

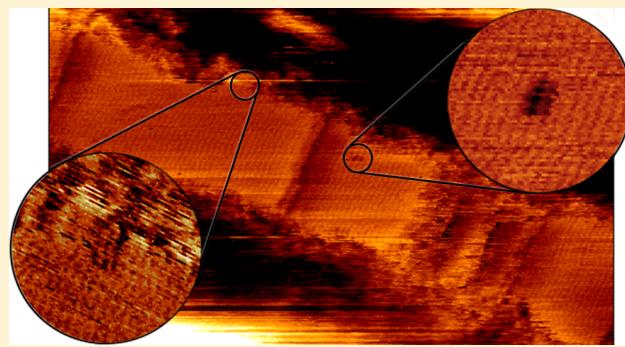
Molecular Conformation at the Crystal–Amorphous Interface in Polyethylene

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 Supporting Information

ABSTRACT: Torsional-tapping AFM with supersharp carbon-whisker tips is used to explore the molecular conformations at the surface of a semicrystalline polymer. Images of the crystal–amorphous interface of oriented polyethylene have allowed us to measure hitherto inaccessible parameters that can be directly compared to polymer crystallization theories and molecular simulations, such as the length of stem-to-stem overhang. It has also been possible to identify both first- and second-neighbor folds and to determine the surface roughness of lamellae which we find approximately doubles the interfacial area. Finally, we calculate the interfacial density profile from the images and find it to be sigmoidal but narrower than values reported by SAXS measurements.



INTRODUCTION

Most semicrystalline polymers consist of hard, elastic, crystalline lamellae with a typical thickness of the order of 10 nm, surrounded by a matrix of rubbery amorphous material, with individual polymer chains having parts in both states.¹ It is this spontaneously formed nanoscale structure that provides many of the desirable properties of polymer materials, such as toughness and strength. Since the 1950s one of the main goals of polymer physics has been to understand these complex structures in terms of the individual chains from which they are formed. Until recently,² direct imaging of chains within the three-dimensional semicrystalline structure has not been possible. Experimental evidence has therefore come from methods that average over many molecules, such as scattering and spectroscopy, which rely on the application of a model to interpret the raw data. This difficulty of directly measuring the behavior of individual molecules has severely limited the development of a verifiable molecular theory of polymer crystallization. Similarly, though computer simulations have provided valuable insights into the crystallization process on the molecular scale, validation of their results is hampered because of the inaccessibility of directly comparable experimental data, to the point that such information is rarely even reported, with authors concentrating instead on larger scale and more readily measurable properties such as average lamella thickness or growth rate.

With the recent development of true molecular resolution imaging,^{2–5} i.e., the ability to resolve single molecular defects,⁶ there is an opportunity to re-examine many of the foundations on which our understanding of semicrystalline polymers are based. By implementing torsional tapping AFM on a commercial instrument equipped with a high precision closed

loop scanner, we have been able to make accurate and traceable measurements at the submolecular scale. Here we have implemented this technique to study an area that is of particular importance to the physical properties of polymer materials—the nature of the crystal–amorphous interface at a molecular level. We find that it is unexpectedly disorganized when compared to textbook schematics and that it may be necessary to re-evaluate the parameters used when interpreting data collected from techniques that average across the entire sample, such as X-ray scattering. Furthermore, we are also able to provide real-space measurements of molecular position against which models of polymer crystallization and computer simulations can be tested or validated.

EXPERIMENTAL METHODS

As in our previous study,² torsional tapping atomic force microscopy (TTAFM) was used to image the archetypal semicrystalline polymer, high-density polyethylene. TTAFM uses T-shaped cantilevers with the tip offset from the oscillation axis. By using a torsional oscillation to provide the tapping motion, TTAFM has significantly improved signal-to-noise ratio and force sensitivity compared to conventional tapping mode AFM.⁷ When combined with supersharp carbon-whisker tips with a radius of curvature typically less than 1 nm,⁸ molecular resolution images can be obtained even on relatively rough surfaces.

The oriented “shish-kebab” morphology was used in order to obtain crystalline chains lying parallel to the sample surface.^{2,9} Samples were prepared from a 1 wt % solution of polyethylene ($M_w = 84\,500$ Da, $M_w/M_n = 1.28$, PSS) in *p*-xylene (puriss. p.a. $\geq 99.0\%$, Sigma-Aldrich) drop-cast onto a glass coverslip on a heating stage (Linkam TP94) held at 160 °C for 20 min to ensure complete melting of the polymer

Received: December 22, 2014

Revised: July 30, 2015

Published: August 19, 2015

and evaporation of the solvent. Thereafter, the stage temperature was lowered to 139 °C and the surface sheared with a blade, orienting the film. Contact with the blade would quench the surface and cause the polymer to crystallize. In order to crystallize lamellae at higher temperatures, the sample was maintained at 139 °C for 13 s, a time period determined from cryo-quenching experiments to be sufficient to melt the lamellar “kebabs” but not the highly oriented “shish” backbone (see SI1). The sample was then slid onto an adjacent heating stage (Linkam TP93) and held at 120 °C for 40 min, allowing new lamellae (“kebabs”) to crystallize.

All AFM imaging was performed under ambient conditions using a JPK NanoWizard III Ultra AFM in a home-built acoustic and vibration isolation system. The microscope was factory modified to reduce the noise floor of the lateral deflection signal to $\sim 10 \text{ fm}/\sqrt{\text{Hz}}$ (see SI2). To reduce thermal drift, samples were placed under the microscope and shut into the isolation hood overnight with the microscope turned on in order to let them reach thermal equilibrium. This resulted in a drift of 1.45 nm/min in the XY plane during measurements, calculated from the apparent change in position of an identifiable point visible in two images, taking account of the time difference between the scan lines crossing them. The drift was calculated from three pairs of images from throughout the session and was found to be consistent in magnitude but varied in direction from 84° to 90° measured from the lamellar axis toward the bottom right of the images. The microscope was operated with the scanner in closed loop (specified positioning accuracy of better than 0.1 nm) and with a reduced scan range in the X and Y directions to reduce noise. Calibration of the scanner in the XY plane was verified by scanning 1 and 3 μm gratings (PG and STR3-1800P, Bruker) in tapping mode at 1 Hz scan rate and confirmed at smaller scales by imaging the atomic lattice of mica in contact mode in water at 16 Hz scan rate. Measurements of the grating pitch were within 1% of the specified value, and measurements on mica were found to be within 10% of the expected value. We also note that the chain spacing measured from the images presented here are in agreement with reported WAXS measurements.¹⁰ The main uncertainty in the positional measurements is due to drift between the AFM tip and the sample. The effect of this on the measured chain spacing was minimized by adjusting the scan angle to ensure that the fast scan axis was substantially perpendicular to the chain axis in the lamella of interest; hence, for measurements of chain spacing the chief uncertainty is the positioning uncertainty of the scanner, specified to be 1 Å. Measurements of stem length and stem end projection were made perpendicular to the fast scan axis and are therefore susceptible to drift. Hence, these measurements are systematically underestimated by approximately 26%. As the measurements of stem length and stem end projection presented here were taken from the images acquired in the same session, the drift is consistent and the relative errors and effects of drift on the shape of length distributions are small. Measurements of stem tilt angle are also systematically affected by the same drift. The extent of the error is dependent on the angle of the chain relative to the drift direction, so uncertainties for chain angle are presented for each measurement.

Measurements of grating depth from the capacitive sensor channel on the Z scanner were within 3% of the specification. The accuracy in this case is limited by the tolerance in the manufacturing process of the grating. All quoted height measurements were made from the Z capacitive sensor channel as this gives a traceable measure of height, but the height images presented are from the Z feedback channel as this does not suffer from capacitive sensor noise.

Tapping mode AFM images were acquired using Bruker TESPA probes and TTAFM images with Micromasch TL01 cantilevers with carbon whisker tips.⁸ TTAFM images were collected with an amplitude set point typically around 0.55 V, within a few tens of millivolts of the free amplitude, corresponding to an amplitude of approximately 5 nm and a mean tip–sample force² on the order of some tens of pN. Height and phase images were recorded in both trace and retrace directions with a pixel density of 1 Å/pixel at a scan rate of 1 Hz, which corresponds to a tip speed of 100 nm/s. Image analysis was performed with Gwyddion or ImageJ software.

RESULTS AND DISCUSSION

Initially, we characterize the crystallography of the exposed surfaces. Overview images acquired in tapping mode (Figure 1)

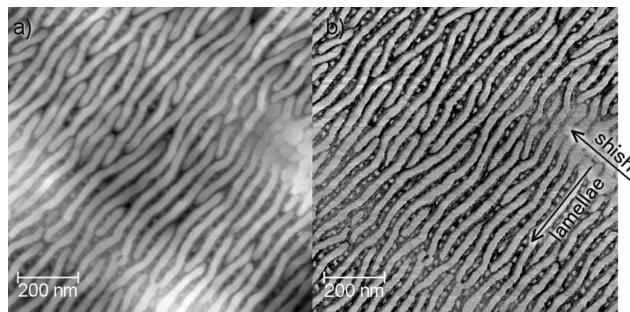


Figure 1. A tapping mode overview image of an oriented sample showing the lamellae growing perpendicularly from shish lying below the surface under the thicker crystalline areas: (a) height image and (b) phase image. Both images have been flattened to first order. Grayscale represents (a) 30.5 nm and (b) a phase lag of 2.4°.

show lamellae growing perpendicularly from the extended chain shish below the surface. The lamellae projected 4–9 nm above the amorphous region (see SI3), and as previously² we find that they present molecularly stepped surfaces (Figure 2a,c) with terraces typically ranging from less than 5 nm up to ~ 20 nm

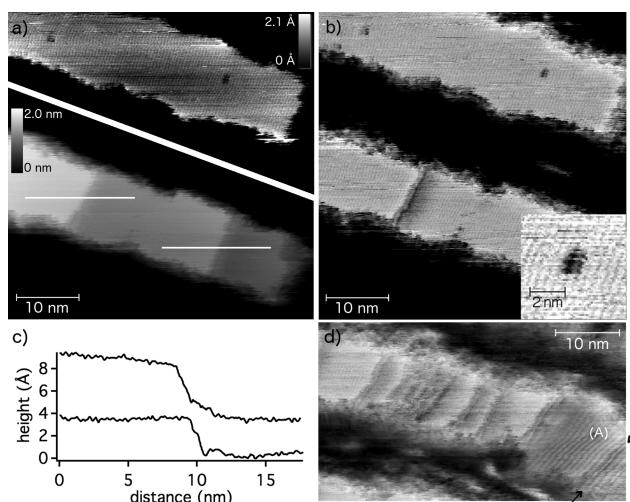


Figure 2. (a) TTAFM height image showing two lamellae at different height scales to emphasize stems (upper) and steps (lower) respectively. The upper image was plane fitted to first order, and median line corrected to the crystal face. The lower image was flattened using the Gwyddion “path level” tool, applying a zeroth-order flatten to scan lines selected on the crystalline terraces. The whole image was subsequently plane-fitted to first order using a plane defined by three points on the central terrace. (b) TTAFM phase image, median line corrected to crystal faces and contrast set to emphasize stems. (inset) Magnified view of the same image showing the right-hand hole in the surface of the upper lamella. (c) Height profiles along lines in (a) showing molecular steps. (d) TTAFM phase image of a lamella with {110} terraces to the left and a section of {010} to the right (labeled A). The darker line (arrowed) is a single-layer step. The unprocessed image is presented in SI4 together with the images from the height and amplitude channels where a further two molecular steps can be seen. Black to white represents (a, top) 0.209 nm, (a, bottom) 2.0 nm, (b) 9°, (b, inset) 4.9°, and (d) 16.4°.

long, though exceptional cases over 50 nm have been observed. Figure 2b shows a high-resolution phase image of two typical lamellae with chains spaced by 4.5–5.0 Å. To determine the visible crystallographic planes, we first considered the most tightly packed planes of polyethylene: the {110} and the {100} which have chains spaced by 4.4 and 4.9 Å respectively.¹⁰ As the chain spacing of these faces differ by only 0.5 Å it was not possible to unambiguously distinguish these planes from chain spacing alone. However, considering also the angle between the stem normal and lamellar direction, we find that half the lamellae have stems oriented at <7° (6.5° accounting for the systematic error) and half have stems oriented at ~18° or 35° (15° or 30° accounting for the systematic error). Both small and large angle lamellae have been observed in the same image; therefore, this variation cannot be due to drift alone. It has previously been shown that melt-crystallized HDPE has a tilt along the *a*-axis ranging from 19° to 41°, with the two most common values being ~34° or ~19°.^{11,12} Projected onto the {110} this would be seen as ~28° or ~16°, whereas the tilt of the {100} would lie in the surface and the stems would appear perpendicular to the direction of the lamellae. This agrees well with our two groups of stem angles. We note also that faces containing chains at angles <7° (now presumed to be the {100} faces) present wide terraces separated by single or double steps, whereas only one with the higher angle {110} plane has similar morphology. All other observations of {110} terraces were <10 nm in length and interspaced by high index faces, suggesting that the {110} plane is less likely to form long terraces on the surface.

Some shorter sections of lamellae show a plane with wider spacing, an example of which is given in Figure 2d. Measurements from 11 areas have an average spacing of 7.6 Å (standard deviation 0.5 Å), corresponding well with the 7.4 Å chain spacing of the {010} crystal face. These sections are less common and considerably shorter than the other low index planes, typically only 4–11 chains long.

On the {100} and {110} crystal faces we frequently observe small defects (inset of Figure 2b and S15). These are typically two chains wide, appear to be 0.5 Å deep or less, stay in the same position for consecutive images, and have been observed in both TTAFM with carbon whisker tips and tapping mode with silicon tips. The tip typically has difficulty tracking the surface when scanning over the holes, suggesting that it is perturbed by loose ends or folds associated with the defect. When there are a few stable lines it is possible to see (part of) a faint chain inside the hole. This appears to be an extension of one of the stems leading up to the hole, suggesting that it is one of the detached chains lying loosely in the hole rather than a chain in the layer below. Considering this, we suggest that the holes may be chain ends or folds causing a point defect in the crystal surface.

In the following sections we concentrate on analysis of individual chains with the aim of using direct stem-by-stem examination of crystalline regions as an analytical tool for improving our understanding of the processes that occur when polymers crystallize. Measurements such as this are very demanding as drift and low-frequency vibration of the microscope stage could create artifacts and lead to false interpretations of the data. Previous AFM studies of polymers have not attempted to characterize chain conformation to this extent or with this level of constraint on the subnanometer measurement precision, so we have carried out several additional analyses to test the data.

To ensure that variations in stem length were a real feature of the sample, several individual lamellae, including the one shown in Figure 2a, were imaged twice, and measurements of the lengths of the same stems, as measured from a clear reference point (such as a step-edge or hole), were compared (see SI6 for details). Qualitatively, outlines of the lamellae, including the roughness of the crystal–amorphous interface, are very similar in the different images, corroborating the impression given from a single image. Measurements of crystalline stems in the paired images reveal an average difference between stem lengths (as measured on two images of the same stem taken at different times separated by at least 10 min) of 0.5 nm, i.e., a statistical error comparable to the chain–chain spacing and approximately 5% of the stem length. A component of this is personal judgment as to where a stem ends. We have attempted to quantify this by analyzing the same images twice and recording the difference in stem length (details can be found in S17) and find it to be smaller than the random error found from measurements taken of the same chains measured in different images. This implies that there are real differences between images taken of the same chain at different times, caused either by motion of the molecules close to the basal plane of the lamella or by small differences in scanning conditions.

Further examination of the images shows a clear artifact in that chains within the images are expected to be straight lines but in fact have some “wiggle” perpendicular to the chain axis, most likely due to mechanical and thermal instability within the experimental setup. Analyzing the “wiggle”, we find that it has an rms amplitude of 0.13 nm (see S18), approximately 25% of the chain–chain spacing and considerably smaller than the features that we will consider as “real” below. We therefore ignore this artifact in the analysis of the results.

To summarize, the uncertainties in our measurements of stem length have been characterized into the following components: (i) a systematic error due to tip–sample drift, causing underestimation of the lengths of molecular segments, but only having a small effect on relative measurements and the shape of distributions of segment length; (ii) a random error due to uncertainty in the position of the end of the crystalline stem, having components due to personal judgment, subtle changes in imaging conditions, and apparent motion of the molecules themselves; and (iii) small scale, time varying drift, which impacts visually on the data, but whose effect on measurements of stem length is negligible. The relative effects of each of these sources of error on measurements derived from our images are discussed with reference to each of our major findings below.

One of the primary observations that any theory of polymer crystallization has to explain is that the crystalline lamellae are considerably thinner than their constituent molecules and must therefore be out of equilibrium. Theories differ as to the nature of the barrier that hinders extended crystal growth, most notably those with a nucleation barrier (e.g., Lauritzen–Hoffman^{13–16}) or those with an entropic barrier (e.g., Sadler–Gilmer¹⁷), and depending on the details of how the various theories are applied^{18–20} different crystal thicknesses are attained at a given crystallization temperature. Furthermore, theories have to allow for the observed variation in stem length within the lamellae, and here also each theory predicts a different distribution of the crystalline stem lengths. In order to compare these to our data, we measured 190 stems across six lamellae (Figure 3a). The mean stem length is 10.1 nm, but as has been noted by previous AFM measurements,²¹ the

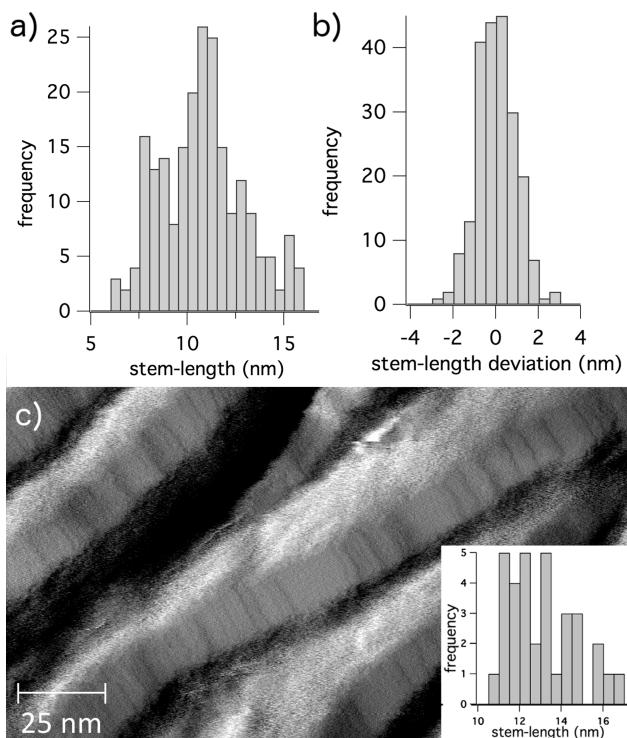


Figure 3. (a) Distribution of stem lengths from six lamellae. (b) Distribution of stem-length deviation from the individual lamella average. (c) One of the tapping mode images showing clearly defined molecular steps from which the stems' orientation could be inferred (amplitude image, grayscale 17 mV). (Inset) Distribution of widths of lamellae measured along the stem direction, obtained from tapping mode images such as (c).

distribution is very broad and shows multiple maxima. For comparison, we also measured widths of lamellae along the stem direction from tapping mode images which showed clearly defined molecular steps (Figure 3c), from which the stems' direction could be inferred. These were found to be slightly wider on average, 13.1 nm (Figure 3c inset), as might be expected due to tip convolution, but the range of values is within the range of those measured from TTAFM images.

The rms deviation from the average of all stem lengths as presented in Figure 3a is 1.72 nm or ~17%. Although these measurements are from many images, they were all subject to the same drift, giving a systematic error affecting the entire data set rather than inducing an apparent variation in stem lengths within it. The dominant error in this measurement is the systematic error which causes the stem length to be underestimated by 26%. Smaller random errors arising from the uncertainty in the actual location of the end point of the stem has the greatest influence at the shorter stem lengths, as it makes up a greater fraction of the total measured length for short stems (approaching 10% for the shortest stems measured). For the modal value of the distribution the random component of the uncertainty is approximately 5% of the total stem length. We also considered the stems' deviation from the average stem length of each individual lamella, which compared to the combined data set of Figure 3a has a more limited range and a very well-defined maxima. This shows that there is a consistent, but limited, variation in stem length within each individual lamella but that this is much smaller than the variation between other, even neighboring lamellae. It was found that on average lamellae had an rms stem length

deviation of 0.73 nm, and the rms deviation of all stem length deviations was 0.90 nm (Figure 3b). While these deviations are close in value, extrapolating the random error calculated in SI6 by the square root of the number of data points to account for the much larger data set suggests that we are able to discern differences in average stem length to approximately 0.4 Å—approximately 25% of the observed difference. The measured values for both single lamella stem length deviation and deviation within several lamellae are in line with the Lauritzen–Hoffman theory's predicted kinetic term which ranges from ~0.6 nm¹⁴ to ~1.2 nm.¹³ Furthermore, both the shape and width of this distribution closely resemble computer simulations based on the Lauritzen–Hoffman theory.^{18,19} It is also worth noting that the relatively large difference in stem lengths from one lamella to another indicates that though current models are good at predicting the behavior of individual lamellae, in practice there is a wide variation across a sample. This could be highly relevant to our understanding of polymer materials since it is the entire range of morphologies present in the material that ultimately determines its mechanical properties.

Turning our attention to the edges of the lamellae, we find not only many first-neighbor folds (Figure 4a) but also a

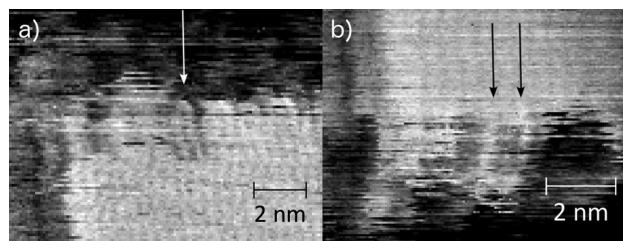


Figure 4. Details from TT-AFM phase images showing (a) a first-neighbor fold, marked by an arrow, and (b) a second-neighbor fold, with arrows marking the two stems. The images have been median line corrected to the area of the terrace. The grayscales represent a phase lag of (a) 7.7° and (b) 9.2°. The entire images from which these were cropped are presented in SI9, together with the corresponding height images, line profiles, and return traces.

smaller number of second-neighbor folds (Figure 4b). That a significant number of stems fold and re-enter the crystal has long been known²² but has as yet not been directly observed in semicrystalline material. That we see fewer second-neighbor folds does not necessarily imply they are fewer in number, but as they must necessarily project farther out from the lamella to complete the fold we would expect them to be less immobilized by their proximity to the crystal and therefore more difficult to image by AFM. Similarly, we do not believe that the number of times we see folds is a good indicator of the total number of chains that fold back into the crystal, as it is likely that for the fold to be resolved by the AFM requires a fortuitous combination of factors, including the packing of nearby chains, the nature of the material in the layer below the folds that cannot be observed with AFM, and the imaging parameters happening to be optimized for that particular region of the image. It is possible that many more folds exist that do not fulfill all of these criteria. Finally, we note that even where "tight" first neighbor folds occur, there are significant steps between adjacent folds.

In both theory and simulation of polymer crystal growth it is clear that the factor inhibiting crystal thickness will limit the

extent to which a depositing chain can overhang its neighbor. Although our data are collected *ex situ*, it provides the closest available experimental insight into this aspect of crystallization. In our images we see that the lamellae edges have a roughness on the order of 1 nm, with stem ends sometimes projecting out by as much as \sim 2 nm. The furthest projecting stem ends were very mobile, moving between successive scans. Those that project more than a few angstroms often bent to one side over the end of their neighbors. It is primarily the longest stem ends that change with successive scans, and therefore this motion and potential ambiguity only affect the tail of the distribution in Figure 5b. This mobility, when combined with the roughness of

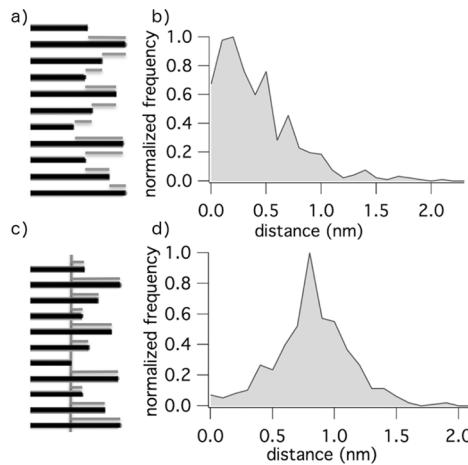


Figure 5. (a) Schematic of a lamella edge, with gray lines marking the stem end projection measured to obtain (b), the normalized distribution of stem end projections. (c) Schematic of a lamella edge with gray lines marking the distances measured to determine roughness. (d) Normalized histogram of lamella edge roughness.

the lamella edge, makes them inherently difficult to scan by AFM, and it is quite likely that stem ends are perturbed by the tip–chain interaction. Nevertheless, we were able to measure how far stem ends projected from the edge of the lamellae (Figure 5a) and found that most of the almost 300 stems measured extended less than 1 nm from their neighbors (Figure 5b). Though we are restricted to a two-dimensional view we find that the distribution closely resembles that of molecular simulations.^{23,24} As above, the dominant error in this measurement is the systematic error in stem length due to dc drift, causing the distance to be underestimated by 26%. There are also smaller random errors, whose influence on the data in Figure 5 are discussed below.

By analyzing the same images twice (SI7), it was found that personal judgment on average affected the value of each data-point in Figure 5b by $\pm 15\%$, but neither the modal value nor range changed significantly between the two measurements. As mentioned above, the effect of motion of the stem ends is expected to mainly influence the stems that project furthest from their neighbors, which are few in number. The roughness of the lamella edge also plays an important role in the mechanical behavior of the material and many simulations have specifically investigated the molecular nature of this interfacial zone.^{23–26} From what we have seen already we can calculate the length of the lamella edge contour, which we define as the sum of the distances between the stem ends' XY coordinates. We find that accounting for the systematic and personal judgment components of our uncertainties, it is 1.38–1.6 times

that of a smooth interface. No significant difference was observed between the {110} and {100} crystal surfaces. If the roughness we observe at the free surface is similar to that of the bulk then the surface area of the lamella would be 2.0–2.7 times greater than that of a planar interface, more than doubling the interaction area between the crystalline lamella and the surrounding amorphous matrix. It is likely that the furthest projecting stem ends are under-represented in this data set due to the difficulty in imaging them, suggesting that the interaction area may be even higher.

We were also able to measure the roughness of the interface analogously to measuring the roughness of a surface by determining the distribution of stem end lengths around the mean (Figure 5c). Measurements from multiple edges were combined by aligning them to their average (details of the procedure can be found in SI10). Over 200 stems from 11 edges were found to have an rms roughness of 3.1 Å (Figure 5d). Again, the dominant error in this rms value is the systematic error causing the roughness to be underestimated by 26%. The different distributions found by analyzing the same images twice are shown in SI7. Again, we suggest that this roughness value might be an underestimate due to underrepresentation of stems that project a long way from their neighbors being more difficult to image with AFM.

Other techniques have previously been used to explore the crystal–amorphous interface, the most common being small-angle X-ray scattering (SAXS). The fitting of SAXS data must make some assumptions about the electron density profile of the lamella edge,^{27,28} and though we cannot directly measure the electron density by AFM we can approximate it by calculating the number density of crystalline chains as a function of distance along the lamella normal. We find that the shape of the number density of over 200 stems projected onto the lamella normal (Figure 6) closely resembles the sigmoidal

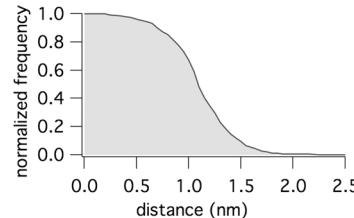


Figure 6. Normalized number density of stems as a function of distance along the lamella normal.

interfacial gradient frequently used for interpreting SAXS data.^{27,29,30} A repeat analysis of the same data was found to influence each data point by less than $\pm 6\%$ on average, and neither the profile nor range of the interfacial density was changed. The shape of the curve relates to the Gaussian standard deviation σ which is used to quantify the width of the interfacial zone and which can be extracted from SAXS data. The sigmoidal interfacial function which is used is obtained by convolving the Heavyside function with a Gaussian curve.³¹

$$f(x) = \frac{A}{2} \left(1 + \text{erf} \left(\frac{x - \mu}{\sigma \sqrt{2}} \right) \right)$$

where erf is the Gauss error function, σ and μ are the Gaussian standard deviation and mean, respectively, and A is a scaling factor. By fitting this function to our two sets of data (see SI11), we find a σ of 2.0 and 3.6 Å, values which are 2 to 3 times

smaller than reported by SAXS investigations.^{27,28} Part of the discrepancy might be accounted for by the different preparation procedure or molecular weight of the material, but it seems likely that most of the difference derives from the imperfect alignment of the lamellae. It can be seen clearly in Figure 1, Figure 3b, and SI1–2 that even in oriented samples the lamellae do not have a well-aligned periodic density profile, and on a smaller scale we see that even the edges do not necessarily align with the main axis of the lamella. This will lead to a widening of the (assumed) lamella profile and an overestimation of the interfacial width with SAXS.

CONCLUSIONS

We have used atomic force microscopy to characterize the crystal–amorphous interface of the archetypal semicrystalline polymer polyethylene. We find that at a chain-by-chain level it is rough but that the maximum step height from the end of one stem to that of its neighbor tends to be less than a nanometer. Nearest- and next-nearest-neighbor folds are observed, although characterization of the degree of chain folding is hampered by chain mobility. We also find that the observed interfacial density profile agrees well with the sigmoidal assumption of small-angle X-ray scattering overall but that the width is rather smaller than reported by SAXS. Furthermore, we present data that can be directly tested against molecular theories of polymer crystallization, opening up the opportunity to develop verifiable theories of the mechanical properties of polymers that fully consider the nature of the crystal amorphous interface.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/ma5025736](https://doi.org/10.1021/ma5025736).

SI1: details of cryo-quenching experiments; SI2: details of the measurement of the lateral deflection noise density of the factory modified AFM; SI3: height image of Figure 2 with a line profile across the lamellae; SI4: the uncorrected version of Figure 2d with the corresponding images from height and amplitude channels; SIS: another example of defects in the crystal surface; SI6: details regarding the measurements of the same stems in different images; SI7: details of the procedure used to estimate the influence of personal judgment on the measurement of stem ends; SI8: the distribution of the stems' deviation from the expected straight line; SI9: the return trace images of Figure 4 together with the entire uncropped figures and their associated height images, also included are line profiles across and along the folds, and line profiles across the nearby molecular steps; SI10: the procedure to align measurements from multiple images; SI11: graphs of the sigmoidal fits to the interfacial density profile ([PDF](#))

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank Paul Kemp-Russell (Physics Workshop, University of Sheffield) for building the vibration isolation and Heiko Haschke and Tilo Jankowski (JPK Instruments) for their factory modifications to the AFM. We also thank Andrey Krayev (AIST-NT) for arranging for the application of carbon whisker tips to the TL01 cantilevers and Dr. Oleksandr Mykhaylyk (Department of Chemistry, University of Sheffield) for helpful conversations. We are grateful to the EPSRC for funding this work, on grants EP/J013005/1 and EP/I012060/1.

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