that the holes, which could be nucleated on defects or were controlled to some extent by properties of the substrate, should not be labelled as heterogeneities.

In their pioneering work, Statton and Geil^[R41] observed the formation of holes in single PE crystals during annealing from which they deduced changes in the folding process. Organ et al.^[R42] visualized the morphology of C₁₉₈H₃₉₈ crystals annealed in solution and revealed that the thickened region spread along the sector boundaries. Moreover, they reported that circular holes were rarely seen in these crystals, even at very advanced stages of thickening. Winkel and coworkers^[R43] demonstrated that dendritic structures were observed after the annealing of once-folded C₁₆₂H₃₂₆ crystals and some kind of holes were often formed at the growth front. However, for extended-chain crystals of the same material, they found no holes formed after comparable treatment. Nakamura et al.^[R44, 45] investigated the morphological changes of PE single crystals on various substrates by AFM. They found that holes were generated in PE single crystals on glass and Pt/Pd substrates, but no holes formed in PE single crystals on HOPG and amorphous carbon.

Magonov et al.^[R46] have studied the thermal behavior of single crystals of ultralong alkanes C₃₉₀H₇₈₂ and single crystals of PE at different temperatures. They observed that thickening proceeded simultaneously with the formation of holes during annealing of

dry C₃₉₀H₇₈₂ crystals. However, in PE the formation of thickened rims did not follow immediately the formation holes. This is probably because the polymer chains require longer time for local reorganization as compared to the alkane. They also suggested that in annealed single crystal holes began to form when sufficient free volume, from vacancy-like defects within the crystal or free volume from pores and channels at the interface between the polymer crystal and the substrate, diffused to the nascent hole. The diffusion of crystallographic defects, such as dislocations or grain boundaries, towards the site of the nascent hole provides a mechanism that can improve the perfection of the crystal by filling small empty spaces in or under the crystal. Once all the free volume related to such defects is accumulated in holes, a process which is probably rather fast, the thickening process can then result in the buildup of rims around the holes, as it is observed.

Accordingly, we propose that the rectangular-shaped holes in the dissolution patterns were initiated by the diffusion and accumulation of vacancy-like defects within the crystal, and then grew by selective dissolution. Most notably, the sites and number density of dissolution holes observed here may be considered to be a measure of the distribution and number density of defects within the crystal, since the competitive processes of lamellar thickening and perfecting of the crystal are not expected to occur under the conditions employed during (rapid) selective dissolution.

Therefore, we modified and improved the manuscript according to above discussion.

The paragraph “In the annealed crystal, a few holes (empty regions) were formed (see Figures 1b). Many previous studies on annealed single crystals have reported the formation of a “Swiss-cheese” morphology with randomly distributed (mostly circular) holes of varying sizes. This morphology (in particular the holes) were attributed to heterogeneities within such crystals, expressed as variations in the degree of metastability. Surprisingly, within the washed crystal several rectangular-shaped holes of various sizes were generated (see Figures 1e). We propose that the removed parts consisted of less stable regions within the lamellar crystal, which could be dissolved in toluene at 21 °C. The dissolution pattern with rectangular-shaped holes, made visible by selective dissolution, may be related to the “Swiss-cheese” morphology formed upon annealing. Both types of holes are probably demonstrating variations in the degree of metastability within the lamellar crystal.” ***has been modified as:***

“The morphology of the annealed crystals revealed the formation of a few holes (see Figures 1b). In fact, many previous studies³⁸⁻⁴³ on annealed single crystals of PE or long-chain alkanes have reported the formation of a “Swiss-cheese” morphology with randomly distributed (mostly circular) holes of varying sizes. Magonov et al.⁴¹ have suggested that the holes in annealed single crystals began to form when sufficient free

volume, from vacancy-like defects within the crystal or free volume from pores and channels at the interface between the polymer crystal and the substrate, diffused to the nascent hole. Once all the free volume related to such defects was accumulated in holes, the thickening process then resulted in the buildup of rims around the holes. In order to minimize the surface energy, the shape of the holes is expected to be circular. Surprisingly, within the washed crystal, several rectangular-shaped holes of various sizes were generated (see Figures 1e). We propose that such rectangular-shaped holes, which may be related to the previously observed “Swiss-cheese” morphology, represent patterns that were initiated by the diffusion and accumulation of vacancy-like defects within the crystal, and then grew by selective dissolution. Due to the rapid diffusion of detached polymer chains into the solvent, the resulting holes are characterized by dissolution along specific crystallographic planes, yielding a rectangular shape of the holes. Most notably, since the competitive processes of lamellar thickening and perfecting of the crystal are not expected to occur under the conditions employed during selective dissolution, the sites and number density of dissolution holes observed here may be considered to be a measure of the distribution and number density of defects within the crystal.” (Page 9 line 175 – Page 10 line 196)

The following references have been added. (Page 26 line 580-587)

38. Statton, W. O.; Geil, P. H. Recrystallization of polyethylene during annealing. *Journal of Applied Polymer Science* **1960**, 3 (9), 357-361.

39. Nakamura, J.; Tsuji, M.; Nakayama, A.; Kawaguchi, A. Substrate-controlled reorganization of solution-grown polyethylene single crystals through partial melting. *Macromolecules* **2008**, 41 (4), 1358-1363.

40. Nakamura, J.; Kawaguchi, A. In situ observations of annealing behavior of polyethylene single crystals on various substrates by AFM. *Macromolecules* **2004**, 37 (10), 3725-3734.

5. L 254 and Figures 2 and S4 e,f: As mentioned above, the seemingly “140” facet is a product of unequal layer spreading rates on (120) planes during crystal growth. The “140” face is thus not regular as drawn in Figure S4f, but has irregularly distributed steps reflecting random growth. It would have been interesting to consider the kinetics of asymmetric dissolution, or “unzipping”, of layers of stems on the (120) face, causing the tilt of the crystal edge to appear like (130) or (140) facets. Of course taking into account, at the same time, that the edge is affected by the dynamic near-equilibrium between stem dissolution and deposition. Instead, while describing Fig 2, the authors keep stating that “different crystallographic planes exhibited different dissolution rates.” What they mean here is that (140) dissolves faster than (120). It is not unexpected that a plane with more steps on it, i.e. the “140”, would dissolve faster

than a plane with no steps (i.e. a smooth 120). Instead, the authors offer a rather vague and uncommitting view of the observations in Fig 2 (L 198-): “In analogy to crystallization, the rate-limiting step of dissolution is associated with the detachment probability of crystalline stems or whole chains from the various crystal faces. The corresponding energy barriers for dissolution is related to the surface free energy of crystalline stems or whole chains on the dissolution front. These energy barriers may depend on the orientation of the crystal surface and may vary with the local degree of metastability, which includes the degree of chain folding.” Just like crystallization does not depend just on attachment rate and attachment barrier, but also on thermodynamic driving force, i.e. free energy difference between the phases and hence the lifetime of the depositions, so dissolution equally depends on its driving force, which is undoubtedly larger for a rough face than for a smooth one.

The referee suggests an excellent way of interpreting our data. As discussed above, the referee is fully right that the apparent (140) facets in our case are in fact rough (120) faces. Therefore, the dissolution of PEO lamellar crystals is along the smooth and rough (120) planes, respectively. In view of this, our observations showed that the rough (120) planes dissolved faster than smooth (120) planes.

Armitstead et al.^[R13] have proposed that the combination of driving force and free energy barrier terms determines the growth rate of lamellar polymer crystals. The driving force of polymer crystallization is related to the difference of free energies between the crystalline state and the amorphous phase in the undercooled melt.^[R47] The main kinetic barrier for the process of depositing a new stem is related to the degree of folding. So, the two main factors that determine the growth rate are the thermodynamic driving force and the kinetic barrier of a deposition of the first stem of appropriate length on a (smooth) crystal surface.^[R48] For example, the driving force for crystallization of extended chains is larger than that for folded chains, but folded-chain crystallization is faster due to a lower kinetic barrier.

Similarly, the dissolution rate of lamellar polymer crystals is also the result of an interplay between kinetic barrier and driving force. It should be noted that these two main factors both depend on the degree of undercooling. For the case of dissolution, which is opposite to crystallization but with some analogy to melting, the free energy difference of a rough face (at any given dissolution temperature in an almost infinitely dilute solution) is higher than that of a smooth one. Therefore, the rough face has a larger driving force for dissolution. Furthermore, dissolving a chain or stem from a rough crystalline face requires to generate less “new” surfaces (on the average, on a rough surface, molecules have fewer nearest crystalline neighbors). Thus, the corresponding kinetic barrier for detachment of a stem or a chain from rough faces is

expected to be lower. Consequently, we agree with the referee that rapid dissolution of rough faces is attributed to a larger thermodynamic driving force and a lower kinetic barrier.

Consequently, we modified and improved the manuscript accordingly.

The sentences “This difference may be related to the variation of growth rates of crystallographic planes resulting from differences in surface nucleation barriers. In analogy to crystallization, the rate-limiting step of dissolution is associated with the detachment probability of crystalline stems or whole chains from the various crystal faces. The corresponding energy barrier for dissolution is related to the surface free energy of crystalline stems or whole chains on the dissolution front. These energy barriers may depend on the orientation of the crystal surface and may vary with the local degree of metastability, which includes the degree of chain folding.” **have been modified as** “Therefore, the difference in dissolution behavior between branches may be related to the changes in the values of the thermodynamic driving force and the kinetic barrier for dissolution of polymer stems or chains from rough faces. Similar to the growth rate⁹, the dissolution rate of lamellar polymer crystals is also the result of an interplay between kinetic barrier and driving force. It should be noted that these two main factors both depend on the degree of undercooling. Dissolution is opposite to crystallization but has some analogy to melting. There, at any given dissolution temperature in an almost infinitely dilute solution, the free energy difference (i.e., the gain) upon dissolving a polymer from a rough face is higher than from a smooth one. Therefore, the driving force for dissolution is larger for rough faces. Furthermore, dissolving a chain or stem from a rough crystalline face requires to generate less “new” surfaces (on the average, molecules have fewer nearest crystalline neighbors on a rough surface). Thus, the corresponding kinetic barrier for detachment of a stem or a chain from rough faces is expected to be lower.” (Page 17 line 341-354)

6. In the paragraph starting on L 228 the difference between dissolution rates of two dendrite branches is attributed to their different orientations relative to the concentration gradient in the solution. “The latter dissolved away in toluene at 20.5 °C within 300 s, but the former remained until 780 s.” What concentration gradient would persist in a toluene solution for 13 minutes and why? And which way was the gradient directed anyway? Decreasing concentration with decreasing distance from the crystal? Evidence from experiments on polymer crystals in solution is in fact opposite – higher local concentration near the crystal surface. By the way, I find the stated analogy with the direction of temperature gradient in quenching metal melts rather irrelevant and unhelpful.

We thank the referee for this highly valuable advice.

Firstly, we apologize for having presented an inaccurate and misleading description. At that point in the manuscript, we are referring to the concentration gradient in the ultrathin molten film during the growth of PEO lamella, not in the solution during the dissolution. Generally, polymer crystallization yields meta-stable patterns which are particularly pronounced in thin films where diffusion-controlled structures can be formed. Due to the slow growth rate of polymer crystals, the latent heat released during crystallization can easily be distributed homogeneously within the system, often on time scales much shorter than the time needed for attaching molecules. There, the transport of thermal energy is typically much faster than the often slow rate of diffusion of polymers within the thin film. Thus, crystallization is not generating significant thermal gradients and temperature can be assumed to be constant throughout the film. Accordingly, growth is essentially driven by density or concentration gradients and the corresponding gradients in the chemical potential.^[R49]

Secondly, we fully agree with the referee that the stated analogy with the direction of temperature gradient in quenching metal melts is indeed irrelevant and not helpful. Our results suggested that the branches oriented along directions different to the (120) normal direction dissolved faster (see Figure 2c and d) than branches grown along the (120) normal direction.

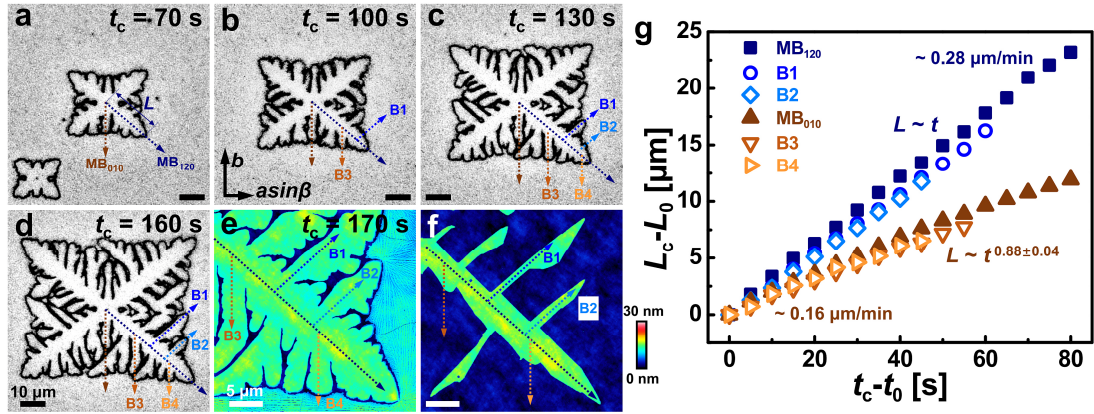


Figure 3. In situ observations of crystal growth. (a-d) Optical micrographs showing the evolution of a PEO crystal growing at 49 °C in a ca. 9 nm thin film. The insert in lower left corner of (a) is the micrograph of the PEO dendritic crystal at $t_c = 40$ s. (e) Height image of the dendritic PEO crystal grown at $(T_c, t_c) = (49 \text{ °C}, 170 \text{ s})$, i.e., the crystal before dissolution experiments. (f) Surface topography of PEO crystal obtained after selective dissolution in toluene at $(T_d, t_d) = (23 \text{ °C}, 30 \text{ s})$. (g) The growth kinetics in terms of branch length ($L_c - L_0$) as a function of $(t_c - t_0)$. L_c and L_0 are the branch length at t_c and t_0 , respectively. Please note that the value of t_0 for MB_{120} , B1 and B2 is the same as for MB_{010} , B3 and B4, respectively.

Further, following crystallization in time, we have investigated the formation of distinct branches and determined their growth rate. In Figure 3, we explored the growth of six individual branches of a PEO dendritic crystal at 49 °C in situ by optical microscopy, starting from the crystallization time of 40 s (see the insert in Figure 3a). Among the six, four main branches were along the (120) normal direction and two along the (010) normal direction (i.e., along the b axis), designated as MB₁₂₀ and MB₀₁₀, respectively. Due to Mullins-Sekerka growth instabilities, dendritic side branches were generated, emerging from the MB₁₂₀ branches and growing along various crystallographic planes (see Figure 3a-c). Most significantly, we found that, mainly due to the difference in growth rates, the growth of side branches, which emerged from the MB₁₂₀ branches, eventually surrounded the MB₀₁₀ branches and thus finally prevented their further growth (see Figure 3c).

To quantitatively corroborate this physical picture, we measured the length, L , of main and side branches along various crystallographic planes. Figure 3g shows the growth kinetics in terms of branch length ($L_c - L_0$) as a function of $(t_c - t_0)$ for different branches. Here, L_c and L_0 are the branch length at t_c and t_0 , respectively. One can clearly see that the length of branches (e.g., the ones labelled as MB₁₂₀, B1 and B2) growing along (120) normal directions increased linearly with time ($L \sim t$), whereas that of branches (e.g., the ones labelled as MB₀₁₀, B3 and B4) growing along (010) normal directions eventually increased in a nonlinear fashion with time (if we would assume a power law dependence, this would yield $L \sim t^{0.88 \pm 0.04}$). The branches along (120) normal directions grew faster ($\sim 0.28 \mu\text{m}/\text{min}$) than the ones along (010) normal directions ($\sim 0.16 \mu\text{m}/\text{min}$). Most interestingly, the former survived but the latter disappeared after selective dissolution at 23 °C for 30 s (see Figure 3f).

Previous studies^[R50-52] showed that for crystals with a size (R) increasing linearly in time (t), i.e., $R \sim t$, their growth is nucleation-limited (NL). By contrast, if R increases in time as $R \sim t^{0.5}$, the crystal growth is diffusion-limited (DL). However, in accordance with the marginal stability criterion of Langer and Müller-Krumbhaar^[R53], Taguchi et al.^[R54, 55] have found that the growth rate of the leading growth tips was constant during growth (linear growth), and proposed, corroborating conclusions previously obtained by Sekerka^[R56], that surface kinetics, transport (diffusion), capillarity and surface nucleation control the growth process. The leading growth tip still advances at a constant velocity even in the diffusion controlled growth. Therefore, we suggest that the growth tip of branches (which follows $L \sim t$) of the branches along (120) normal directions is mainly controlled by (secondary) nucleation, while other branches of the dendritic crystal, including the branches along (010) normal directions, are profoundly affected by temporal changes in the number of polymers diffusing towards the growing branches.

In the diffusion-limited regime, growth is controlled by the diffusion of polymer to the growth face. In this case, the growth front may become unstable (Mullins-Sekerka instability) and thus may become roughened.^[R57] Especially when the degree of undercooling is increased, the crystal growth fronts are becoming increasingly rough, leading to the generation of a multitude of crystalline branches.^[R51] On the other hand, for example at low supercooling, nucleation controlled growth may generate flat growth faces, i.e., facets.^[R58]

In summary, branches in a direction different to the (120) normal direction grow slower but dissolve faster. Their growth is significantly affected by diffusion of a deficient number of polymer to the growing branch, resulting in the formation of rough (120) faces. By contrast, tips of branches along (120) normal directions exhibit growth of molecularly smooth interfaces (see Figure 3g), while the curved portion on the sides of these growth tip are influenced by diffusion resulting in a kinetically roughened growth front^[R59]. Similarly, Toda et al.^[R60] have observed that the melting velocity shows strong anisotropy in the directions of long and short axes for both PE and PVDF crystals. Such an anisotropy suggests that the rate determining process differentiates the lateral surfaces of different crystal indices.

We have modified and improved the manuscript accordingly. *The analysis and discussion presented above has been added.* (Page 14 line 280 – Page 17 line 340)

7. *Much of the subsequent text and figures concern the slowing down of dissolution with time. As seen in Fig 3a the main reason for the slowdown is the fact that “140” faces dissolve faster than the 120 faces, and as the former also approach the regularity of the 120 faces, i.e. as the faces become less rough and more resistant to dissolution, the whole dissolution process slows down, as shown in Fig 3b. The fact that the rough high-energy “140” faces dissolve faster than the smoother low-energy 120 faces is hardly surprising. The intriguing thing is that, by page 15, the authors seem to have forgotten about Figure 3b and the cause of the retardation of cumulative (overall) dissolution. Instead, they now attribute the slowdown to the crystal lamellae being thicker in the center of crystal than at the periphery. Incidentally, for the latter the authors provide no experimental evidence, even though they measure the crystal thickness by AFM. Then, by the time we reach the Conclusions, the authors change their minds again, and say (L 439): “This decay in dissolution velocity reflects that, due to reorganization in the course of their growth, the centre parts of the crystal were more stable than the peripheral ones.” Not clear what is now meant by “reorganization”, but this line is also repeated in the Abstract. But no mention at all any more about the early depletion of the fast-dissolving “140” faces.*

Thank you for your valuable advice and the clear criticism of the inadequate presentation of the interpretation of our observations. We fully agree that rough (120) faces dissolve faster than smooth (120) faces. Thus, in the course of time, the crystal faces become less rough and gradually approach the smooth (120) faces, so the overall dissolution rate slows down.

As shown in Figure 2b, the branches grown along (120) normal directions firstly dissolved along R(120) faces. These rough faces of variable tilt were consumed (almost) completely with time (see Figure 2e). Thus, eventually the dissolution of the remaining crystal was along S(120) faces. Accordingly, we denoted the initial dissolution velocity of the branches grown along (120) normal directions as $V_{d,R-S(120)}$, representing the transition from the dissolution of R(120) planes to the dissolution of S(120) planes. Besides, Figure 2c shows that the branches grown along (010) normal directions dissolved mainly along the contour line with a dissolution velocity equal to $V_{d,R(120)}$, as they most likely consisted of a number of serrated, microscopic R(120) planes. Figure 2 also shows that the grooves between the final trunks of dendritic branches widened with $V_{d,S(120)}$ along S(120) planes (see Figure 2f).

We traced the dissolution velocities as a function of t_d along the R(120) and S(120) faces, respectively. In Figure 2g, we plotted the value of $V_{d,R(120)}$, $V_{d,S(120)}$ and $V_{d,R-S(120)}$ against t_d . Both, $V_{d,R(120)}$ and $V_{d,S(120)}$ showed initially a slight decrease and then stayed constant during further dissolution. Such a slight reduction in $V_{d,R(120)}$ and $V_{d,S(120)}$ at the very beginning of dissolution can probably be attributed to stages of accelerated crystal growth occurring in the course of the quenching process after isothermal crystallization, generating a transition zone with a width of ca. 1 μm , which is less stable and thus dissolves somewhat faster. However, crystalline structures grown at constant temperature dissolved at a constant velocity. Remarkably, $V_{d,R(120), \text{const}} = V_{d,R}$ was about five times faster than $V_{d,S(120), \text{const}} = V_{d,S}$. Interestingly, the initial value of $V_{d,R-S(120)}$ was quite similar to $V_{d,R}$, then dropped by a factor of 5 during the first 400 s and eventually became constant at a value of $V_{d,S}$. As the referee correctly pointed out, our observations indicate that the transition from the dissolution of rough to the dissolution smooth planes is responsible for the decay of the total dissolution velocity ($V_{d,\text{total}}$) with time, which averages the dissolution velocity of all crystalline faces.

We have modified and improved the manuscript accordingly. The sentences in the manuscript related to “reorganization” have been deleted.

The sentences “The work by Hu et al. has reported that variations in crystal thickness (increasing gradually from edges to the centre of the crystals) of the single crystals could be responsible for two stages of crystal melting with different speeds at intermediate melting temperatures. In analogy to these observations, we conjecture that

the changes in $V_{d,\text{total}}$ with t_d is presumably reflecting the spatially varying degree of metastability within lamellae (e.g., the lamellar thickness or the local degree of order may increase towards the centre of the crystalline lamellae).” *have been deleted.*

The following paragraphs have been added. (Page 13 line 242 – Page 14 line 279)

“Figure 2 revealed that the dissolution of dendritic PEO crystals occurs along specific crystallographic planes. Computing the growth habit of PEO crystals with the help of the Frank-Seto model, Ungar et al.^{48, 49} concluded that the fold planes in PEO crystals are (100) and (120). They also proposed that the apparent (140) facets of PEO crystals grown from the melt are in fact rough (120) faces of variable tilt, which resulted from a high secondary nucleation rate and unequal spreading rates of layers in opposite directions due to the asymmetry of the (120) crystallographic planes. Therefore, we suggest that during early stages the dissolution of PEO dendritic crystals is mainly along the rough and smooth (120) planes, designated as R(120) and S(120), respectively. The branches grown along the (120) normal directions firstly and rather fast dissolved along R(120) faces (see Figure 2b). As these rough faces of variable tilt were consumed (almost) completely with time (see Figure 2e), dissolution of the crystal was eventually along S(120) faces. Accordingly, we denoted the initial dissolution velocity of the branches grown along (120) normal directions as $V_{d,R-S(120)}$, representing the transition from the dissolution of R(120) planes to the dissolution of S(120) planes. Besides, Figure 2c shows that branches grown along (010) normal directions dissolved mainly along the contour line with a dissolution velocity equal to $V_{d,R(120)}$, as they most likely consisted of a number of serrated, microscopic R(120) planes. Figure 2 also shows that the gaps between the final trunks of dendritic branches widened with $V_{d,S(120)}$ along S(120) planes.

We traced the dissolution velocities as a function of t_d along R(120) and S(120) faces, respectively. In Figure 2g, we plotted the value of $V_{d,R(120)}$, $V_{d,S(120)}$ and $V_{d,R-S(120)}$ against t_d . Both, $V_{d,R(120)}$ and $V_{d,S(120)}$ showed initially a slight decrease and then stayed constant during further dissolution. Such a slight reduction in $V_{d,R(120)}$ and $V_{d,S(120)}$ at the very initial stages of dissolution can probably be attributed to accelerated crystal growth occurring in the course of the quenching process after isothermal crystallization, generating a transition zone with a width of ca. 1 μm , which is less stable and thus dissolves somewhat faster. However, crystalline structures grown at constant temperature dissolved at a constant velocity. As shown in Figure 2g, the brown and blue dashed lines correspond to the eventually reached constant values of the dissolution velocity along the R(120) and S(120) faces, respectively, which we designated as $V_{d,R}$ and $V_{d,S}$. Remarkably, $V_{d,R}$ was about five times faster than $V_{d,S}$. Interestingly, the initial value of $V_{d,R-S(120)}$ was quite similar to $V_{d,R}$, then dropped by a factor of 5 during the

first 400 s and eventually became constant at the value of $V_{d,s}$. Therefore, our observations indicate that the transition from the dissolution of rough to the dissolution of smooth planes is responsible for the decay of the total dissolution velocity ($V_{d,total}$) with time (see Figure 2h), which averages the dissolution velocity of all crystalline faces.”

8. *Next the temperature dependence of the dissolution rate is considered. In Fig 5 a parameter related to the reciprocal of the speed of dissolution (denominator in the exponent in exponential decay of crystal with time) is plotted as log against $1000/T$ in an Arrhenius-type fashion. From the slope of the linear fit the authors obtain an activation energy E for dissolution, which is very high indeed. However, one has to be sceptical about the E -value derived in this way. At best, it is an estimate of the upper limit. The rate of dissolution does not depend only on the rate of detachment, but also on the rate of re-attachment. The net rate is the difference between the two. The authors’ method would only be valid if the back-reaction could be neglected, i.e. at infinite or very high dilution. Importantly with polymers, what matters is local, not global concentration, and that is rarely low. We should really know the polymer-solvent phase diagram, i.e. its liquidus curve. For polymers that curve is almost horizontal for most of the concentration range, so that one even talks about equilibrium dissolution temperature of a polymer in a solvent, as if it did not depend on concentration. In other words, the concentration should be really low indeed, and the solution should be vigorously stirred, for the re-attachment rate to be ignored. Satisfying neither of these requirements were mentioned in the text. It is therefore clear that the re-attachment rate and the lifetime of the unstable re-attachments may be strongly dependent on temperature and thus influence the determination of E via Arrhenius. A vivid illustration of the simultaneous dissolution and recrystallization for polymer crystals held in solution are the well-documented “picture-frame” crystals, which should also be mentioned in the paper.*

Again, this is an excellent suggestion. In the present study, PEO dendritic crystals were generated by isothermal crystallization in ultrathin films (ca. 9 nm) on silicon substrates. Then, the crystallized sample was dipped into a **PURE** solvent kept at a set temperature (T_d) for a period of time and subsequently retracted from the solvent and dried in a flow of nitrogen. For a given T_d , this dissolution step was repeated several times, adding up to a total dissolution time t_d . Please note that **PURE** solvent was used for **EACH** dissolution step.

Firstly, the referee is right that the global concentration during dissolution is extremely low (= the number of dissolved polymers in the total volume of solvent bath).

In this work, the samples have an area of $0.5 \times 0.5 \text{ cm}^2$ and a thickness of $\sim 9 \text{ nm}$, and the volume of solvent used for dissolution is 5 ml. Assuming that the polymer was completely dissolved in the solvent, then, the highest concentration can be calculated to be $4.8 \times 10^{-6} \%$. Since pure solvent was used for each dissolution step, the global concentration during dissolution should be significantly below $4.8 \times 10^{-6} \%$.

Besides, a control dissolution experiment as suggested by reviewer was carried out by rapidly oscillating the sample in the solvent vial, and the results were shown in Figures R1 and R2. To avoid temperature-induced changes in the diffusion constant of polymers in the solvent, the dissolution temperature was set to $19.5 \text{ }^\circ\text{C}$. Both, from the morphological changes of PEO dendrites and the overall dissolution velocity ($V_{d,\text{total}}$), it became clear that the dissolution velocities at quiescent and oscillation conditions were comparable within the uncertainty of the experiment (see Figure R2). Therefore, we assume that the local concentration around the crystals is extremely low, and the re-attachment rate can be ignored. In other words, reflecting the enormous gain in translational entropy, once a polymer is detached from the crystal front, it only has a negligible probability to find its way back to the crystal, like an astronaut once detached from the spaceship will basically never get back to the spaceship.

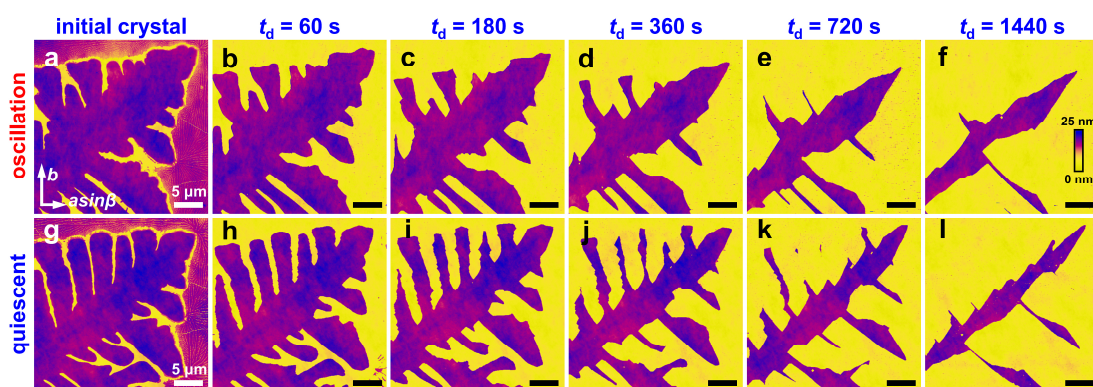


Figure R1. Temporal evolution of changes in morphology in PEO crystals, which were induced by selective dissolution. (a, g) Height images of the initial dendritic PEO crystals grown at $[(T_c, t_c) = (49 \text{ }^\circ\text{C}, 120 \text{ s})]$. Successive AFM height images showing the surface topographies of the PEO crystals after selective dissolution at (b-f) quiescent and (h-l) oscillation conditions, respectively, in toluene at the dissolution temperature $T_d = 19.5 \text{ }^\circ\text{C}$ for different times (t_d). Oscillation condition: the sample was manually shaken vigorously twice every 5 seconds.

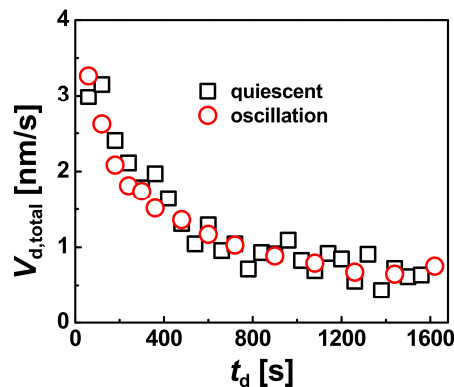


Figure R2. Plots of the overall dissolution velocity ($V_{d,total}$) as a function of dissolution time (t_d) in the course of dissolution in toluene at quiescent and oscillation conditions.

Furthermore, we have carefully read the references about the “picture-frame” crystals. On the one hand, when solution grown single crystals of poly-4-methyl-pentene-1^[R61] or polyethylene^[R10, 41, 62, 63] are heated in solution well above their crystallization temperature and kept at high temperature, the remaining (i.e., undissolved) polymer crystal exhibits the form (morphology) of a picture-frame which is considered to be associated with a solution-mediated process (i.e., by partial dissolution followed by recrystallization). On the other hand, Hobbs and Barham et al.^[R64] have reported that annealing long alkanes ($C_{294}H_{590}$) single crystal in dilute solutions can induce a picture-frame morphology. They suggested that large-scale cooperative rearrangements were involved within the solid-state of the crystal. They concluded that this was a faster process than dissolution and recrystallization. It should be noted that the “picture-frame” crystals observed in these references have generally been the result of annealing the solution-grown crystals in a dilute solution of finite concentration, no matter whether they are caused by recrystallization or solid-state thickening.

In contrast, the morphological changes which were observed in the present work are different from those reported for “picture-frame” crystals. This is probably because a pure solvent is used in each dissolution step, which makes both global and local concentrations extremely low, which does not allow for any significant re-attachment during dissolution. Furthermore, given that the samples were kept at maximum (after multiple steps) only up to ca. 1000 s in pure solvent, we do not anticipate any significant reorganization processes to occur. We have modified and improved the manuscript accordingly.

The sentences “It should be noted that the morphological changes which take place in this work are different from those reported for “picture-frame” crystals. “Picture-frame” crystals have generally been the result of recrystallization or solid-state thickening caused by annealing crystals supported on a substrate, which were

previously grown in a dilute solution.^{6, 38, 44-47} In contrast, since we used a pure solvent for each dissolution step, the corresponding global and local polymer concentrations around the crystal were extremely low, causing a negligible re-attachment rate during dissolution.” **have been added.** (Page 12 line 234-241)

The following references have been added. (Page 26 line 596-605)

44. Frank, F. C.; Keller, A.; O'Connor, A. Observations on single crystals of an isotactic polyolefin: Morphology and chain packing in poly-4-methyl-pentene-1. *The Philosophical Magazine: A Journal of Theoretical Experimental and Applied Physics* **1959**, 4 (38), 200-214.

45. Holland, V. F. Dislocations in Polyethylene Single Crystals. *J Appl Phys* **1964**, 35 (11), 3235-3241.

46. Blackadder, D. A.; Schleinitz, H. M. The dissolution and recrystallization of polyethylene crystals suspended in various solvents. *Polymer* **1966**, 7 (12), 603-637.

47. Hobbs, J. K.; Hill, M. J.; Barham, P. J. Isothermal thickening of single crystals of C294H590 in dilute solution. *Polymer* **2000**, 41 (25), 8761-8773.

Less important but needing attention:

9. *L 52: “Generally speaking, heterogeneity within a polymer lamellar crystal is reflecting differences in packing of molecules, varying somewhere between perfectly arranged crystalline structures and fully amorphous chain segments. [8]” This statement is dubious and contradicts the well-accepted 2-phase model of semicrystalline polymers. It reminds one of the very early days of studies of semicrystalline polymers, where a view existed that those polymers adopt a state between crystal and amorphous, denying the 2-phase structure.*

Thank you for your suggestion! We apologize for this imprecise description. Accordingly, we have modified and improved the manuscript.

The sentence “Generally speaking, heterogeneity within a polymer lamellar crystal is reflecting differences in packing of molecules, varying somewhere between perfectly arranged crystalline structures and fully amorphous chain segments.” **has been modified as** “For polymer crystals, Keller and Cheng¹⁵ have proposed a particular hierarchy of metastabilities: One class of metastable states is related to differences in the lattice parameters (sometimes called classical metastable states) and another class of metastable states is related to the finite and often only nanometer small thickness of lamellar polymer crystals bounded by fold surfaces, which can be described as states of metastable morphologies.” (Page 3 line 56-61)

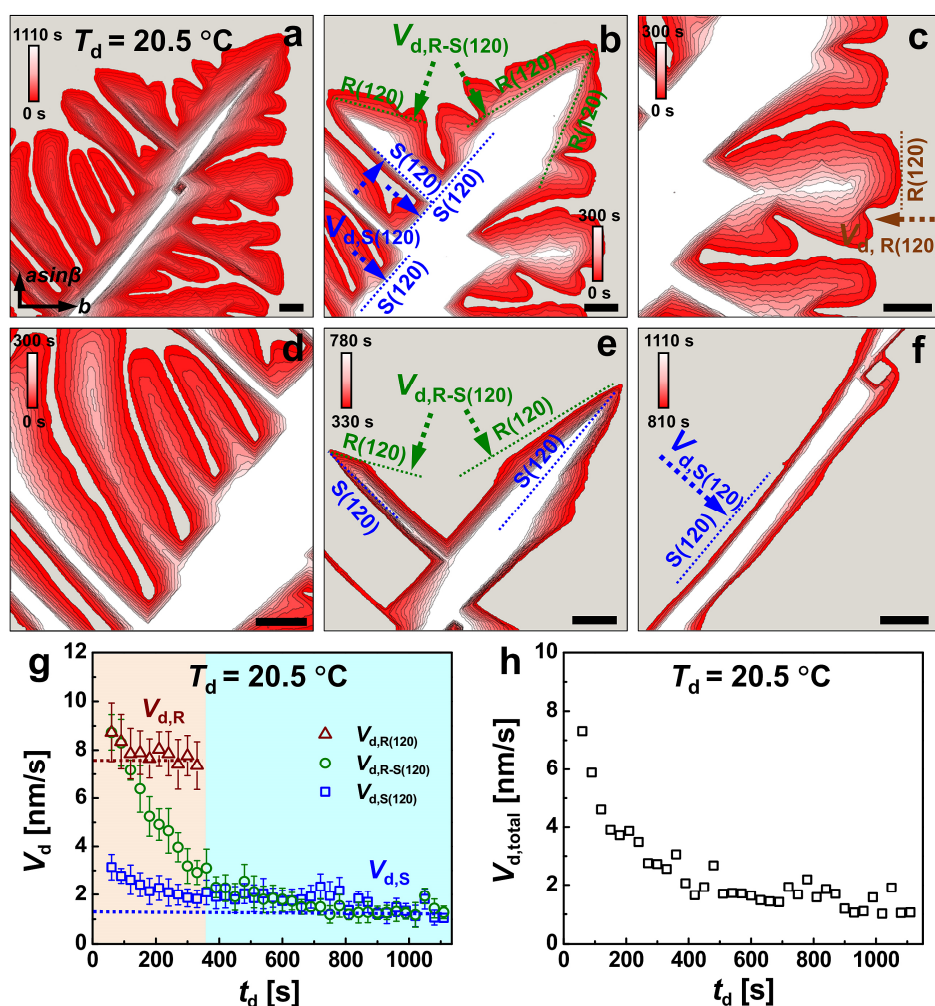
The following references have been added. (Page 24 line 514-516)

15. Cheng, S. Z. D.; Keller, A. The Role of Metastable States in Polymer Phase Transitions: Concepts, Principles, and Experimental Observations. *Annual Review of Materials Research* **1998**, 28, 533-562.

10. *It is unfortunate that the authors use symbol a^* for $a \sin(\beta)$ in describing the real space unit cell. a^* is normally used for a reciprocal lattice parameter, in $1/\text{nm}$ or $1/\text{\AA}$ units. $a \sin(\beta)$ should be used instead.*

Thank you for your suggestion! We have modified it in Figure 2 accordingly.

Figure 2 has been modified as: (Page 11 line 200)



11. *There are superfluous sentences like, when describing crystal dissolution, the authors say (L 187) “Most obviously, the size of crystal became smaller as the cumulative dissolution time increased.”*

Thank you for your suggestion!

The sentence “Most obviously, the size of crystal became smaller as the cumulative dissolution time increased.” ***has been deleted.***

12. ***More on superfluous text and inappropriate references: L 147: “This indicated that annealing at an elevated temperature (e.g., at 51 °C), which is still below the melting point, resulted in a thickening of the metastable crystal, causing an increase of its stability.[27]” Everyone vaguely familiar with semicrystalline polymers would be aware that increasing lamellar thickness lowers the free energy. So why do we have to be reminded, and are even given a reference (27) to a 2005 article? And just a little further (L 153): “The lamellar thickness is widely accepted to be the characteristic feature that determines crystal stability.” And the rather overused and not very meaningful phrase “degree of metastability”, used 21 times in this paper.***

Thank you for your suggestion!

The sentence “This indicated that annealing at an elevated temperature (e.g., at 51 °C), which is still below the melting point, resulted in a thickening of the metastable crystal, causing an increase of its stability.” ***has been deleted.***

The reference has been deleted.

27. Zhai, X. M.; Wang, W.; Ma, Z. P.; Wen, X. J.; Yuan, F.; Tang, X. F.; He, B. L. Spontaneous and inductive thickenings of lamellar crystal monolayers of low molecular weight PEO fractions on surface of solid substrates. *Macromolecules* **2005**, 38 (5), 1717-1722.

The parts related to “degree of metastability” in the manuscript have been modified accordingly.

Detailed response on the comments (*written in blue*) by Reviewer #2

In this manuscript the authors introduce time dependent dissolution measurements as a method to investigate the local (meta)stability of polymer crystals in thin films. Polymers crystallize as thin lamellar crystals, in which the chains take on a folded conformation. It is well known that these crystals are a non-equilibrium structures, their stability depends on their thickness, which is typically lying in the nanometer range. Isolated crystals form in thin films, and if the films are very thin, the crystals are dendritic. The stability of these crystals can vary depending on the distance to the growth front due to reorganization going on in parallel to crystal growth. The reorganization is typically related to the existence of intracrystalline mobility, which is high for PEO, used as a model substance here. Reorganization becomes faster during heating, it is therefore difficult to use heating as a measure of stability, unless it takes place very fast. At this point the idea introduced here sets in: dissolution in a solvent at ambient temperatures takes place without reorganization and dissolution speed therefore reflects the local stability of the crystals. The crystals are mostly dissolved in the lateral direction, inverse to the path crystal growth has taken place before with a few exceptions, in which holes form in the middle of the crystals. In this paper the authors demonstrate the application this approach on a model system consisting of dendritic crystals grown in thin films of PEO of relatively low molecular weight using AFM and optical microscopy as experimental methods.

The paper is based on previous work of the authors, in which polymer crystals grown in thin films have already been studied and also washing has been introduced as a technique for partial dissolution. To use this approach for a systematic investigation of the dissolution kinetics is to my knowledge novel and provides an interesting illustration of the spatially varying stability of the crystals. Furthermore, the measured temperature dependence (activation energy) of the dissolution speed gives insights about the molecular process of dissolution, provided the corresponding questions below can be answered. In general, the paper is well written, the experimental design is convincing, and the experiments seem carefully performed. I can mostly follow the arguments and interpretation of the results that the authors put forward with a few but important exceptions that need further clarification. These points are listed below.

We thank the reviewer for the positive feed-back, the useful comments and the highly valuable advice. A detailed response to all points raised can be found in the subsequent reply.

1. *In line 191 and Fig. S4 the authors identify some surfaces of the crystals as specific crystallographic planes. It is not clear, how this assignment is done. I assume it rests on previous work, which should then either be cited or explained again here.*

The referee is fully right that the identification of specific crystallographic planes is based on previous works by Kovacs^[R21], Cheng^[R27, 38] and Ungar^[R39, 40].

Kovacs et al.^[R19, 20] and Cheng et al.^[R27] have found that within a narrow range of supercooling the shape of PEO single crystals, which were grown from the melt, change from faceted to circular and back. In view of the observed habit, which involves two (100) and four (140) growth faces,^[R19, 20] Kovacs et al.^[R21] have proposed a molecular model for chain packing in a PEO single lamellar crystal. In this model, the folds are supposedly parallel to the (120) planes as in solution-grown crystals.^[R37] Though (100) folds may also be conceived in the (100) sectors, Cheng et al.^[R27] have proved later that the (100) folds are less favorable. Folds parallel to (140) are, however, unrealistic, since they would involve a fold packing which is too dense in the corresponding sectors. In addition, on a molecular scale, the growth faces of the PEO single crystals are highly serrated rather than smooth.^[R21] Cheng et al.^[R27] have suggested that the (120) growth faces are molecularly smooth, in contrast to other faces. Additionally, the apparent (140) facets do not represent densely packed planes. In contrast, single crystals of PEO grown from dilute solutions are bounded by (100) and (120) facets, both densely packed.^[R37] Further, Cheng et al.^[R38] have shown that chain folding in high molecular weight PEO lamellar single crystals grown from solution is mostly along the (120) growth planes.

To explain these morphological features, Ungar et al.^[R39, 40] computed the growth habit of PEO crystals using the Frank-Seto model. They proposed that the apparent (140) facets are in fact (120) growth faces with steps traveling toward the outlying (100) faces 4 times faster than away from them. This causes a pileup of growing layers toward the borders with (100) faces, causing the (120) faces to tilt. In contrast, crystals growing from a dilute solution tend to have a low initiation-to-propagation ratio and thus display crystallographic facets. Therefore, Ungar et al.^[R39, 40] have suggested that the fold planes in PEO crystals are (100) and (120). Specifically, these planes have the highest lateral surface energy and the lowest growth rate. Moreover, they calculated that PEO single crystals are constructed from two symmetric (100) planes and four asymmetric (120) planes.

Consequently, we suggest that the apparent (140) facets in our case are, in fact, rough (120) faces. We have modified and improved the manuscript accordingly.

The Figures 2 and 3 have been modified as: (Page 11 line 200-215)

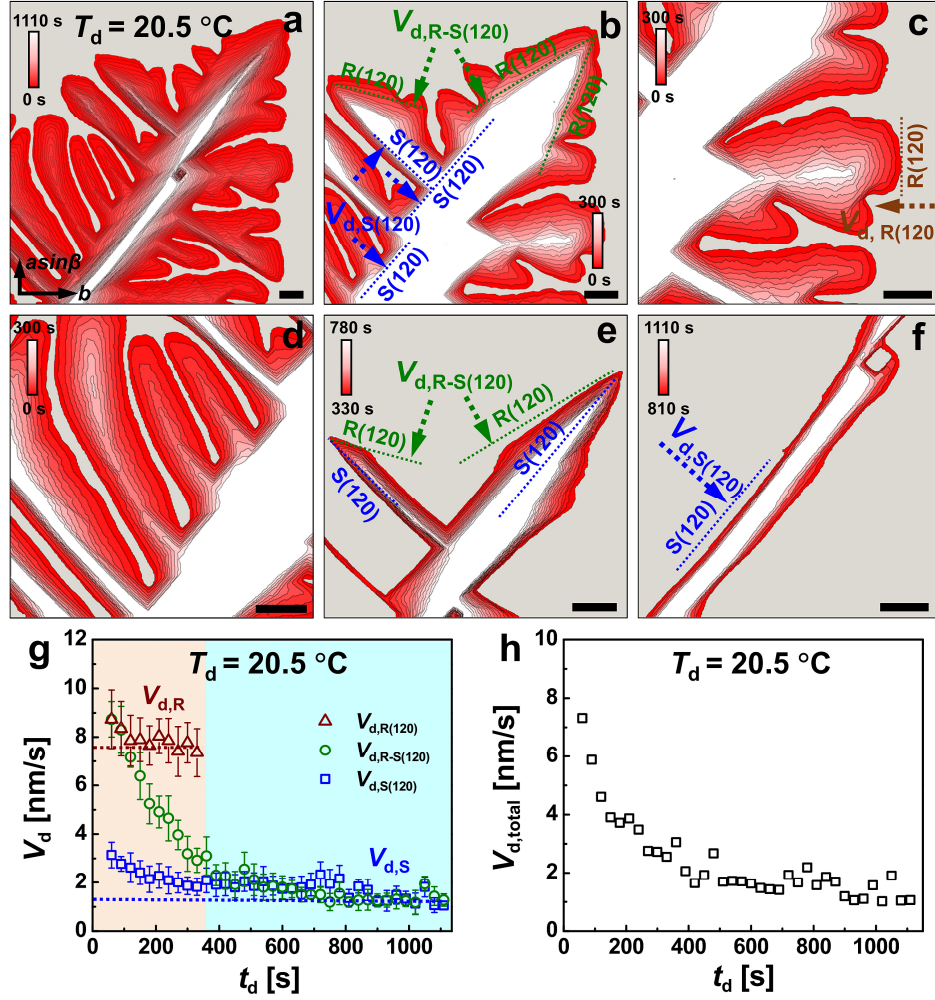


Figure 2. Temporal evolution of morphology in PEO lamellar crystals induced by selective dissolution and the dissolution kinetics of PEO lamellar crystals. (a) A false-colour overlay of AFM images showing the contour of a PEO crystal taken at different times (t_d) in the course of selective dissolution in toluene at $T_d = 20.5\text{ °C}$. The bare substrate is represented in a grey colour. The initial PEO crystal was grown at $(T_c, t_c) = (49\text{ °C}, 120\text{ s})$. Overlays of AFM images for the t_d -range of: (a) 0 ~ 1110 s, (b-d) 0 ~ 300 s; (e) 330 ~ 780 s and (f) 810 ~ 1110 s, respectively. The time intervals (Δt) between two successive layers for (a-e) and (f) are 30 s and 60 s, respectively. The scale bars represent 2 μm . (g) Time dependence of the dissolution velocity (V_d) along individual rough (120) and smooth (120) faces, respectively. The error bars indicate standard deviation. The brown and blue dashed lines correspond to the constant values, reached after a certain time, of the dissolution velocity along the R(120) and S(120) faces, respectively, which are designated as $V_{d,R}$ and $V_{d,S}$. The dissolution velocity of the branches grown along directions normal to (120) planes is denoted as $V_{d,R-S(120)}$, representing the transition from the dissolution of R(120) planes to the dissolution of S(120) planes. (h) Plot of the overall dissolution velocity ($V_{d,total}$) versus time during dissolution at $T_d = 20.5\text{ °C}$.

The sentence “In accordance with previous studies^{33, 34} on the molecular model of

chain packing in a lamellar PEO single crystal, the coordinate system in lower left corner of panel (d) indicates the orientation of the $a \cdot \sin\beta$ - and b -axis of the monoclinic crystal unit cell (see also Figure S3). The two black arrows labelled $a \cdot \sin\beta$ and b indicate the (100) and (010) planes, respectively.” **has been added.** (Page 8 line 148-152)

The sentences “Figures 2b-d show the morphological changes of the crystal within $t_d = 300$ s. It is visible that the crystal started to dissolve along the contour line. Later on, it shrank along particular crystallographic planes, i.e., the (120) and (140) planes (see Figure 2b and 2c).” **have been modified as** “Figures 2b-f and S5a-c show that the morphological changes of the crystal at different dissolution stages. In the early stage of dissolution (i.e., within $t_d = 300$ s), two distinct pathways were clearly observed in the dissolution of dendritic crystal. It is visible that the branches grown along the (120) normal directions started to dissolve along the contour lines. Later on, they shrank along particular crystallographic planes (see Figure 2b).” (Page 12 line 220-225)

The paragraph “Figure 2 revealed that the dissolution of dendritic PEO crystals occurs along specific crystallographic planes. Computing the growth habit of PEO crystals with the help of the Frank-Seto model, Ungar et al.^{48,49} concluded that the fold planes in PEO crystals are (100) and (120). They also proposed that the apparent (140) facets of PEO crystals grown from the melt are in fact rough (120) faces of variable tilt, which resulted from a high secondary nucleation rate and unequal spreading rates of layers in opposite directions due to the asymmetry of the (120) crystallographic planes. Therefore, we suggest that during early stages the dissolution of PEO dendritic crystals is mainly along the rough and smooth (120) planes, designated as R(120) and S(120), respectively.” **has been added.** (Page 13 line 242-250)

The following references have been added.

33. Kovacs, A.; Straupe, C.; Gonthier, A. Isothermal growth, thickening, and melting of poly(ethylene oxide) single crystals in the bulk. II. *Journal of Polymer Science: Polymer Symposia* **1977**, 59 (1), 31-54. (Page 25 line 565-567)

34. Cheng, S. Z. D.; Chen, J. Nonintegral and integral folding crystal growth in low-molecular mass poly (ethylene oxide) fractions. III. Linear crystal growth rates and crystal morphology. *Journal of Polymer Science Part B: Polymer Physics* **1991**, 29 (3), 311-327. (Page 25 line 568-571)

48. Shcherbina, M. A.; Ungar, G. Asymmetric Curvature of Growth Faces of Polymer Crystals. *Macromolecules* **2007**, 40 (3), 402-405. (Page 26 line 606-607)

49. Shcherbina, M. A.; Chvalun, S. N.; Ungar, G. Effect of crystallization conditions on the shape of polymer single crystals: Experimental and theoretical approaches. *Crystallography Reports* **2007**, 52 (4), 707-720. (Page 26 line 608-610)

2. **In the paragraph starting at line 228 the authors claim that the observed higher**

dissolution tendency of some crystals is due to a competition between preferred crystal orientation and the concentration gradient direction. A few lines above they (line 200) they state that the barrier for dissolution is related to the surface free energy (of crystalline stems or whole chains on the dissolution front). First, it seems to me that surface energy is a concept, which applies to a larger region of the surface than a single chain. Furthermore, it seems obvious to me that a crystal surface with a certain inclination to a crystal plane will in general always be less stable than a surface which is parallel to a crystal plane due to the microscopic roughness caused by the inclination. I would think that this fact explains the faster dissolution. I am not sure if the authors mean just this fact or something else, I find the text not very clear at this point. This issue should be addressed.

Again, this is an excellent suggestion!

Firstly, as we discussed above in the context of comment #1, the observed apparent (140) facets are in fact rough (120) faces of variable tilt^[R39, 40]. Therefore, we completely agree with the referee that the parts of lamellar crystals with microscopic roughness caused by the inclination dissolve faster. For our experiments, we mainly observed the dissolution of PEO lamellar crystals along the smooth and rough (120) planes, respectively. In view of this, our observations showed that rough (120) planes dissolved faster than smooth (120) planes.

Armitstead et al.^[R13] have proposed that the combination of driving force and free energy barrier terms determines the growth rate of lamellar polymer crystals. The driving force of polymer crystallization is related to the difference of free energies between the crystalline state and the amorphous phase in the undercooled melt.^[R47] The main kinetic barrier for the process of depositing a new stem is related to the degree of folding. So, the two main factors that determine the growth rate are the thermodynamic driving force and the kinetic barrier of a deposition of the first stem of appropriate length on a (smooth) crystal surface.^[R48] For example, the driving force for crystallization of extended chains is larger than that for folded chains, but folded-chain crystallization is faster due to a lower kinetic barrier.

Similarly, the dissolution rate of lamellar polymer crystals is also the result of an interplay between kinetic barrier and driving force. It should be noted that these two main factors both depend on the degree of undercooling. For the case of dissolution, which is opposite to crystallization but with some analogy to melting, the free energy difference of a rough face (at any given dissolution temperature in an almost infinitely dilute solution) is higher than that of a smooth one. Therefore, the rough face has a larger driving force for dissolution. Furthermore, dissolving a chain or stem from a

rough crystalline face requires to generate less “new” surfaces (on the average, on a rough surface, molecules have fewer nearest crystalline neighbors). Thus, the corresponding kinetic barrier for detachment of a stem or a chain from rough faces is expected to be lower. Consequently, we agree with the referee that rapid dissolution of rough faces is attributed to a larger thermodynamic driving force and a lower kinetic barrier.

Besides, the distinctly different dissolution rates of the two side branches in Figure 2 should be attributed to the difference in growth kinetics along different crystallographic planes. As shown in Figure 3, following crystallization in time, we explored the growth of six individual branches of a PEO dendritic crystal at 49 °C in situ by optical microscopy, starting from the crystallization time of 40 s (see the insert in Figure 3a). Among the six, four main branches were along the (120) normal direction and two along the (010) normal direction (i.e., along the b axis), designated as MB₁₂₀ and MB₀₁₀, respectively. Due to Mullins-Sekerka growth instabilities, dendritic side branches were generated, emerging from the MB₁₂₀ branches and growing along various crystallographic planes (see Figure 3a-c). Most significantly, we found that, mainly due to the difference in growth rates, the growth of side branches, which emerged from the MB₁₂₀ branches, eventually surrounded the MB₀₁₀ branches and thus finally prevented their further growth (see Figure 3c).

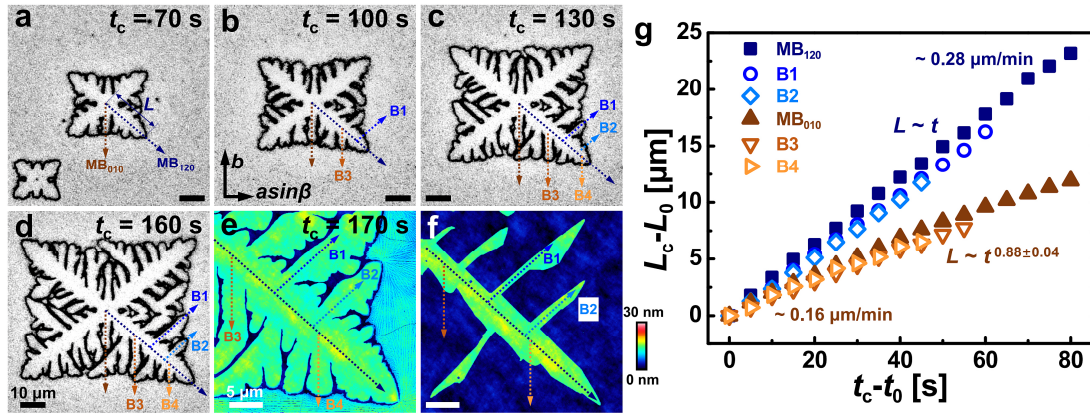


Figure 3. In situ observations of crystal growth. (a-d) Optical micrographs showing the evolution of a PEO crystal growing at 49 °C in a ca. 9 nm thin film. The insert in lower left corner of (a) is the micrograph of the PEO dendritic crystal at $t_c = 40$ s. (e) Height image of the dendritic PEO crystal grown at $(T_c, t_c) = (49$ °C, 170 s), i.e., the crystal before dissolution experiments. (f) Surface topography of PEO crystal obtained after selective dissolution in toluene at $(T_d, t_d) = (23$ °C, 30 s). (g) The growth kinetics in terms of branch length ($L_c - L_0$) as a function of $(t_c - t_0)$. L_c and L_0 are the branch length at t_c and t_0 , respectively. Please note that the value of t_0 for MB₁₂₀, B1 and B2 is the same as for MB₀₁₀, B3 and B4, respectively.

To quantitatively corroborate this physical picture, we measured the length, L , of main and side branches along various crystallographic planes. Figure 3g shows the growth kinetics in terms of branch length ($L_c - L_0$) as a function of $(t_c - t_0)$ for different branches. Here, L_c and L_0 are the branch length at t_c and t_0 , respectively. One can clearly see that the length of branches (e.g., the ones labelled as MB₁₂₀, B1 and B2) growing along (120) normal directions increased linearly with time ($L \sim t$), whereas that of branches (e.g., the ones labelled as MB₀₁₀, B3 and B4) growing along (010) normal directions eventually increased in a nonlinear fashion with time (if we would assume a power law dependence, this would yield $L \sim t^{0.88 \pm 0.04}$). The branches along (120) normal directions grew faster ($\sim 0.28 \mu\text{m/min}$) than the ones along (010) normal directions ($\sim 0.16 \mu\text{m/min}$). Most interestingly, the former survived but the latter disappeared after selective dissolution at 23 °C for 30 s (see Figure 3f).

Previous studies^[R50-52] showed that for crystals with a size (R) increasing linearly in time (t), i.e., $R \sim t$, their growth is nucleation-limited (NL). By contrast, if R increases in time as $R \sim t^{0.5}$, the crystal growth is diffusion-limited (DL). However, in accordance with the marginal stability criterion of Langer and Müller-Krumbhaar^[R53], Taguchi et al.^[R54, 55] have found that the growth rate of the leading growth tips was constant during growth (linear growth), and proposed, corroborating conclusions previously obtained by Sekerka^[R56], that surface kinetics, transport (diffusion), capillarity and surface nucleation control the growth process. The leading growth tip still advances at a constant velocity even in the diffusion controlled growth. Therefore, we suggest that the growth tip of branches (which follows $L \sim t$) of the branches along (120) normal directions is mainly controlled by (secondary) nucleation, while other branches of the dendritic crystal, including the branches along (010) normal directions, are profoundly affected by temporal changes in the number of polymers diffusing towards the growing branches.

In the diffusion-limited regime, growth is controlled by the diffusion of polymer to the growth face. In this case, the growth front may become unstable (Mullins-Sekerka instability) and thus may become roughened.^[R57] Especially when the degree of undercooling is increased, the crystal growth fronts are becoming increasingly rough, leading to the generation of a multitude of crystalline branches.^[R51] On the other hand, for example at low supercooling, nucleation controlled growth may generate flat growth faces, i.e., facets.^[R58]

In summary, branches in a direction different to the (120) normal direction grow slower but dissolve faster. Their growth is significantly affected by diffusion of a deficient number of polymer to the growing branch, resulting in the formation of rough (120) faces. By contrast, tips of branches along (120) normal directions exhibit growth

of molecularly smooth interfaces (see Figure 3g), while the curved portion on the sides of these growth tip are influenced by diffusion resulting in a kinetically roughened growth front^[R59]. Similarly, Toda et al.^[R60] have observed that the melting velocity shows strong anisotropy in the directions of long and short axes for both PE and PVDF crystals. Such an anisotropy suggests that the rate determining process differentiates the lateral surfaces of different crystal indices.

We have modified and improved the manuscript accordingly. *The analysis and discussion presented above has been added.* (Page 14 line 280 – Page 17 line 340)

3. *In the further part of the manuscript, the authors analyze in detail the observation that the dissolution becomes slower during the process with the advent of time. It is probably caused by an increasing stability with distance from the outer lateral surface of the crystal. The time dependent dissolution speed can be modeled with an exponential decay. The authors interpret the temperature dependence in terms of an activation energy for the transport of a molecule from the crystal to the solvent. I am not sure if I can follow this argument. It seems to me that something is wrong with the equation in line 327. τ_d describes the spatial variation of stability of the crystal. Should the temperature dependence of the dissolution velocity, if it is caused by the barrier for the transport to the solvent, not show up in the temperature dependent prefactor $v_d(T_d)$ instead of in τ_d ? A temperature dependence of τ_d means that the spatial variation of stability changes with temperature. Why should this be related to the activation energy of dissolution? The authors should please check and clarify this issue and provide a more detailed explanation in their text.*

We thank the referee for this highly valuable advice.

Previous studies^[R65-67] obtained activation energies from Arrhenius plots of the crystal growth velocities versus temperature, when the isothermal crystal growth velocity was observed to be time-independent (i.e., constant). However, in the present work, the (averaged) dissolution velocity (V_d) was not constant but decreased over time. Therefore, we needed to define an alternative parameter that characterizes the dissolution velocity.

For each dissolution temperature (T_d), the variation of dissolution velocity (V_d) as a function of time (t_d) can be approximated by an exponential function: $V_d(T_d, t_d) = \Delta V_d(T_d) \cdot \exp[-t_d/\tau_d(T_d)] + V_{d,\infty}$. There, τ_d is a characteristic time reflecting the time required for a decay of the dissolution velocity to a value of 1/e of the difference between the highest value at $t_d = 0$ and the lowest value at $t_d = \infty$ (i.e., $\Delta V_d = V_{d,0} - V_{d,\infty}$).

Thus, as an alternative parameter, we defined the dissolution velocity corresponding to the time τ_d as the characteristic dissolution velocity, V_d^* , at that given dissolution temperature.

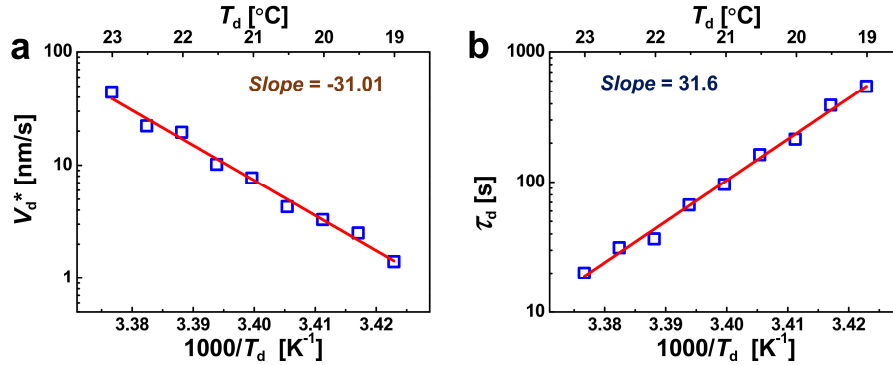


Figure R3. Dependences of (a) characteristic dissolution velocity (V_d^*) and (b) characteristic time (τ_d) versus the reciprocal dissolution temperature ($1000/T_d$) for PEO lamellar crystals generated at 49 °C.

The temperature dependence of V_d^* followed the Arrhenius equation: $V_d^*(T_d) = V_{d,0}^* \exp(E_d/RT_d)$, as shown in Figure R3a. The corresponding activation energy E_d can be obtained by plotting the logarithm of the characteristic dissolution velocity V_d^* versus the reciprocal dissolution temperature ($1000/T_d$). The linear relationship in Figure R3a gives a value of E_d of around 600 kJ/mol, which is in accordance with the value of E_d calculated from the Arrhenius plot of the characteristic time τ_d versus $1000/T_d$ (see Figure R3b). Since the contribution of diffusion of molecular chains in extremely dilute solutions is negligible, such a high value of E_d reflects the substantial energy required for the detachment of a crystalline stem or a whole chain from the lateral surface of the crystal.

The value of $V_{d,\text{total}}$, which is defined as the mean difference in length between two successive contour lines divided by the time interval (Δt) at which the two successive contour lines were measured. This mean difference in length was derived by calculating the total (dissolved) area between these two successive contour lines and dividing it by the perimeter of the earlier contour line. We note that $V_{d,\text{total}}$ includes the dissolution of both rough and smooth faces. However, as shown in Figures 2g and 2h, it is possible to distinguish between the dissolution velocities of rough and smooth faces, allowing to derive $V_{d,R}$ and $V_{d,S}$. Therefore, instead of using τ_d , we now chose $V_{d,R}$ and $V_{d,S}$ as parameters characterizing the dissolution process. By plotting $V_{d,R}$ and $V_{d,S}$ against the dissolution temperature (T_d), we estimate the activation energies for dissolution of rough and smooth faces, respectively, as shown in Figure 4.

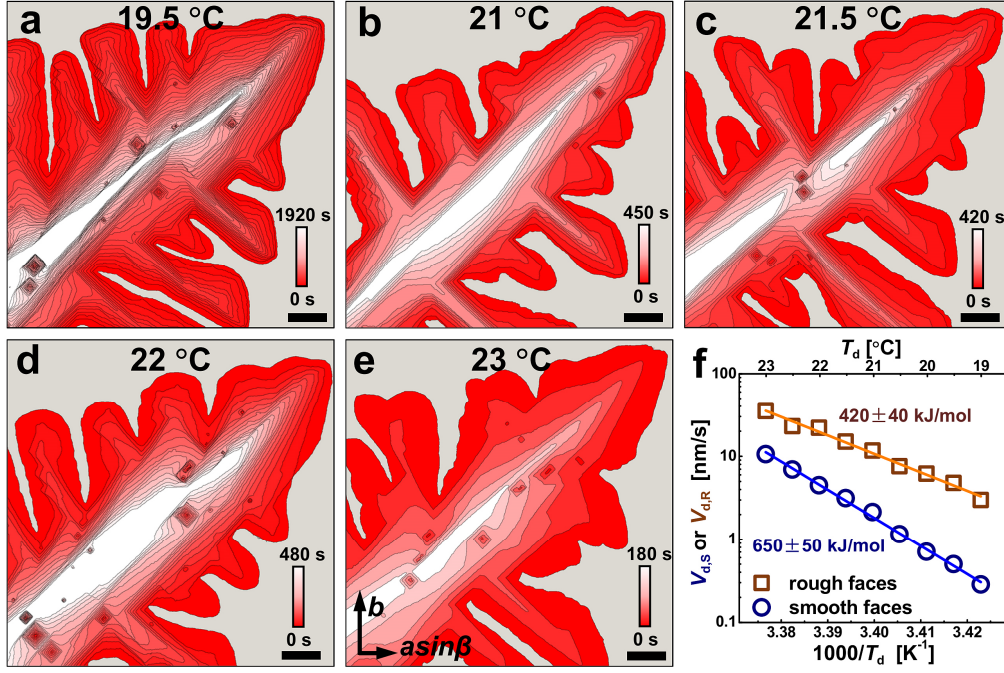


Figure 4. Changes in morphology of PEO lamellar crystals induced by selective dissolution in toluene at different temperatures (T_d). Initial PEO crystals were grown at $(T_c, t_c) = (49\text{ }^\circ\text{C}, 120\text{ s})$. The false-colour overlay of the contour of AFM height images of PEO crystals during selective dissolution in toluene at $T_d =$ (a) $19.5\text{ }^\circ\text{C}$; (b) $21\text{ }^\circ\text{C}$, (a) $21.5\text{ }^\circ\text{C}$; (b) $22\text{ }^\circ\text{C}$ and (c) $23\text{ }^\circ\text{C}$ for different times. The bare substrate is represented in a grey colour. The time intervals (Δt) between two contour lines for (a) and (b-e) are 60 s and 30 s , respectively. The scale bars represent $2\text{ }\mu\text{m}$. (f) Dependence of $V_{d,R}$ and $V_{d,S}$ versus the reciprocal dissolution temperature ($1000/T_d$) for PEO lamellar crystals generated at $49\text{ }^\circ\text{C}$.

We have modified and improved the manuscript accordingly.

Figure 4 has been added. (Page 18 line 368-376)

The sentences “For each dissolution temperature T_d , the variation of $V_{d,\text{total}}$ as a function of t_d can be fitted by an exponential function: $V_d(T_d, t_d) = V_{d,0}(T_d) \cdot \exp[-t_d/\tau_d(T_d)]$, where τ_d is a characteristic time (see Figure S6). Figure 5 shows the derived values of τ_d as a function of T_d . For the temperature range from $19\text{ }^\circ\text{C}$ to $23\text{ }^\circ\text{C}$, τ_d clearly decreased with T_d , following an Arrhenius law: $\tau_d(T_d) = \tau_{d,0} \exp(E_d/RT_d)$, where E_d is the activation energy for the transport of one mole of chains from the crystal lattice to the solvent, and $\tau_{d,0}$ is assumed to be independent of temperature. The activation energy E_d for the dissolution of PEO lamellar crystals can be obtained by plotting in Figure 5 the logarithm of the values of τ_d versus the reciprocal dissolution temperature ($1000/T_d$). From this plot, we obtain a value of $E_d = 610 \pm 50\text{ kJ/mol}$.” **have been modified as** “For each dissolution temperature T_d , it is possible to distinguish between the dissolution velocities of rough and smooth faces, allowing to derive $V_{d,R}$ and $V_{d,S}$. Figure 4f shows

as a function of T_d the obtained values of $V_{d,R}$ and $V_{d,S}$, respectively. For the investigated temperature range from 19 °C to 23 °C, both $V_{d,R}$ and $V_{d,S}$ clearly decreased with T_d . This decrease followed an Arrhenius law: $V_d(T_d) = V_{d,0} \exp(E_d/RT_d)$, where E_d is the detachment energy for the transport of one mole of polymer chains from the crystal lattice to the solvent, and with $V_{d,0}$ being a constant assumed to be independent of temperature. In Figure 4f, the activation energy E_d for the dissolution of PEO lamellar crystals is obtained by plotting the logarithm of the values of $V_{d,R}$ and $V_{d,S}$ versus the reciprocal dissolution temperature ($1000/T_d$). From these plots, we concluded that the value of E_d for the dissolution of rough and smooth faces are 420 ± 40 kJ/mol and 650 ± 50 kJ/mol, respectively.” (Page 19 line 392-403)

Detailed response on the comments (*written in blue*) by Reviewer #3

The authors report on experiments to sequentially dissolve a single lamellar crystal grown on a solid substrate. By analyzing the patterns after each step of dissolution they can calculate the speed of dissolution. The authors argue that the experiments indicate a spatial variation of “metastability” of the crystalline polymer which is not reflected by the height of the crystal. Although the experiments are certainly of interest for the polymer community the conclusions are speculative, and to some extent the work is premature for presentation to a larger audience. Key concepts used by the authors like “metastability” remain vague and it is difficult for me to take a clear message home after reading. Therefore, I do not recommend publication. Below, I address some issues in more detail which may help the authors to improve the manuscript for submission in a more specialized journal.

We are very grateful for the attention the referee has paid to our work and the useful comments provided. The stability of crystalline polymer structures has always been a major concern of polymer science. Besides, we agree with the referee that the concept of metastability was not defined clearly in the original version of our manuscript. Our key message was not presented convincingly due to our insufficient comparison and discussion with previous results and observations published in the classical literature on growth of rough and smooth crystalline surfaces. In the revised version of our manuscript, we have modified and improved these parts of the manuscript accordingly. In the following, we provide responses to the comments and suggestions in a point-by-point fashion. **Again, we are much indebted to the referee for the highly valuable advice!**

- 1. I do not understand the argument “From the constant lamellar thickness revealed by time-resolved in situ AFM measurements in Figure S3, we can safely assume that, in contrast to thermal annealing, selective dissolution does not change the degree of metastability of the crystal.” Obviously, the author made a difference between height (thickness) of the crystal and “metastability”. If so, how can the authors conclude from the missing height difference during dissolution that the metastability has not changed?*

We thank the referee for this highly valuable advice.

In order to quantitatively describe metastable states, we need to precisely define metastability in first place.^[R36] The polymer single crystal of infinite size and without

defects represents the equilibrium state which is always taken as our reference state. Here, we quantify metastability as the difference in stability (reflected by a lower melting temperature or a higher dissolution rate at a given temperature) between the investigated crystal and this reference state. In the pioneering work by Keller and Cheng^[R68], they proposed a particular hierarchy of metastabilities: One class of metastable states is related to differences in the lattice parameters (sometimes called classical metastable states) and another class of metastable states is related to the finite and often only nanometer-small thickness of lamellar polymer crystals, which can be designated as states of metastable morphologies.

The concept of metastable states is important for both, a profound scientific understanding of the related physical processes and for designing and controlling material properties in practical applications. Many polymers possess more than one crystalline form and thus exhibit several polymorphs. Essentially, such polymorphs belong to the class of classical metastable states, or the first level in the hierarchy of metastability. Such metastable crystals are characterized by crystal lattices with different symmetries or crystalline structures which may include (a few) defects. When classical metastable states are discussed, we consider that crystals of these states have a large (infinite) size. Besides, there is a broad class of metastable states dictated by the finite size of the crystalline phase (usually, at least one of the three dimensions of the crystal has a size (much) less than one micrometer). There are many reasons for this class of metastability: exhaustion of available material, geometric restrictions (i.e., imposed by crystallization in thin films or cavities like cylindrical pores), limited molecular mobility (i.e., upon approaching the glass transition - vitrification), and crystallization kinetics (i.e., the origin of the growth rate dependence of the thickness of polymer lamellar crystals). In our study, the thickness of the polymer crystal was constant in space and time. Thus, these crystals correspond to classical metastable states, however of limited thickness, i.e., classical metastable states interlinked with states of metastable morphologies. A finite crystal thickness may be recognized as a distinct feature of a metastable structure. Therefore, as discussed by Cheng et al.^[R69], polymer crystals of finite lamellar thickness can be considered states of metastable morphologies, the second level in the hierarchies of metastability.

In our study, the finite lamellar thickness of the crystals did not change upon selective dissolution. There are also no indications of any change in crystal lattice parameters. Thus, we assume that the metastability of the crystal remains constant. However, our results showed that these metastable crystals exhibited different dissolution rates for two types of side branches, both having the same thickness. We will discuss this aspect in detail in the context of the next question.

2. *In order to explain the different speed of dissolution of two side-branches they write: “I may suggest that it was preferentially grown at a smaller angle with respect to the direction of the concentration gradient. Thus, although they have a similar thickness, these two side branches possessed different thermal stabilities as demonstrated by their selective dissolution, allowing classifying them as “favourably oriented” and “unfavourably oriented” “First of all, why the side branch should not grow in the direction of the (local) concentration gradient? I note that the speed of grow is very low in the thin film where the grow is taken place in 2D and is diffusion-controlled. But the key question is: What should be the molecular origin in the different stability given that both branches have the same height?”*

Again, this is a highly relevant and insightful question. We fully agree with the referee that the difference in stability of branches, characterized by the corresponding difference in dissolution velocity, having the same thickness needs to be explained in detail, invoking features differing at the molecular level.

Firstly, as we discussed above in the context of comment #1, the apparent (140) facets in our case are in fact rough (120) faces of variable tilt^[R39, 40]. Similarly, referee #2 also points out that the faces of lamellar crystals with microscopic roughness dissolve faster. In our experiments, dissolution of PEO lamellar crystals is along smooth and rough (120) planes, respectively (see Figure 2). In view of this, our observations showed that rough (120) planes dissolved faster than smooth (120) planes.

Secondly, we found that the branches oriented along directions different to the (120) normal direction dissolved faster (see Figure 2c and d) than branches grown along the (120) normal direction. Further, following crystallization in time, we have investigated the formation of distinct branches and determined their growth rate. In Figure 3, we explored the growth of six individual branches of a PEO dendritic crystal at 49 °C in situ by optical microscopy, starting from the crystallization time of 40 s (see the insert in Figure 3a). Among the six, four main branches were along the (120) normal direction and two along the (010) normal direction (i.e., along the b axis), designated as MB₁₂₀ and MB₀₁₀, respectively. Due to Mullins-Sekerka growth instabilities, dendritic side branches were generated, emerging from the MB₁₂₀ branches and growing along various crystallographic planes (see Figure 3a-c). Most significantly, we found that, mainly due to the difference in growth rates, the growth of side branches, which emerged from the MB₁₂₀ branches, eventually surrounded the MB₀₁₀ branches and thus finally prevented their further growth (see Figure 3c).

To quantitatively corroborate this physical picture, we measured the length, L , of main and side branches along various crystallographic planes. Figure 3g shows the

growth kinetics in terms of branch length ($L_c - L_0$) as a function of ($t_c - t_0$) for different branches. Here, L_c and L_0 are the branch length at t_c and t_0 , respectively. One can clearly see that the length of branches (e.g., the ones labelled as MB₁₂₀, B1 and B2) growing along (120) normal directions increased linearly with time ($L \sim t$), whereas that of branches (e.g., the ones labelled as MB₀₁₀, B3 and B4) growing along (010) normal directions eventually increased in a nonlinear fashion with time (if we would assume a power law dependence, this would yield $L \sim t^{0.88 \pm 0.04}$). The branches along (120) normal directions grew faster ($\sim 0.28 \mu\text{m}/\text{min}$) than the ones along (010) normal directions ($\sim 0.16 \mu\text{m}/\text{min}$). Most interestingly, the former survived but the latter disappeared after selective dissolution at 23 °C for 30 s (see Figure 3f).

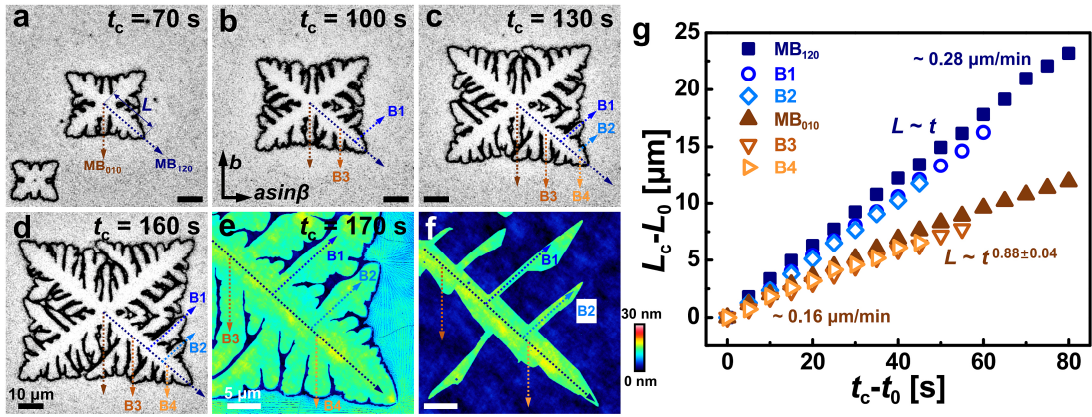


Figure 3. In situ observations of crystal growth. (a-d) Optical micrographs showing the evolution of a PEO crystal growing at 49 °C in a ca. 9 nm thin film. The insert in lower left corner of (a) is the micrograph of the PEO dendritic crystal at $t_c = 40$ s. (e) Height image of the dendritic PEO crystal grown at $(T_c, t_c) = (49 \text{ °C}, 170 \text{ s})$, i.e., the crystal before dissolution experiments. (f) Surface topography of PEO crystal obtained after selective dissolution in toluene at $(T_d, t_d) = (23 \text{ °C}, 30 \text{ s})$. (g) The growth kinetics in terms of branch length ($L_c - L_0$) as a function of ($t_c - t_0$). L_c and L_0 are the branch length at t_c and t_0 , respectively. Please note that the value of t_0 for MB₁₂₀, B1 and B2 is the same as for MB₀₁₀, B3 and B4, respectively.

Previous studies^[R50-52] showed that for crystals with a size (R) increasing linearly in time (t), i.e., $R \sim t$, their growth is nucleation-limited (NL). By contrast, if R increases in time as $R \sim t^{0.5}$, the crystal growth is diffusion-limited (DL). However, in accordance with the marginal stability criterion of Langer and Müller-Krumbhaar^[R53], Taguchi et al.^[R54, 55] have found that the growth rate of the leading growth tips was constant during growth (linear growth), and proposed, corroborating conclusions previously obtained by Sekerka^[R56], that surface kinetics, transport (diffusion), capillarity and surface nucleation control the growth process. The leading growth tip still advances at a constant velocity even in the diffusion controlled growth. Therefore, we suggest that the growth tip of branches (which follows $L \sim t$) of the branches along (120) normal

directions is mainly controlled by (secondary) nucleation, while other branches of the dendritic crystal, including the branches along (010) normal directions, are profoundly affected by temporal changes in the number of polymers diffusing towards the growing branches.

In the diffusion-limited regime, growth is controlled by the diffusion of polymer to the growth face. In this case, the growth front may become unstable (Mullins-Sekerka instability) and thus may become roughened.^[R57] Especially when the degree of undercooling is increased, the crystal growth fronts are becoming increasingly rough, leading to the generation of a multitude of crystalline branches.^[R51] On the other hand, for example at low supercooling, nucleation controlled growth may generate flat growth faces, i.e., facets.^[R58]

In summary, branches in a direction different to the (120) normal direction grow slower but dissolve faster. Their growth is significantly affected by diffusion of a deficient number of polymer to the growing branch, resulting in the formation of rough (120) faces in the molecular scale. By contrast, tips of branches along (120) normal directions exhibit growth of molecularly smooth interfaces (see Figure 3g), while the curved portion on the sides of these growth tip are influenced by diffusion resulting in a kinetically roughened growth front^[R59]. Similarly, Toda et al.^[R60] have observed that the melting velocity shows strong anisotropy in the directions of long and short axes for both PE and PVDF crystals. Such an anisotropy suggests that the rate determining process differentiates the lateral surfaces of different crystal indices.

We have modified and improved the manuscript accordingly. *The analysis and discussion presented above has been added.* (Page 14 line 280 – Page 17 line 340)

3. *The authors speculate about the observed decrease of dissolution velocity: “Therefore, we believe that the exponential decay of $V_{d,total}$ with td revealed an exponential decrease of the degree of metastability from the initial edge to the centre of the lamellar crystal.” What means “exponential decrease of the degree of metastability from the initial edge to the centre of the lamellar crystal.”? Exponential with respect to what? I can only speculate the the authors assume with respect to the distance within the crystal? Since V_d is exponentially decreasing in time this cannot be mapped to an exponential decrease of “metastability” (a term which was never defined exactly) as a function of the distance.*

We sincerely appreciate this valuable comment. In fact, we now explicitly attribute the decay of dissolution velocity with time to the distinctly different dissolution rates of rough and smooth (120) faces. As the rough (120) faces dissolve rapidly and

progressively, the crystal faces become less rough and gradually approach the smooth (120) faces, which dissolve more slowly. Thus, the overall dissolution rate slows down in time.

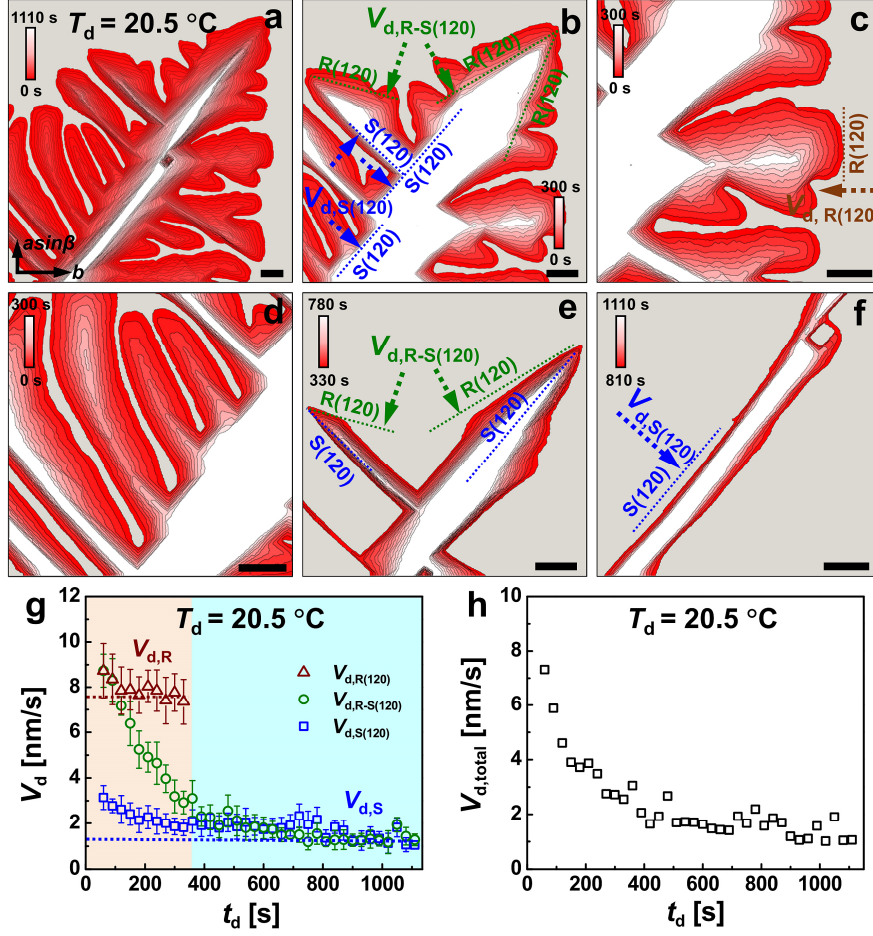


Figure 2. Temporal evolution of morphology in PEO lamellar crystals induced by selective dissolution and the dissolution kinetics of PEO lamellar crystals. (a) A false-colour overlay of AFM images showing the contour of a PEO crystal taken at different times (t_d) in the course of selective dissolution in toluene at $T_d = 20.5$ °C. The bare substrate is represented in a grey colour. The initial PEO crystal was grown at $(T_c, t_c) = (49$ °C, 120 s). Overlays of AFM images for the t_d -range of: (a) 0 ~ 1110 s, (b-d) 0 ~ 300 s; (e) 330 ~ 780 s and (f) 810 ~ 1110 s, respectively. The time intervals (Δt) between two successive layers for (a-e) and (f) are 30 s and 60 s, respectively. The scale bars represent 2 μ m. (g) Time dependence of the dissolution velocity (V_d) along individual rough (120) and smooth (120) faces, respectively. The error bars indicate standard deviation. The brown and blue dashed lines correspond to the constant values, reached after a certain time, of the dissolution velocity along the R(120) and S(120) faces, respectively, which are designated as $V_{d,R}$ and $V_{d,S}$. The dissolution velocity of the branches grown along directions normal to (120) planes is denoted as $V_{d,R-S(120)}$, representing the transition from the dissolution of R(120) planes to the dissolution of S(120) planes. (h) Plot of the overall dissolution velocity ($V_{d,total}$) versus time during dissolution at $T_d = 20.5$ °C.

As shown in Figure 2b, the branches grown along (120) normal directions firstly dissolved along R(120) faces. These rough faces of variable tilt were consumed (almost) completely with time (see Figure 2e). Thus, eventually the dissolution of the remaining crystal was along S(120) faces. Accordingly, we denoted the initial dissolution velocity of the branches grown along (120) normal directions as $V_{d,R-S(120)}$, representing the transition from the dissolution of R(120) planes to the dissolution of S(120) planes. Besides, Figure 2c shows that the branches grown along (010) normal directions dissolved mainly along the contour line with a dissolution velocity equal to $V_{d,R(120)}$, as they most likely consisted of a number of serrated, microscopic R(120) planes. Figure 2 also shows that the grooves between the final trunks of dendritic branches widened with $V_{d,S(120)}$ along S(120) planes (see Figure 2f).

We traced the dissolution velocities as a function of t_d along the R(120) and S(120) faces, respectively. In Figure 2g, we plotted the value of $V_{d,R(120)}$, $V_{d,S(120)}$ and $V_{d,R-S(120)}$ against t_d . Both, $V_{d,R(120)}$ and $V_{d,S(120)}$ showed initially a slight decrease and then stayed constant during further dissolution. Such a slight reduction in $V_{d,R(120)}$ and $V_{d,S(120)}$ at the very beginning of dissolution can probably be attributed to stages of accelerated crystal growth occurring in the course of the quenching process after isothermal crystallization, generating a transition zone with a width of ca. 1 μm , which is less stable and thus dissolves somewhat faster. However, crystalline structures grown at constant temperature dissolved at a constant velocity. Remarkably, $V_{d,R(120), \text{const}} = V_{d,R}$ was about five times faster than $V_{d,S(120), \text{const}} = V_{d,S}$. Interestingly, the initial value of $V_{d,R-S(120)}$ was quite similar to $V_{d,R}$, then dropped by a factor of 5 during the first 400 s and eventually became constant at a value of $V_{d,S}$. As the referee correctly pointed out, our observations indicate that the transition from the dissolution of rough to the dissolution smooth planes is responsible for the decay of the total dissolution velocity ($V_{d,\text{total}}$) with time, which averages the dissolution velocity of all crystalline faces.

We have modified and improved the manuscript accordingly.

The following paragraphs have been added. (Page 13 line 242 – Page 14 line 279)

“Figure 2 revealed that the dissolution of dendritic PEO crystals occurs along specific crystallographic planes. Computing the growth habit of PEO crystals with the help of the Frank-Seto model, Ungar et al.^{48, 49} concluded that the fold planes in PEO crystals are (100) and (120). They also proposed that the apparent (140) facets of PEO crystals grown from the melt are in fact rough (120) faces of variable tilt, which resulted from a high secondary nucleation rate and unequal spreading rates of layers in opposite directions due to the asymmetry of the (120) crystallographic planes. Therefore, we suggest that during early stages the dissolution of PEO dendritic crystals is mainly along the rough and smooth (120) planes, designated as R(120) and S(120), respectively. The

branches grown along the (120) normal directions firstly and rather fast dissolved along R(120) faces (see Figure 2b). As these rough faces of variable tilt were consumed (almost) completely with time (see Figure 2e), dissolution of the crystal was eventually along S(120) faces. Accordingly, we denoted the initial dissolution velocity of the branches grown along (120) normal directions as $V_{d,R-S(120)}$, representing the transition from the dissolution of R(120) planes to the dissolution of S(120) planes. Besides, Figure 2c shows that branches grown along (010) normal directions dissolved mainly along the contour line with a dissolution velocity equal to $V_{d,R(120)}$, as they most likely consisted of a number of serrated, microscopic R(120) planes. Figure 2 also shows that the gaps between the final trunks of dendritic branches widened with $V_{d,S(120)}$ along S(120) planes.

We traced the dissolution velocities as a function of t_d along R(120) and S(120) faces, respectively. In Figure 2g, we plotted the value of $V_{d,R(120)}$, $V_{d,S(120)}$ and $V_{d,R-S(120)}$ against t_d . Both, $V_{d,R(120)}$ and $V_{d,S(120)}$ showed initially a slight decrease and then stayed constant during further dissolution. Such a slight reduction in $V_{d,R(120)}$ and $V_{d,S(120)}$ at the very initial stages of dissolution can probably be attributed to accelerated crystal growth occurring in the course of the quenching process after isothermal crystallization, generating a transition zone with a width of ca. 1 μm , which is less stable and thus dissolves somewhat faster. However, crystalline structures grown at constant temperature dissolved at a constant velocity. As shown in Figure 2g, the brown and blue dashed lines correspond to the eventually reached constant values of the dissolution velocity along the R(120) and S(120) faces, respectively, which we designated as $V_{d,R}$ and $V_{d,S}$. Remarkably, $V_{d,R}$ was about five times faster than $V_{d,S}$. Interestingly, the initial value of $V_{d,R-S(120)}$ was quite similar to $V_{d,R}$, then dropped by a factor of 5 during the first 400 s and eventually became constant at the value of $V_{d,S}$. Therefore, our observations indicate that the transition from the dissolution of rough to the dissolution of smooth planes is responsible for the decay of the total dissolution velocity ($V_{d,\text{total}}$) with time (see Figure 2h), which averages the dissolution velocity of all crystalline faces.”

The following references have been added. (Page 26 line 606-610)

48. Shcherbina, M. A.; Ungar, G. Asymmetric Curvature of Growth Faces of Polymer Crystals. *Macromolecules* **2007**, 40 (3), 402-405.

49. Shcherbina, M. A.; Chvalun, S. N.; Ungar, G. Effect of crystallization conditions on the shape of polymer single crystals: Experimental and theoretical approaches. *Crystallography Reports* **2007**, 52 (4), 707-720.

4. *In the analysis of the characteristic time for the decay of dissolution velocity the authors observe an Arrhenius-like relation with respect to temperature which they*

associate with the energy barrier to dissolve a chain or a stem. I cannot see how this can be concluded if the process of dissolution is more complex and involves dissolution of whole clusters of chains, or maybe only parts of chains. The argument of considering the barrier as given by the heat of fusion seem not striking. this would indicate that the solvent does not have any impact on the state of the chains exposed to the surface. It also means that different solvents should have the same barrier. In order to substantiate the claim, experiments with shorter and longer chains should be performed, and also with different solvents.

How does the predicted constant energy barrier (heat of fusion per chain) relate with the original observation that the speed of dissolution is higher at the border of the crystal?

We thank the referee for this highly valuable advice. Accordingly, we have performed dissolution experiments in different solvents, and a series of dissolution experiments of polymer crystals having different lamellar thicknesses and resulting from different molecular weights of PEO.

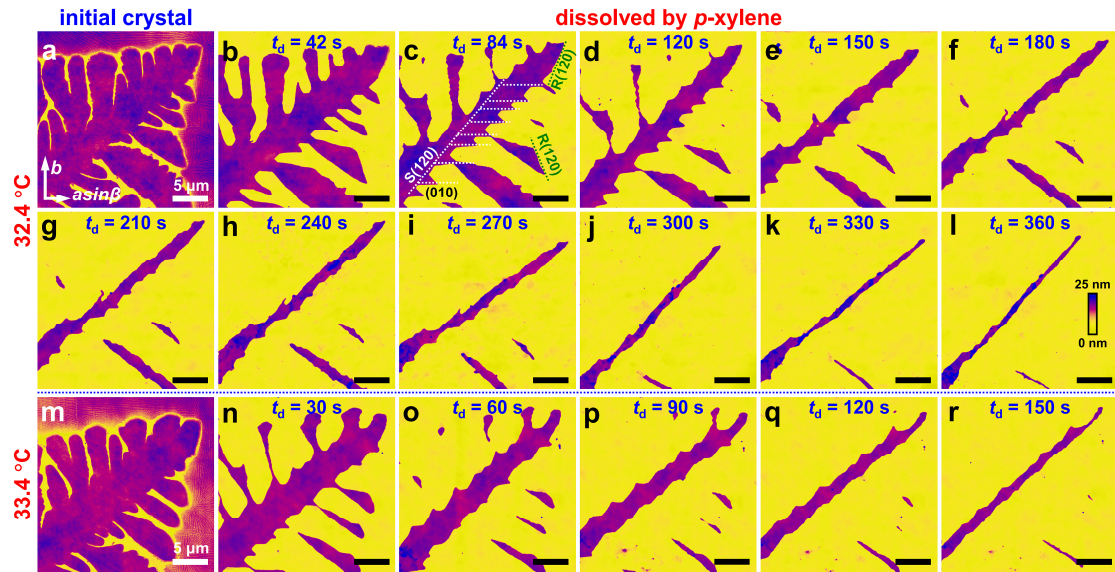


Figure R3. Temporal evolution of changes in morphology in PEO crystals, which were induced by selective dissolution. (a, m) Height images of the initial dendritic PEO crystals grown at $[(T_c, t_c) = (49\text{ }^{\circ}\text{C}, 120\text{ s})]$. Successive AFM height images showing the surface topographies of the PEO crystals after selective dissolution in *p*-xylene for different times (t_d) at a dissolution temperature $T_d = 32.4\text{ }^{\circ}\text{C}$ for images (b-l) and $T_d = 33.4\text{ }^{\circ}\text{C}$ for images (n-r), respectively.

Firstly, dissolution experiments of PEO crystals in *p*-xylene were carried out at temperatures ranging from 30.8 °C to 33.4 °C. The corresponding results are shown in Figure R3. From the morphological changes of PEO dendrites after selective

dissolution in *p*-xylene, one can clearly see that initially the dissolution is along the contour line, and then along specific crystallographic planes. In particular, apart from the smooth and rough (120) planes, the dissolution is also along the (010) planes (see Figure R3c). Additionally, a distinct difference in dissolution behavior between the various side branches can be observed.

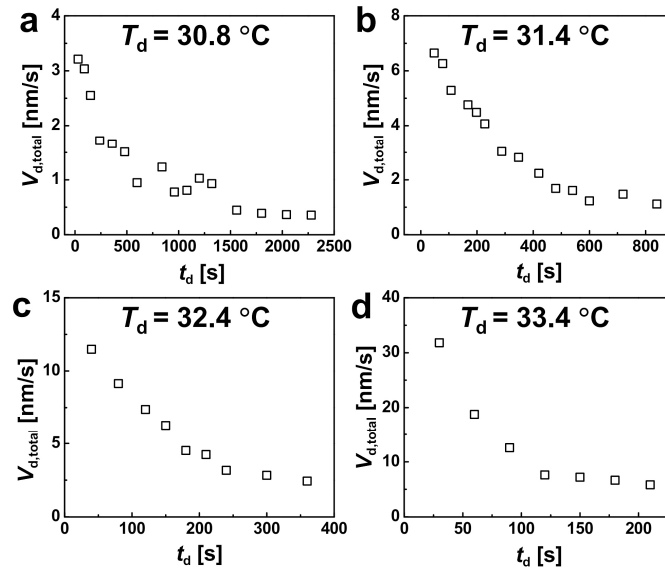


Figure R4. Plots of the overall dissolution velocity ($V_{d,\text{total}}$) as a function of dissolution time (t_d) in the course of dissolution in *p*-xylene at different temperatures (T_d). The initial PEO crystals were grown at $[(T_c, t_c) = (49\text{ °C}, 120\text{ s})]$.

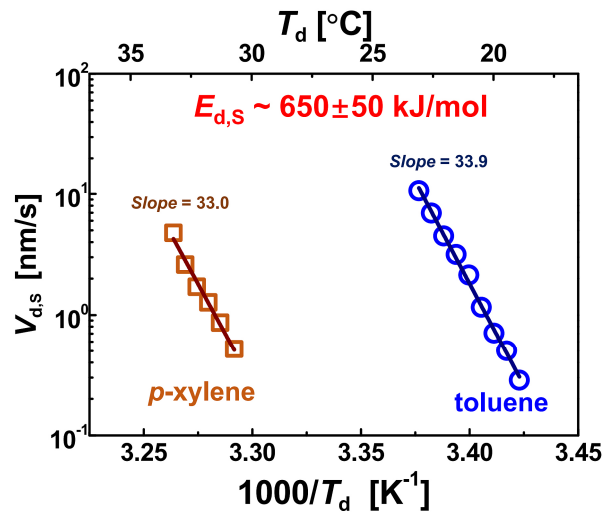


Figure R5. Dependence of the dissolution velocity, which approached a constant value, i.e., $V_{d,s}$, along the S(120) faces, versus the reciprocal dissolution temperature ($1000/T_d$) for PEO lamellar crystals generated at 49 °C in the course of dissolution in *p*-xylene and toluene, respectively.

The overall dissolution velocities ($V_{d,\text{total}}$) for all samples in *p*-xylene at different T_d initially decreased with increasing t_d (see Figure R4), but approached at long t_d a constant value along the S(120) faces, i.e., $V_{d,s}$. Figure R5 shows the temperature

dependence of $V_{d,S}$, which suggested an Arrhenius-like relation. From this plot, we obtain a value of $E_{d,S} \sim 630 \pm 50$ kJ/mol, which is close to the value obtained for dissolution in toluene (ca. 650 ± 50 kJ/mol). As anticipated by the referee, the solvent has no appreciable effect on the “*state of the chains exposed to the surface. In the two studied solvents*”. For both solvents, the energy barrier for dissolution (detachment) of a chain or a stem from the crystalline surface is rather similar (within the uncertainty of the measurements we cannot detect significant differences). We tentatively believe that the relevant energy for this process is related to the number of detached monomer-monomer interactions at the crystal surface. However, our results clearly indicate that different solvents have different (maximum) dissolution temperatures.

Furthermore, lamellar crystals resulting from different molecular weights of PEO (ranging from $M_n = 2$ kg/mol to $M_n = 20$ kg/mol) were prepared at different crystallization temperatures in ca. 9 nm thin films. Subsequently, these crystals were dissolved in toluene at varying temperatures. As shown in Figure R6, the overall dissolution velocities ($V_{d,total}$) for all samples at different M_n initially decreased with increasing t_d and then tended to be constant at long t_d . Figure R7 shows the dependence of the $V_{d,S}$ versus the reciprocal dissolution temperature ($1000/T_d$) for lamellar crystals prepared from different molecular weights of PEO.

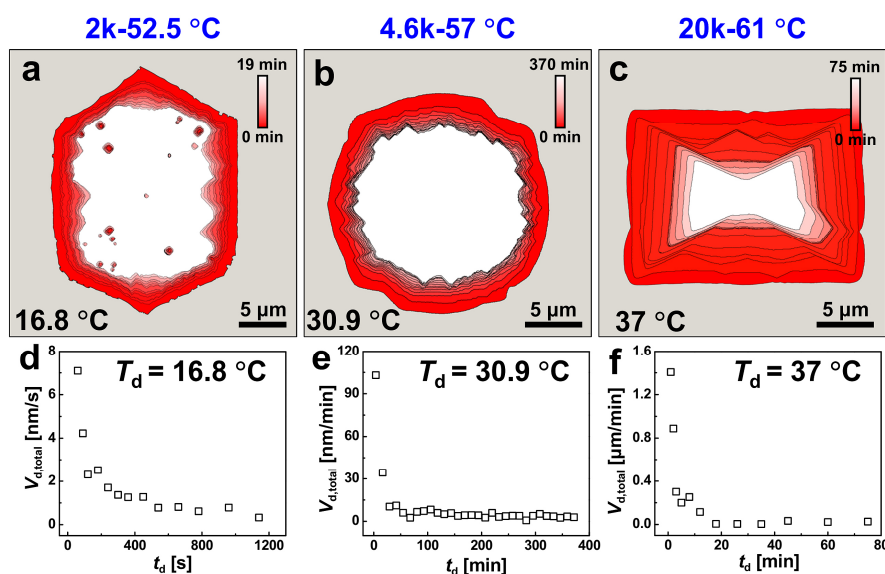


Figure R6. (a-c) The false-colour overlays of the contours of PEO crystals of different molecular weight derived from AFM images, taken in the course of selective dissolution. Please note that crystals were grown at different temperature (labelled in blue) and accordingly dissolution took place at different temperatures T_d (labelled in black). The bare substrate is represented in a grey colour. The initial PEO crystals were grown at (a) $[(T_c, t_c) = (52.5 \text{ °C}, 120 \text{ s})]$, (b) $[(T_c, t_c) = (57 \text{ °C}, 180 \text{ min})]$ and (c) $[(T_c, t_c) = (61 \text{ °C}, 240 \text{ min})]$. (d-e) Plots of the overall dissolution velocity ($V_{d,total}$) in toluene for the crystals of the three different molecular weights as a function of dissolution time (t_d) at the indicated dissolution temperatures (T_d).

For PEO with $M_n = 4.6$ kg/mol, the dissolution of extended chain crystals grown at 57 °C, IF(0), was probed by *in situ* AFM measurements at different dissolution temperatures. The slopes shown in Figure R7 for IF(0) and IF(2) are similar. This suggests that the activation energy required for the respective processes, namely, the removal of three stems of a folded-chain from the surface [slope IF(2)] as well as the detachment of an extended chain [slope IF(0)], is the same, indicating that dissolution requires the detachment of whole chains and not proceeding as a detachment of stem after stem. The two Arrhenius-like relations in Figure R7 give a value of $E_{d,s}$ around 650 ± 50 kJ/mol.

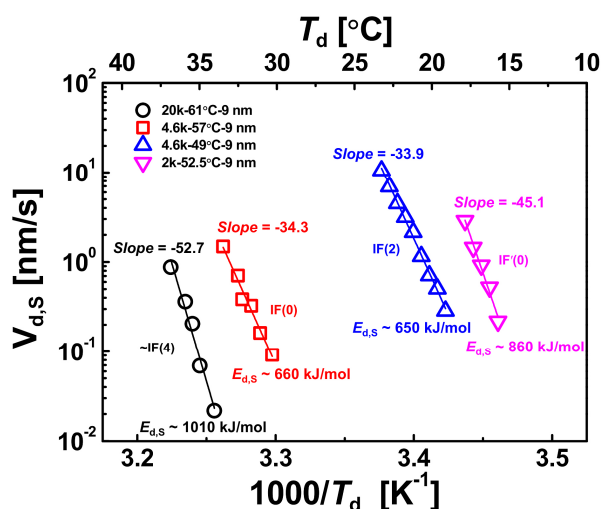


Figure R7. Dependence of the dissolution velocity in toluene, which approached a constant value, i.e., $V_{d,s}$, along the S(120) faces, versus the reciprocal dissolution temperature ($1000/T_d$) for lamellar crystals of PEO with different molecular weights.

For the cases of $M_n = 2$ kg/mol and 20 kg/mol, respectively, the dissolution experiments of lamellar crystals were performed in toluene at different temperatures. As shown in Figure R7, the value of $E_{d,s}$ ($\sim 860 \pm 100$ kJ/mol) obtained from the dissolution of extended chain crystals [IF(0)] with $M_n = 2$ kg/mol, corresponds to the simultaneous detachment of three stems (chains) from the crystalline substrate. However, the value of $E_{d,s} \approx 1010$ kJ/mol for the folded chain crystals with $M_n = 20$ kg/mol refers to the detachment of two stems from the crystalline substrate.

The results in Figures R6-R7 show that the dissolution temperature increases with molecular weight, but there is no significant and clear molecular weight dependence of the value of $E_{d,s}$.

5. *The term “metastability” as imposed by the authors (as an orthogonal property to the crystal thickness) is indeed very difficult to understand. The authors argue that this might have to do with unfavorable growth direction, or with the effective time of*

transport of the chains through the depletion zone. But this should lead to crystalline structure which also should display different energy barriers (and heat of fusion). Could the decrease of dissolution velocity be related to the more stable attachment to the substrate of the “earlier” crystalline parts?

Thank you for your suggestion!

Figure 3 shows that the branch B2 emerges significantly later than branch B3 (Figure 3c), but it exhibits a considerably slower dissolution rate compared to B3 (Figure 3f). These observations suggest that the decrease of dissolution velocity does not depend on the time when the polymers became crystalline at the growth front.

Although phase transitions are controlled by thermodynamic parameters, in the majority of experimentally observed cases, the kinetics of the transitions practically determines the properties of the finally obtained metastable states.^[R15, 70] As a consequence of the complexity of the resulting metastable states of chain-folded polymer crystals, they possess an intrinsically broad temperature range for the so-called melting region and exhibit processes of recrystallization and reorganization, affecting also the melting kinetics of superheated crystals^[R60, 71]. In our study, the presented results confirm that the growth kinetics during crystallization affects metastability and dissolution kinetics of different branches in dendritic crystals, resulting in a significant difference in dissolution velocity of the various crystalline branches.

Accordingly, we have modified and improved the manuscript. The parts related to “degree of metastability” in the manuscript have been modified.

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Detailed response on the comments (written in blue) by Reviewer #1

I have checked the extensive and detailed response to my comments by the authors and am satisfied that they have responded satisfactorily in full, and made the appropriate changes. There is just one minor detail which I would like them to correct. On page 17, line 341-, there is the sentence “There, at any given dissolution temperature in an almost infinitely dilute solution, the free energy difference (i.e., the gain) upon dissolving a polymer from a rough face is higher than from a smooth one.” Upon dissolution above the dissolution temperature the free energy drops rather than gains, otherwise the process would not go ahead. The drop is caused by the increase in entropy of the system. Otherwise, I do not have any further objections and am recommending publication of this fine paper.

We are deeply grateful to the reviewer for their encouraging remarks and constructive feedback, which have greatly contributed to enhancing the quality of our manuscript. Their thoughtful suggestions have provided us with valuable insights and have been instrumental in refining our work. We sincerely appreciate the time and effort they dedicated to reviewing our submission and offering such meaningful guidance.

We fully agree with the reviewer that the free energy drops rather than gains when dissolution above the critical dissolution temperature. Accordingly, we have modified it in the revised version.

The sentence “There, at any given dissolution temperature in an almost infinitely dilute solution, the free energy difference (i.e., the gain) upon dissolving a polymer from a rough face is higher than from a smooth one.” ***has been modified as*** “Above the critical dissolution temperature $T_{d,cr}$, the free energy drops caused by the increase in entropy of the system induced by dissolving the ordered crystal. There, at any given dissolution temperature in an almost infinitely dilute solution, the free energy difference upon dissolving a polymer from a rough face is higher than from a smooth one.” (Page 17 line 347-349)

The sentence “Consequently, at any given temperature above $T_{d,cr}$, dissolution of rough faces is faster than that of smooth faces.” ***has been added.*** (Page 17 line 354)

Detailed response on the comments (written in blue) by Reviewer #2

I have checked the authors' answers to the comments of Reviewer 2. Some of the answers and changes made to the manuscript are already given in response to comments by reviewers 1 and 3. Regarding comment 3 by reviewer 2, the answer given clarifies the situation, at least clarifies the method used. Taking the average dissolution velocity when the velocity varies significantly with time may not be an ideal technique when it comes to Arrhenius fitting.

We sincerely appreciate your professional and thorough review of our article. Your insightful feedback has been invaluable in refining our work and improving its quality. We sincerely appreciate the time and effort you dedicated to evaluating our manuscript, and we are truly thankful for your constructive suggestions.

- 1. However, I suppose there is some justification for it, given the dissolution kinetics in this system. Why the velocity drops so drastically with time is still something of a puzzle to me. Separating the contributions from rough and smooth surfaces makes a lot of sense, as rough faces dissolve earlier than smooth ones. Yet even after separation, the individual components $V(R)$ and $V(S)$ still decay with time. By the way I cannot see the shapes of separate $VR(t)$ and $VS(t)$ – am I missing something? So what is the reason these separate rates should slow down as dissolution front approaches the center of the crystal? During the growth of the crystal, has the center perfected while the periphery was still growing? But on the timescale of the experiment, all parts of the crystal would have had time to perfect before the dissolution experiment. And also, in their rebuttal the authors say: “Furthermore, given that the samples were kept at maximum (after multiple steps) only up to ca.1000 s in pure solvent, we do not anticipate any significant reorganization processes to occur.” So what causes the increased resistance of the crystal center? I suggest that serious consideration should be given to fractionation during growth of the crystal. It is true that, on the scale of commercial polymers, PDI of 1.14 is a rather narrow fraction. Nevertheless, the polymers used are not monodisperse, and the higher MW fraction is expected to crystallize first forming the crystal center, while the lower MW fraction would have been left at the periphery. The consequences for dissolution process are obvious.*

Undoubtedly, this is an excellent question. Given the current understanding, we propose there might be two potential causes for the decay of $V(R)$ and $V(S)$ over time. First, as highlighted by the reviewer, the crystallization process may result

in fractionation due to a PDI greater than 1. Our study shows that the dissolution temperature of high molecular weight PEO crystals is higher, while their dissolution rate is lower. Consequently, the peripheral regions consisting of the lower M_w fraction exhibit faster dissolution, whereas the crystal center with higher M_w fraction dissolves more slowly. Another potential explanation might be that the diffusion effects resulting from high undercooling produce imperfectly smooth faces at the periphery. We deeply thank the reviewer for identifying this, as it has clarified the path for our future research, and we will address this issue in our upcoming work.

2. *One comment about the “degree of metastability”, which has been discussed at some length in the correspondence between the author and the reviewers. Like the other reviewers, I also do not like this fuzzy term. But if it has to be used, I see no problem in defining it. Surely it must be the excess free energy of phase 1 above the most stable phase, phase 2. So if phase 1 is an imperfect or a small crystal and phase 2 the perfect infinite crystal then the excess free enthalpy can be expressed, to a good approximation, as $\Delta G = \Delta T * \Delta S$, where ΔT is melting point depression and ΔS is melting entropy. Similar for dissolution.*

Again, this is an excellent suggestion. Accordingly, we have defined “degree of metastability” following the description of “metastability” in the Introduction section of the submitted revised manuscript.

The sentences “The degree of metastability refers to how far a metastable state deviates from its equilibrium state.” *has been added.* (Page 3 line 55)

Moreover, to make minimal changes to the manuscript, we still have written (e.g., in the abstract) spatial variations in metastability, which may reflect different “degrees” of metastability.

I advise the authors to consider these comments. If they feel they are helpful and making changes to the paper in response to them would improve the paper, please make those changes at your discretion.

We would like to express our heartfelt gratitude for your positive evaluation and invaluable suggestions, which have significantly contributed to improving the quality of our manuscript. Your thoughtful feedback has been instrumental in refining our work, and we deeply appreciate the time and effort you have dedicated to reviewing our submission. We are committed to incorporating your

insights into our research and ensuring that the manuscript meets the highest standards. Thank you once again for your encouragement and constructive advice, which have been truly inspiring for our team.

Detailed response on the comments (*written in blue*) by Reviewer #4

A method based on the selective dissolution at constant temperature in a pure solvent of isothermally grown poly(ethylene oxide) (PEO) dendritic single crystals is described. The method allows to probe differences in the metastability of PEO crystals, while providing information on the relationships between growth kinetics and the “degree of metastability” of different single crystal regions. The revised manuscript correctly accommodated the changes proposed by the initial reviewers, resulting in an excellent work that highlights unsolved problems in polymer physics. In my opinion it should be published unchanged.

We are deeply grateful for the reviewer’s recognition of our efforts and their positive evaluation of our work. Their encouraging feedback not only validates the direction of our research but also inspires us to continue striving for excellence. We are deeply grateful for their thoughtful comments, which have provided valuable insights and motivation for our ongoing and future endeavors. Such recognition is truly rewarding and reinforces our commitment to advancing this field of study.

- 1. I think it would be nice to complement the approach, using selected area electron diffraction (SAED) of the single crystals dissolved for different times, coupled with dark field imaging, in order to map the coherent contribution to ED reflections from the different stem layers and to visualize the defects.*

We thank the referee for this highly valuable advice. The referee has proposed a valuable technique to refine and expand our investigation. We fully intend to incorporate SAED characterization in our future studies, as we believe it will offer profound insights into our study. This thoughtful suggestion has inspired us to further enhance the quality and depth of our research endeavors.