AFM study of the nanostructure of quenched isotactic polypropylene

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Atomic force microscopy (AFM) is an important tool for characterization of the morphology of semicrystalline polymers. These consist of crystals of nanometer dimensions, being surrounded by amorphous phase. The relative fractions of the amorphous and crystalline phases, as well as the shape, size, and structure of crystals can effectively be controlled by the conditions of crystallization. In this review, the effect of variation of the conditions of crystallization on the crystal morphology of isotactic polypropylene (iPP), as examined by AFM, is demonstrated. It has been found that slow cooling of the melt leads to formation of lamellar crystals while rapid cooling results in formation of isometric nodular domains. Subsequent annealing at elevated temperature does not affect the habit of the ordered phase but can be employed for fine-tuning of the size, number and perfection of crystals. Beside detailed information about the structure of iPP at the nanometer scale, this review contains information about the procedures of sample preparation and AFM imaging. In particular, the importance of the tip geometry on observation of quantitative metrological data is demonstrated.

Keywords atomic force microscopy; isotactic polypropylene; crystallization; crystal morphology; AFM tip radius

1. General information about the structure of isotactic polypropylene

Isotactic polypropylene (iPP) is a multiple-phase semicrystalline polymer at ambient temperature. It is a polymorphic material, that is, crystals can adopt different structure [1, 2]. In case of absence of constitutional and configurational chain defects, and absence of special heterogeneous nucleators, typically, the monoclinic α-form develops. In the α-form, molecules adopt a 3,1 helix conformation, are parallel aligned, and left-handed and right-handed helices form separate layers [3]. Crystallization occurs by supercooling of the liquid state to a temperature between the equilibrium melting temperature, which is about 461 K [4], and the glass transition temperature at about 250–270 K [5, 6]. The ordering process of macromolecules can only be prevented by rapid transfer of the liquid structure into the glassy state, which in case of the relatively fast crystallizing iPP requires an extremely high cooling rate of order of magnitude of 105 K s⁻¹ [7–9]. In order to prevent crystallization, however, the polymer then needed to be kept below the glass transition temperature.

The ordering process of macromolecules in the temperature range between the glass transition temperature and the equilibrium melting temperature is largely controlled by the supercooling. Qualitatively, crystallization of iPP at low supercooling of the liquid state obeys classical rules of polymer crystallization [10, 11]. The crystallization process is separated into the stages of nucleation, growth, and perfection, and ultimately leads to the formation of rather well-ordered monoclinic crystals of lamellar shape, being organized in a higher-order spherulitic superstructure [12, 13]. In spherulites, in general, the lamellae are oriented with their long dimensions parallel to the radius. However, in case of iPP, there is often observed so-called cross-hatching due to epitaxial growth of lamellae [14, 15], leading to spherulites in which lamellae are radially and tangentially oriented. In contrast, structure formation at high supercooling is not connected with the formation of well-ordered crystals and spherulites. It has been found that at high supercooling the quiescent liquid partially transforms into a mesophase of nodular geometry, with the nodules being not organized in a higher-order superstructure [16–18]. The latter observation points to absence of a distinct nucleation and growth mechanism, and simultaneous appearance of these domains. Regarding the internal structure of the mesophase, there has not been achieved consensus yet. Initially, at its discovery, the mesophase was classified as being a paracrystalline smectic phase, consisting of parallel aligned molecular stems arranged in a pseudo-hexagonal lattice [19, 20]. Alternatively, it has been suggested that the mesophase are fine crystallites of hexagonal structure [21, 22], or monoclinic microcrystals [23]. Recently, based on in-depth X-ray analysis of fiber pattern it has been proposed that the mesophase contains bundles of parallel aligned chains with an identical helical conformation as in monoclinic α-crystals. In longitudinal direction, that is, chain direction, order is terminated by helix reversals or other conformational chain defects, while in cross-chain/lateral direction the correlation between different chain segments has been described to be closer to a monoclinic rather than a hexagonal lattice [24, 25]. Finally, based on detailed calorimetric analyses, the mesophase of iPP formed at high supercooling has been classified as a conformationally disordered crystal [26, 27]. At ambient temperature, the conformationally disordered mesophase is in its glassy state and therefore metastable, and only on heating above its glass transition temperature, a transformation into the monoclinic crystal form can occur.

The thermodynamic stability of the monoclinic α-form is controlled by both bulk properties of the crystalline and amorphous phases, and the area and structure of the crystal surface. The bulk enthalpy and entropy of fusion define the equilibrium melting temperature, which can be interpreted as the temperature of melting of a crystal of infinity size, being about 461 K [4, 28]. The equilibrium melting point is decreased due to presence of crystal defects, which results in a lowering of the bulk heat of fusion, or — more important — due to presence of surfaces with a specific surface free
energy. The effect of the specific morphology of crystals on the melting temperature can be quantified with the Gibbs-Thomson equation [29, 30], which also has been used to describe the melting behavior of α-crystals of iPP [28]. As is typical for many semicrystalline polymers, the experimentally observed melting temperature of α-crystals in semicrystalline iPP is about 10–30 K lower than the equilibrium melting temperature, that is, it is often reported of being around 430 K. The stability of the mesophase of iPP, formed at high supercooling, cannot as straightforward be characterized as the stability of the α-crystal phase by analysis of the temperature of transition into the liquid phase. Research about the stability of the mesophase of iPP included the analysis of the temperature dependence of structure by X-ray techniques [31–34], differential scanning calorimetry (DSC) [26, 27, 31, 35–39], and microscopy [40, 41]. Heating of semimesomorphic iPP at low or moderate rate leads to a transformation of the mesophase into monoclinic structure. Additionally, on heating occurs classical crystal reorganization, that is, crystal perfection including an increase of the volume to surface ratio, and cold crystallization of supercooled liquid. All of these processes are thermodynamically irreversible, and may superimpose on each other, complicating the analysis of the stability of the mesophase. Recently, the transformation of the mesophase into monoclinic crystals, the crystal reorganization, and the cold crystallization have been suppressed by heating the semimesomorphic structure of iPP at extremely high rate of 40,000 K s⁻¹ using fast scanning calorimetry (FSC) [42]. The suppression of these processes resulted in direct transformation of the mesophase into liquid structure, which occurred at about 350 K at the selected rate of heating.

The exact condition of solidification of the quiescent liquid of iPP to obtain a fully amorphous glass, a semimesomorphic structure consisting of mesophase and amorphous phase, or semicrystalline structure consisting of monoclinic α-crystals and amorphous phase have quantitatively been evaluated by either FSC [7, 8] or combined analysis of the X-ray pattern and density of samples of iPP of different history of solidification [43–46]. Figure 1 shows necessary boundaries regarding the rate of cooling the liquid state of iPP to obtain such structures, with the information taken from the literature. Fully amorphous iPP can only be obtained by cooling the equilibrium liquid at a rate of about 1,000 K s⁻¹, or faster, to a temperature lower than the glass transition temperature. Cooling at such high rate prevents formation of both monoclinic crystals at low supercooling and mesophase at high supercooling of the liquid. As was outlined before, devitrification of the glassy structure by re-heating immediately leads to formation of either mesophase or monoclinic crystals, depending on the heating rate applied, and the final temperature of the heating scan. Formation of monoclinic crystals is observed only at temperatures higher than about 330 K, and if the liquid is not cooled faster than about 50–100 K s⁻¹. If the cooling rate is higher, then monoclinic crystals cannot form due to the specific kinetics of formation of such crystals. Instead, mesophase develops on cooling between about 100 and 1,000 K s⁻¹ in the temperature range between the glass transition temperature and about 330 K. A necessary condition for mesophase formation is the prevention of formation of crystals at low supercooling/high temperature. The temperature range between 330 K and the melting temperature must therefore be passed at a rate faster than 50–100 K s⁻¹. To allow mesophase formation between 330 K and the glass transition temperature, in this temperature range cooling must be slower than 1,000 K s⁻¹, however, can even approach zero cooling rate.

Fig. 1 Conditions of cooling the quiescent liquid of iPP to obtain a fully amorphous glass (left), a semimesomorphic structure (center), or a semicrystalline structure (right). The cooling rates provided need to be considered as estimates. Detailed explanation is given in the text.
2. Morphology of quenched isotactic polypropylene

First studies about the morphology of quenched form of iPP, or of the mesophase, respectively, were done about half a century ago in 1960ies [16, 47, 48]. It was found that the structure of iPP after quenching and ageing at ambient temperature was non-spherulitic, containing “small clusters” with a size of order of 20–50 nm [47], or “nodules” with a size of about 12.5 nm [16]. Remarkably, in the latter investigation thin films of only 5 to 15 nm thickness were directly floated onto an electron microscope grid, heated together with the grid to 473 K, held for a period of two minutes and then quenched into ice-water, followed by Pt/C shadowing before TEM observation. These early reports about the observation of granular structures of size of a few nanometers in quenched polymers using electron microscopy, initially, were not unequivocally agreed upon [49, 50], and also discussed as being an instrumentally caused artefact. To date, the formation of nodules in quenched and subsequently at ambient temperature aged iPP has been re-proven by numerous independent studies using different preparation techniques for generation of semimesomorphic iPP and different instrumentation to gain morphological information. Beside direct observation of structure by microscopy, indirect structure information at the nanometer length scale was also collected by wide-angle and small-angle X-ray scattering [23, 51–53]. The many reports consistently confirm the nodular shape of mesomorphic domains, however, information about the exact size and shape still are not available. This may be caused by different preparation/quenching techniques, by different chemical architectures of iPP grades employed for investigation, and, naturally, by the different specific tools used for analysis of structure. For example, ultra-quenching of films of 100 nm thickness below the glass transition temperature resulted in formation of domains with a size less than 2.5 nm [18]. Subsequent heating to ambient temperature then produced nodules with a size between 7.5 and 10 nm. Similarly, a size of nodules of 10 nm has been found in 0.25 mm thick films of iPP, prepared by melt-extrusion on a chill roll kept at a temperature of 281 K [35]. Films of iPP with a thickness between 0.10 and 0.15 nm were quenched into ice-water, in which equi-axed domains of size of about 20 nm were observed [54]. A final example of quantitative information about the morphology of the mesophase is the study of the structure of a film of 14 μm thickness which was quenched in a mixture of dry ice and ethanol. This preparation technique yielded micro-crystalline regions of size of 10–20 nm [38].

![Image](image_url)

**Fig. 2** Structure of quenched iPP as examined using TEM. The images represent an area of 500×500 nm². Details about the quenching/preparation technique are described in the text. Left image: Reprinted in part from reference [35], Copyright 2001, with permission from Elsevier. Right image: Reprinted in part from reference [55], with kind permission from Springer+Business Media.

Imaging of the fine-structure of the quenched form of iPP at the nanometer length scale mainly was performed using electron microscopy in the past. Figure 2 shows two selected examples of such electron-microscopy investigations, with the images representing an area of 500×500 nm². The left image was obtained from a cast film of 250 μm thickness with was extruded onto a chill roll of temperature of 281 K. In a first preparation step, the cast film was cryofaced using a glass knife at a temperature of 243 K. Then, the cryofaced sample was stained in the vapor space of a RuO₄ solution for a period of 7 hours. Finally, after staining, ultra-thin sections with a thickness of 70–75 nm were cut at ambient temperature, using a diamond knife. In the original reference, the image observed is described as showing “cluster-like” structures with an average size of about 10 nm, with some clusters being of distinctly smaller dimension. The dark and bright appearing regions were attributed to the amorphous phase and the mesophase, respectively, based on the knowledge that the amorphous phase is of lower density and being therefore more susceptible for staining than the mesophase [35]. The right image was observed from a film of iPP of thickness of 100 μm, which was quenched from 473 K to about ambient temperature by spraying with cold water. The non-linear cooling curve, temperature as a function of time, recorded during quenching, revealed for this particular sample a cooling rate of 750 K s⁻¹ at a temperature of 343 K. As such, the requirement of cooling at a rate faster than 100 K s⁻¹ in the temperature range of...
potential formation of monoclinic crystals, for observation of the mesophase, is fulfilled (see Figure 1). The image shows the center of the cross-section of the film. The sample has been contrasted using RuO$_4$, and thin sections of thickness of about 75–80 nm were taken at ambient temperature. The structure of this preparation has been described as being heterogeneous, containing particle-like domains with a typical dimension of about 5 nm, which in addition seem aligned to form short strings [55]. The long period of close to 12 nm was estimated from the Fourier transform, and was only slightly larger than frequently observed by SAXS. For comparison, reports of the SAXS long period of semimesomorphic iPP at ambient temperature revealed values of about 8 nm [51], 9 nm [56], 10.5 [31], or 11 nm [35].

Atomic force microscopy (AFM) has frequently been applied for evaluation of various structural features of semicrystalline iPP at different length scales — starting at the length scale of molecular segments, for example to obtain details of the helical structure, up to the length scale of spherulites [57–61]. Recently, investigations were published revealing details of the melting and crystallization processes, as were measured in situ, using hot stage microscopy [62, 63]. AFM investigations about the nanostructure of semimesomorphic iPP, in order to confirm the morphological data obtained by electron microscopy, are not available and have therefore been collected on a series of specimens of iPP of different history of crystallization [64]. Samples have been prepared by solidification the quiescent liquid state at different rate of cooling between 0.1 and 1.000 K s$^{-1}$, and subsequent storing at ambient temperature. The ultimate goal of this study was the establishment of a relation between the condition of non-isothermal solidification/crystallization and the nanostructure of iPP. Present-day knowledge is restricted to information about the effect of systematic variation of the cooling conditions of iPP on the X-ray structure, macroscopic density, and superstructure at the micrometer scale, however, structure information at the nanometer scale on such differently crystallized specimens were not systematically collected yet.

![AFM structure of semicrystalline (left) and semimesomorphic iPP (right). The semicrystalline structure was obtained by cooling the quiescent melt at a rate of 0.1 K s$^{-1}$ to ambient temperature, while the semimesomorphic structure was obtained by cooling the material at a rate of 750 K s$^{-1}$ to ambient temperature. The images represent an area of 1×1 µm². Left image: Reprinted with permission from reference [6], Copyright 2008 American Chemical Society.](image)

**Fig. 3** AFM structure of semicrystalline (left) and semimesomorphic iPP (right). The semicrystalline structure was obtained by cooling the quiescent melt at a rate of 0.1 K s$^{-1}$ to ambient temperature, while the semimesomorphic structure was obtained by cooling the material at a rate of 750 K s$^{-1}$ to ambient temperature. The images represent an area of 1×1 µm². Left image: Reprinted with permission from reference [6], Copyright 2008 American Chemical Society.

Figure 3 shows two selected examples of AFM structures of iPP. The left image represents a semicrystalline structure which was prepared according to cooling scheme (III) in Figure 1, and the right image represents a semimesomorphic structure, prepared according to cooling scheme (II) in Figure 1. The structures are shown at identical scale of 1×1 µm². The left image of the semicrystalline preparation shows with the bright objects lamellar α-crystals which are viewed edge-on, and which are embedded in amorphous phase. The lateral extension of lamellae is two-fold; mother lamellae are of length of several 100 nm, while expitaxially grown daughter lamellae are distinctly shorter and almost perpendicular oriented with respect to the mother lamellae. The long mother lamellae are oriented parallel and the short daughter lamellae are oriented tangentially to the radius of the spherulite which is too large to be shown at the selected magnification. The thickness of lamellae, as expected, is of the order of 10–20 nm. The right image of the semimesomorphic sample, in contrast, shows non-lamellar and apparently isometric objects, being assigned to the mesophase of iPP. The size of these nodular domains is of the order of 15–20 nm. The AFM image of the semimesomorphic iPP, at least qualitatively, confirms the observations collected earlier by transmission electron microscopy (TEM) though quantitative differences regarding the size of detected objects are obvious. It will be shown below that by variation of the AFM instrumentation differences can be minimized.

The images of Figure 3 were collected with a Quesant Universal SPM instrument, being equipped with a 5×5 µm² scanner. The instrument was operated in intermittent contact mode, employing standard, general-purpose silicon tips NSCl4 from MikroMasch [65] with a resonant frequency of 160–170 kHz and force constant of 5 N m$^{-1}$. The shape of the tip is conical, with a typical radius at its front-end of about 10 nm, tip height of 20–25 nm, and cone angle of 40°. The ratio between the set-point amplitude and free-oscillation amplitude of the tip, for feedback control, was adjusted to
be 0.70–0.75. Post-processing of images included tilt-removal only. Smoothing, or Fourier filtering, respectively, in order to enhance specific features, or to remove noise, was not applied. Regarding sample preparation, it is worthwhile to note that images represent the surface structure of the differently crystallized iPP films. Special emphasis was put on preparation of smooth surfaces of the specimens in order to avoid a priori any misinterpretation of observed structures, for example, generated by improper height profile or surface roughness. As such, samples were crystallized in contact with a flat and smooth substrate. In most cases, either freshly-cleaved mica or carefully cleaned glass cover slips — used for preparation of specimens in optical microscopy — were employed. There has not been detected any influence of the type of substrate on structure formation during solidification of iPP, that is, epitaxial crystal growth has been excluded. Though it is not as convenient as the use of a substrate on sample preparation, AFM surface imaging of iPP can also be done on samples solidified in absence of a solid substrate [39].

3. Morphology of quenched and annealed isotactic polypropylene

The morphology of initially quenched and subsequently at elevated temperature annealed iPP at the nanometer scale was in the past directly be observed by TEM only. It has been found that annealing at for example 411 K led to an increase of the size of domains to 20–30 nm, with nodules merging and forming “short fibers”/“lath-like lamellae” as a function of time. There was detected a distinct effect of the annealing temperature and time on the observed structure, such that major structure reorganization only occurred at temperatures above 383 K [18]. It is important to note that in this study films where shadowed before TEM analysis, that is, the structure detected represented the surface morphology. In a different study [35], TEM imaging of initially quenched iPP was done after annealing at 373 K, with the TEM specimen prepared by staining with RuO₄. The observed structure was described as showing coexistence of lamellar crystals and clusters, with the short lamellae appearing as being formed by “aggregation of several cluster domains”. In this investigation, the film surface of the specimen was oriented parallel to the electron beam, that is, the true bulk structure has been assessed. Despite quantitative differences regarding the size of objects, sample preparation procedure, and imaging technique, both studies led to similar conclusions regarding growth of domains, and their aggregation to form lamellae during the annealing procedure.

Recently, for the first time, AFM has been applied to study the effect of annealing on the structure of semimessomorphic iPP [66], with selected major results presented in Figures 4 to 6. In Figure 4 — for comparison — is shown with the left and right images the change of structure of a semicrystalline and initially semimesomorphic preparation, respectively, caused by annealing at a temperature of 433 K for a period of 1 hour. The insets in both micrographs represent the structure before annealing, which has been shown in Figure 3. The images show a sample area of 1×1 μm², with the insets scaled to permit direct comparison of the size of objects. Regarding the initially slowly cooled semicrystalline sample, in which crystals are of lamellar shape and arranged in a higher-order spherulitic superstructure, annealing results as expected in an increase of the thickness of lamellae. The observation of thickening of lamellae in semicrystalline polymers, in general, has been well-described in the literature from the points of view of thermodynamics, phenomenology, and kinetics [11, 30, 68, 69]. In short, thickening is thermodynamically driven since crystals are more stable if the volume-to-surface ratio is increased and since crystal growth in thickness-direction does not lead to an increase of the surface with the highest free energy. Furthermore, thickening can be achieved either by so-called chain-sliding diffusion within existing lamellae and/or a melting-recrystallization mechanism. From kinetics point of view, it has been found that crystal growth on isothermal annealing obeys a logarithmic time dependence, that is, a temperature-dependent equilibrium value of the crystal size is approached. While semicrystalline polymers which contain lamellae as dominant crystal form have been explored numerous times regarding structure reorganization on annealing, there is only minor knowledge available about temperature-triggered reorganization of structure for systems with ordered domains of nodular geometry, based on microscopy observations. Initial work on this subject [18, 35] is now extended more systematically using AFM. For qualitative discussion, the right image of Figure 4 clearly reveals that the habit of ordered mesomorphic domains, obtained by quenching, does not change on subsequent annealing. The only observation is a distinct increase of the size of objects. The size of mesomorphic domains after quenching, as was observed by AFM, is of the order of 15–20 nm, and about doubles on annealing at 433 K. This result is not a priori expected, since heating of semimessomorphic iPP initiates several processes which could have an effect on the crystal habit: (i) the mesophase is replaced by monoclinic crystals as is evidenced by X-ray studies, (ii) the amorphous phase partially crystallizes as is evidenced by calorimetry, and (iii) crystals reorganize/stabilize as is evidenced by calorimetry or microscopy. Obviously, all of these processes do not affect the crystal shape. Consequently, it has been proposed that the mesophase – crystal phase transition, which is observed at relatively low temperature below 370 K, occurs at very local scale within existing domains, perhaps involving a local melting process. It seems settled that the phase transition does not involve global melting of mesomorphic domains and subsequent recrystallization of amorphous phase. Furthermore, formation of lamellae on cold-recrystallization of unstable supercooled liquid does not occur due to geometrical constraints. In simple words, formation of lamellae is not possible since space is occupied already by the many evident crystals of limited lateral size. As such cold-recrystallization may result in formation of crystals of similar nodular/particle-like geometry, or — which is more likely from point of view of nucleation — it occurs at the surface of the existing crystals.
The qualitative discussion of annealing-triggered changes of the nanostructure of initially quenched iPP has been extended, to additionally gain quantitative information about the effects of both temperature and time on the size of ordered domains. In Figure 5 is shown as an example the evolution of structure as a function of time of initially quenched iPP during isothermal annealing at elevated temperature. The left image shows the structure before annealing, after the sample has been quenched at a rate of 750 K s\(^{-1}\) in cold-water and aged at ambient temperature. The images of the top and bottom rows show the effect of annealing time on isothermal annealing at 393 K and 433 K, respectively. Note that the images actually were not taken at these temperatures rather than were cooled after annealing to room temperature before image collection. The images of Figure 5 reveal that the size of ordered domains/nodules increases with both (i) increasing temperature of annealing, and (ii) increasing time of annealing. As was pointed out before, the shape of domains or their aspect ratio, respectively, almost does not change during annealing. Lamellae, as are typically observed on melt-crystallization at slow or moderate cooling, shown with the left images in Figures 3 and 4, are not detected. Nodules, however, in particular on annealing at high temperature, tend to aggregate or align, respectively, and to ultimately form string- or ribbon-like objects. This observation is in accord with the earlier microscopic investigations on this subject.

The AFM images obtained on quenched and subsequently annealed samples were systematically analyzed to obtain functional relationships between the size of mesomorphic domains/crystals and both the temperature and time of annealing. Since convenient data reduction via Fourier transformation was successful only in few cases, images were manually evaluated using classical approaches like line analysis. Figure 6 shows with the left and right graphs the evolution of the AFM nodule size as a function of the annealing temperature and the annealing time, respectively. The plots contain different sets of data which serve for illustration of the statistics of experimentation/data reduction. In detail, the different symbols in the left graph represent data obtained on samples quenched at different rate between 50 and 1,000 K s\(^{-1}\). However, as long as formation of monoclinic crystals is suppressed at rather low supercooling [see cooling scheme (II) in Figure 1], the rate of quenching apparently does not affect the formation of semimesomorphic structure at high supercooling, and structure reorganization during subsequent annealing. It can be seen that a major increase of the nodule size is only obtained on heating and annealing at temperatures higher than about 390–400 K. Below this temperature, which also covers the temperature range of the mesophase – crystal phase transition, the nodule size almost stays constant, supporting the notion that the phase transition is not connected with global/complete melting of domains. The right plot, which shows the evolution of the nodule size versus time at two different annealing temperatures, reveals a non-linear exponential increase of the size of domains/crystals, similar as has been observed in systems with lamellar crystals [67–69]. Comparison of the TEM and AFM images shown in Figures 2–5 reveals distinct differences of the size of observed objects. Though it could be argued that these differences may be due to different preparation/quenching conditions, or different location analyzed in the sample, there remain specific instrument-related reasons. Therefore it is emphasized in Figure 6 that the observed nodule size has been measured by AFM. It will be demonstrated below that AFM imaging is largely affected by the geometry of tip, in particular if the size of objects is of similar order as the front curvature of the tip.
Effect of temperature and time of annealing of initially quenched and therefore semimesomorphic iPP on the AFM structure. The left image shows the structure before annealing, and the images of the top and bottom rows show the structure after annealing at the indicated temperature and for the indicated time. The images represent an area of $1 \times 1 \mu m^2$. Reprinted in part from reference [66], Copyright 2007, with permission from Elsevier.

Effect of temperature and time of annealing of initially quenched and therefore semimesomorphic iPP on the AFM structure. The left plot shows the AFM nodule size as a function of the annealing temperature, with the samples annealed for 60 min. The right plot shows the AFM nodule size as a function of the annealing time, for two different temperatures as indicated in the plot. The various symbols represent different quenching conditions/samples. Left graph: Reprinted in part from reference [64], Copyright 2006, with permission from Elsevier. Right graph: Reprinted in part from reference [66], Copyright 2007, with permission from Elsevier.

4. Effect of AFM tip geometry on the evaluation of the crystal size

There have been published numerous reports in which it is demonstrated that the AFM tip geometry affects the images collected [70–78]. In general, due to interaction of the AFM tip and structural details of the sample, objects appear larger than they are in reality, with the error being increased with the tip radius. The effect of the AFM tip geometry on observed images can be removed/corrected for by mathematical deconvolution [74, 75], which, however, is only possible if the tip geometry is exactly known. Otherwise, there is the option to test and apply tips of different geometry to estimate the error on determination of quantitative size data. Recently, there have been developed tips with a radius of only a few nanometers, and extreme high aspect ratio, by attaching an extra tip at the front end of standard tips. These extra tips, for example, can be zinc oxide whiskers [76, 77], carbon nanotubes [78, 79], or tungsten spikes [80]. With such extra tips, the limitations of standard silicon or silicon nitride tips for observation of exact size data can
strongly be reduced. As far as we are aware, high-resolution tungsten-spike tips have not yet been employed for the analysis of the nanostructure of semicrystalline polymers. We used therefore the iPP samples of different history of crystallization to evaluate the effect of the tip geometry on the imaging results, employing a standard tip with a radius of 10 nm and a high-resolution tip with a tungsten spike of only 1 nm radius at its front for comparison [81].

In Figure 7 are shown with the top images nodular crystals (left) and lamellar crystals (right) which both were collected using the standard silicon tip NSC14. At the bottom, identical preparations were scanned using the high-resolution tip DP14. The images clearly illustrate that the size of objects — in both cases nodules and lamellae in thickness direction — apparently is reduced in case of the high resolution tip. Quantitative estimation of the nodule size revealed values of 30–35 nm and 22–25 nm in case of using the tips NSC14 and DP14, respectively. Similar, for the system with lamellar crystals, thicknesses of 26 nm and 20 nm were obtained in case of using the standard and high-resolution tips, respectively. In accord with theoretical considerations, there is expected an additive overestimation of the size of objects by a magnitude close to the radius of the tip [82], which is clearly confirmed with the experimental data shown in Figure 7. The standard silicon tip of 10 nm front curvature leads to an overestimation of the true size of crystals by about 5–10 nm. Therefore, quantitative evaluation of dimensions of crystals requires the use of a high-resolution tip, if a mathematical deconvolution of the effect of the tip in experimentally observed images is not possible.

5. Summary

Isotactic polypropylene can be crystallized along different thermodynamic pathways. Classical melt-crystallization occurs at relatively low supercooling by direct transformation of supercooled liquid into monoclinic crystals, which are of lamellar shape and arranged within spherulites. Alternatively, iPP can be crystallized via formation of a metastable mesophase at high supercooling, and subsequent transformation of the mesophase into crystals of nodular geometry, being not arranged in a superstructure. These qualitatively different semicrystalline structures exhibit distinctly different properties [82, 83], which — from point of view of materials science — requires detailed knowledge about critical parameters of the condition of formation, and about the structure and morphology of crystals. AFM is a superior tool to be employed for such investigations since it allows systematic analysis of the nanostructure of a rather large number of samples in timely and affordable manner due to relative simple specimen preparation and procedure of data collection. This is in particular true since it has been shown that the surface structure as obtained by AFM and the bulk structure as

Fig. 7 AFM phase-mode images of semicrystalline iPP, containing nodular crystals (left), or lamellar crystals (right). The images shown in the top row were measured with a general purpose silicon tip NSC14, and the images shown in the bottom row were collected with a high-resolution tip DP14. The tip DP14 has a sharp tungsten spike of high aspect ratio and extreme small tip radius of only 1 nm attached at the front end of a standard tip. The images represent an area of 1×1 μm². Reprinted/adapted with permission from reference [81], Copyright 2009, IOP Publishing.
obtained by TEM are qualitatively indifferent [55]. There have been prepared a large number of iPP films which were solidified at different rate of cooling. AFM analysis allowed to determine a critical rate of cooling which enforces a transition from formation of lamellar crystals to formation of mesomorphic domains, being about 50–100 K s⁻¹ [64]. Subsequent heating of at ambient temperature semimesomorphic samples leads to irreversible changes of the nanostructure which have quantitatively been characterized by AFM in relation to both temperature and time [66].

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1949


