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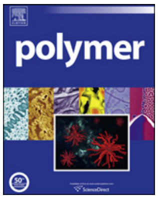

Insight into growth details and characteristics of windmill-like polyethylene crystals

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ABSTRACT

The crystallization detail of polyethylene (PE) has been scarcely studied via in-situ approach since it is an extremely fast process. In this work, optical microscopy is used to investigate crystallization details and characteristics of windmill-like polyethylene crystals. It has been shown that the straight edges of the petals appear firstly and grow in pairs from their central junctions, which subsequently induce the surrounding domains in between each pairs of petals to nucleate and crystallize into twisted lamellar overgrowths. The remaining terrace-stacked lamellae which form curved edges of the petals start to develop only after the straight edges of the petals together with the twisted lamellar overgrowths have completed their growth. It is confirmed that the preferential growth direction of these petals are along crystallographic [113] axis, which has an angle of 65° with the typical direction along *b*-axis adopted also by the twisted lamellar overgrowths. The crystallization kinetics is analyzed in terms of Avrami equation and an Avrami exponent $n = 2$ is thus obtained, which is consistent with the morphological observations of heterogeneous nucleation and 2-dimensional growth for these PE crystals. The melting behaviors of these crystals are exactly the reversed process of crystallization.

1. Introduction

Crystallization is the dominant driving force towards the formation of various morphologies observed in polymers. Understanding the crystallization behaviors and characteristics is a key topic to design appropriate production parameters and to extend the properties of polymer materials. As one of the most well-known semicrystalline polymer, polyethylene is the most widely and thoroughly studied polymeric material, in particular its morphology. In the previous paper [1] we have reported a novel morphology of polyethylene, the windmill-like crystals prepared via melt crystallization within hot spin-coated film [2]. Though the crystal orientation and detailed conditions to achieve such novel PE morphology have been revealed [1], many open questions still remain, some of which are critical to help us to better understand this unusual morphology of the most intensively studied polymer and to disclose the formation details and mechanism of these interesting crystals.

As it is considered to be the simplest polymer to date in terms of molecular structure, polyethylene usually adopts orthorhombic stacking during crystallization, which leads to a preferential growth direction along the crystallographic [110] direction based on the periodic bond chain theory [3,4]. Accordingly, the molecular chains can conveniently diffuse to both the fold surface and growth front plane according to the results of Bassett et al. [5]. Consequently, polyethylene crystals show {112} fold surface and {110} growth face [6], which is consistent with most of the observations reported. However, the preferential growth direction is dependent on the crystallization conditions, and other growth styles along crystallographic [530], [540] [7] and [310] directions [8] have also been observed. Besides, it has been proven that, polyethylene single crystal grown from the melt typically adopts a preferential growth direction along crystallographic *b*-axis [9]. The windmill crystals and associated twisted lamellar overgrowths are actually crystallized from the melt within the thin films. Both of these two crystals adopt an identical orientation of *b*-axis, which is the preferential growth direction of the twisted lamellar overgrowths. However, it is not the preferential growth direction of the petals as directly shown by the microscopy images. Therefore, it is interesting to get deeper insight into this novel morphology of polyethylene, e.g. what is the preferential growth direction, how does this morphology develop from kinetic point of view and crystallization sequence of the crystals involved in the windmill and associated twisted lamellae [10–16]. In the present work, by resorting to other morphological characterization tools such as atomic force

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microscopy (AFM), scanning electron microscopy (SEM) and optical microscopy (OM), in particular temperature-controller integrated OM and live image recording system, the detailed crystallization process has been revealed.

2. Experimental section

2.1. Materials and sample preparations

The high-density polyethylene (HDPE) ($M_n = 8.6 \times 10^3$ g/mol; PDI = 30.1) with partial substitute of butyl branches was kindly supplied by China petroleum & Chemical Corporation. The polymer solution was prepared by dissolving HDPE in xylene at 180 °C under stirring so as to achieve the solution with a concentration of 10 mg/ml. Polymer films were prepared by hot spin coating of this polymer solution onto a well-cleaned glass substrate. Film thickness was evaluated by AFM and its average thickness was ca. 300 nm, which is confirmed to be one of the requisite conditions for the formation of this novel crystal in our previous paper [1]. Afterwards, a small portion of the film was transferred to copper grids coated with a thin layer of amorphous carbon by using flotation technique. The more detailed specimen preparation procedures have been provided in our previous paper [1].

The crystallization of the specimen was performed on a silver hot-stage (Linkam THMS 600, England), which was equipped to the optical microscopy. The temperature of this hot-stage is controlled through a Linkam TMS 94 controller with a temperature variation within 0.1 °C. The prepared specimens were firstly melted at 180 °C for ca. 5 min, afterwards the hot-stage was rapidly cooled to isothermal crystallization temperature at a rate of 130 °C/min, which is the fastest cooling rate within the controllable range of the hot-stage used in this work. In order to avoid degradation, the chamber where hot-stage locates was filled with dry nitrogen.

2.2. Instruments

SEM was performed on an FEI XL30 ESEM-FEG operated at an accelerating voltage of 15 kV. BF-TEM observation was conducted by a JEOL JEM-1011 working on an accelerating voltage of 100 kV. AFM measurements were carried out on a SPA300HV with a SPI 3800 controller Seiko instruments industry Co. Ltd., and images were recorded with intermittent contact mode at room temperature. OM or polarized optical microscopy (POM) images were acquired by a Carl Zeiss A1m microscope equipped with an Infinity 4–11 digital camera from Lumenera Co., Canada.

3. Results and discussion

The windmill-like crystals of polyethylene obtained via melt crystallization have been extensively investigated by various morphological characterization tools. Fig. 1 presents the typical images of these morphologies obtained by using bright-field TEM, SEM, OM, POM and topographic AFM. For the crystals obtained via isothermal crystallization at different temperatures, no intrinsic morphological difference except variations of crystal growth rate and petal number could be found. The lower the isothermal crystallization temperature is applied, the higher the crystallization rate for the windmill crystals and the associated twisted lamellar overgrowths. For instance, the morphology shown in Fig. 1 is the

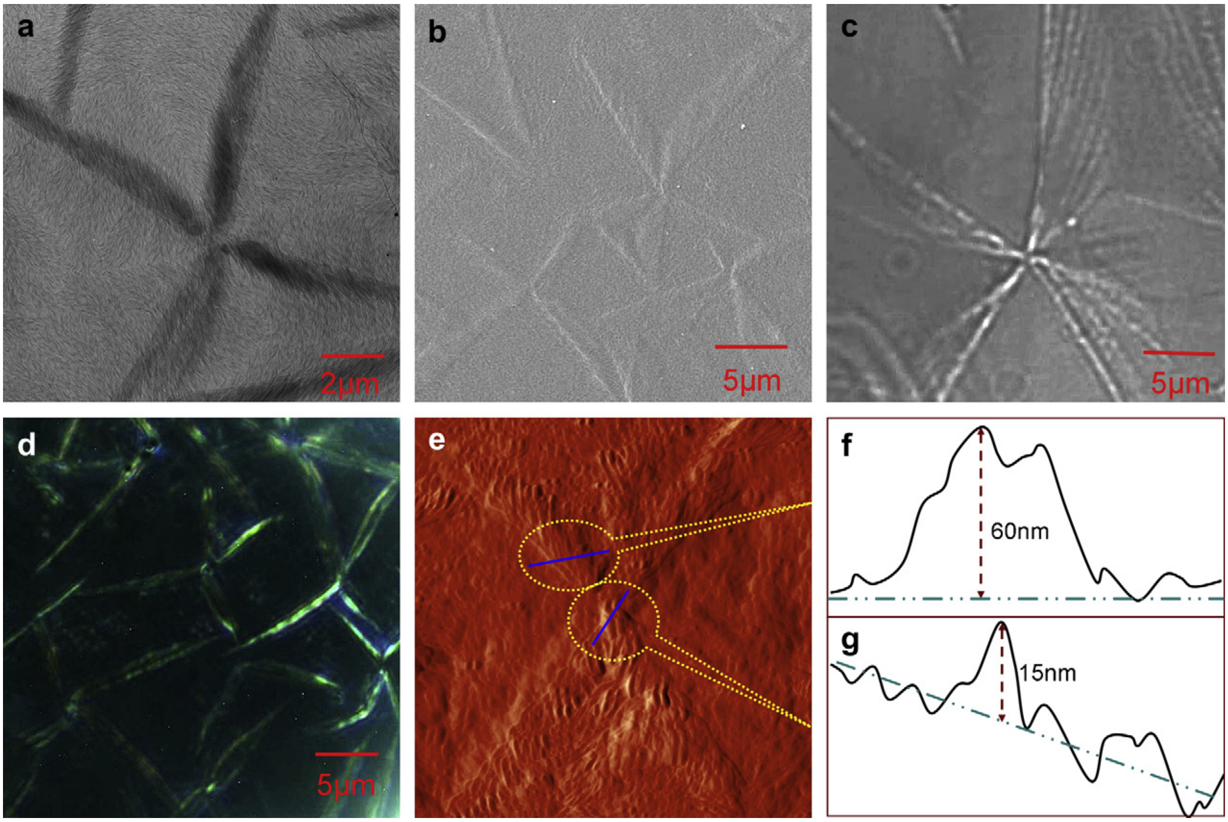

Fig. 1. (a) Bright-field TEM, (b) SEM, (c)OM, (d) POM and (e) AFM topographic images of windmill-like polyethylene crystals prepared via isothermal crystallization at 114 °C for 60 min. Cross-section profiles of the petal (f) and the central junction (g) from AFM topographic image as indicated in part e.

crystals obtained via isothermal crystallization at 114 °C. As prompted by the SEM image (Fig. 1b) obtained at an accelerating voltage of 15 kV, the relatively brighter contrast of the petals in windmill crystals hints that the windmills are higher than the associated twisted lamellar overgrowths. This assumption is further confirmed by the AFM topography shown in Fig. 1e. As is clearly demonstrated by the cross-section profiles (Fig. 1f), the petals are about 60 nm higher than the twisted lamellar overgrowths. Besides, a more interesting result that the central junction of the windmill is even ca. 15 nm higher than the petals (Fig. 1 g) can be observed. Based on these observations, we can draw a preparatory conclusion that the formation of the windmill crystal could be attributed to the preservation of the hardly melted cores upon heating, which afterwards act as nuclei during crystallization process towards windmill morphology. Due to the intrinsic resolution limitation of optical microscope, only the petals of the windmill crystals could be clearly resolved in both bright-field and polarized images. However, the OM resolvable morphology of the petals opens the possibility of the investigation on the growing process of the windmill crystals by optical microscope equipped with a hot-stage, which allows us to get deeper insight into the formation details of this novel morphology of polyethylene.

Actually, the formation details of windmill crystals could be vividly recorded by a digital camera equipped to the optical microscope and thus a video is obtained (See Supporting Information). A series of bright-field optical micrographs are snapped according to certain time interval from the video sequence, which reveals every important process during the formation of the windmill crystals. As shown in Fig. 2, for the specimen isothermally crystallized at 114 °C, which was pre-melted at 180 °C for 5 min and subsequently quenched to the isothermal temperature, only after about 5 s the temperature has reached this crystallization temperature, nucleation happens as an occurrence of bright dots within the field investigated, and all the specimens will not crystallize until the appearance of these bright dots, which are the central junction parts for the windmill crystals. This phenomenon strongly hints that nucleation plays a very important role in the crystallization of PE in this work. During the subsequent crystal growth process, we find that only when the straight edge of the petals comprised by lamellae grows in pairs firstly, the region in between each pair of the petals immediately crystallizes into the twisted lamellar overgrowths. The crystallographic relationship between both lamellae and twisted lamellar overgrowths has been intensively addressed in our previous publication [1], in which they have an identical orientation along crystallographic *b*-axis. As observed in polyethylene lamellae obtained via melt-crystallization within a thin film, the long direction, which is also the preferential growth direction of twisted lamellar overgrowths in this work, is along *b*-axis. In contrast, the long direction of petals lamellae is not along *b*-axis anymore. Based on the crystals growth details, the identical crystallographic orientation in between the petal lamellae and the twisted lamellar overgrowths, together with crystallization sequence between them, we can conclude that the crystallization of the twisted lamellar overgrowths is nucleated by the straight edge of the petals.

For a clearer demonstration, Fig. 3 gives schematic illustrations of the crystal growth details shown in Fig. 2. As has already been stated previously [1], the angle ω between the petals and the long direction of associated twisted lamellar overgrowths is fixed to 65° during the evolution process of these crystals. However, the angle θ between the petal and the growing frontier of the twisted lamellar overgrowths gradually becomes smaller with crystallization time increasing, which is due to the increased distance from the straight edge of the petal to the middle site in between a pair of petals during crystallization. Only after the straight edge of the petal has reached considerable size (length), for example, encountering with

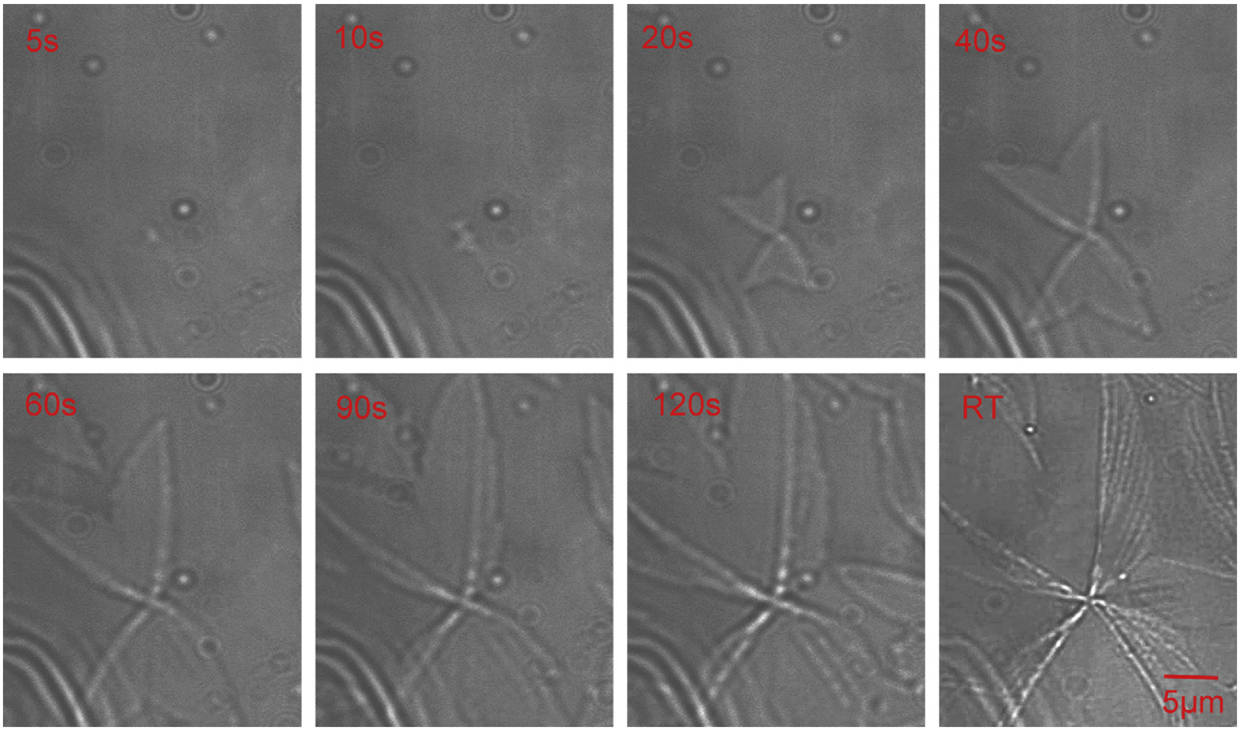

Fig. 2. A series of OM snapshots indicating growth details of the windmill crystals and associated twisted lamellar overgrowths of polyethylene isothermally crystallized at 114 °C for given crystallization times and at room temperature. The image RT was taken by using a conventional objective with NA (Numerical Aperture) = 0.8, the other images at elevated temperature were taken by using long working-distance objective with NA = 0.55, which produces different quality of the images.

the petals from the neighbor windmills, the other lamella starts to grow subsequently one by one, using the same mode as that of the straight edge. Finally, the development of the remaining lamellae gives rise to the integrated windmill crystals. The eventual length of each lamella associated to a petal decreases with time, which is attributed to the formation of straight and curved edges for a petal. It should be noted that technically, for all the OM images taken at elevated temperature shown in Fig. 2, they were recorded by using a long-distance (LD) objective with an numerical aperture (NA) of 0.55 for the observations using a hot-stage, the image quality is therefore limited by the resolution of this objective. In contrast, the last OM image, which was taken at room temperature by using a conventional high-ranking objective with an NA of 0.8, shows higher resolution and all the lamellae for a petal can be clearly distinguished.

As has already been shown in the previous study [1], the twisted lamellar overgrowths always take an angle of 65° with the straight edge of the petal. Upon tilting the specimen along *b*-axis for 45°, this angle changes to 56°. Upon relating these angles to the unit cells of orthorhombic crystal of polyethylene, together with the well-aligned electron diffraction pattern obtained from [001] axis after tilting the specimen for 45° [1], we conclude that the folding surface of the petals corresponds to crystallographic $(\bar{3}01)$ plane, which exactly has an angle of 45° with crystallographic (001) plane around *b*-axis. Correspondingly, by considering the 65° angle between the twisted lamellar overgrowths and the straight edge of the petals, it could be concluded that the preferential growth direction of the petals is along [113] axis, which has an angle of 65° with *b*-axis. This conclusion could be further verified by the fact that the projection of [113] axis on crystallographic (001) plane corresponds to [110] axis, which exactly takes an angle of 56° with *b*-axis, as observed in the projected BF-TEM image from 45° tilted specimen. All these relations have been schematically shown in Fig. 4.

With respect to this unusual growth direction of [113] axis for the petals, it might be a consequence of steep free-energy barriers both in enthalpy and in entropy for the petals in the initial stage since they grow in pair. In such a case, chains bend in the transverse direction so as to reduce free enthalpy is not possible any more, which is the typical growth behaviors adopted by the melt crystallized polyethylene in a thin film. Alternatively, the chains within the lamellae of the petals choose a tilting of 45° around crystallographic *b*-axis, which results in novel preferential growth direction along [113] axis instead of the conventional [110] axis for solution crystallized polyethylene. Therefore, the petals of the windmill crystals adopt a preferential growth direction along [113] axis.

The studies on kinetics of isothermal or non-isothermal polymer crystallization in bulk, which usually results in the formation of spherulites [17,18], are typically carried out by differential scanning calorimetry (DSC) measurements. Generally, the determination of the crystallization kinetics by morphological method, e.g. optical microscopy, is only possible for those semi-crystalline polymers with very low crystallization rates. This is attributed to the reason that low crystallization rates in these materials will ensure the specimen being quenched to the desired temperatures without any remarkable crystallization. However, high-density polyethylene, which is undoubtedly the most widely studied polymer in terms of crystallization, is not the case. Due to the inherent rapid crystallization rates that are typically orders of magnitude higher than that found in other semi-crystalline polymers, it is really a challenge to quench polyethylene to the temperatures lower than 108 °C while simultaneously measuring the growth rate of crystals. Only after these limitations have been overcome, the crystallization process of the windmill crystals and associated twisted lamellar overgrowths could be investigated in real time. Since the crystallization of the twisted lamellar overgrowths is nucleated by the straight edge of the petal, the growth rates of the lamella in straight edge is of highly interest. It has been shown that this lamella adopts a constant linear growth rate during the crystallization process before it is impinged by the other petals. Fig. 5 gives a plot showing the linear growth rates versus crystallization temperatures. The inset confirms that the growth rate is a constant value with time at a given crystallization temperature. Within the temperatures used for isothermal crystallization ranging from 108 °C to 114 °C, the linear growth rate of this straight edge rapidly decreases from 2.5 μm/s at 108 °C to 0.12 μm/s at 114 °C. Based on the two observations that the

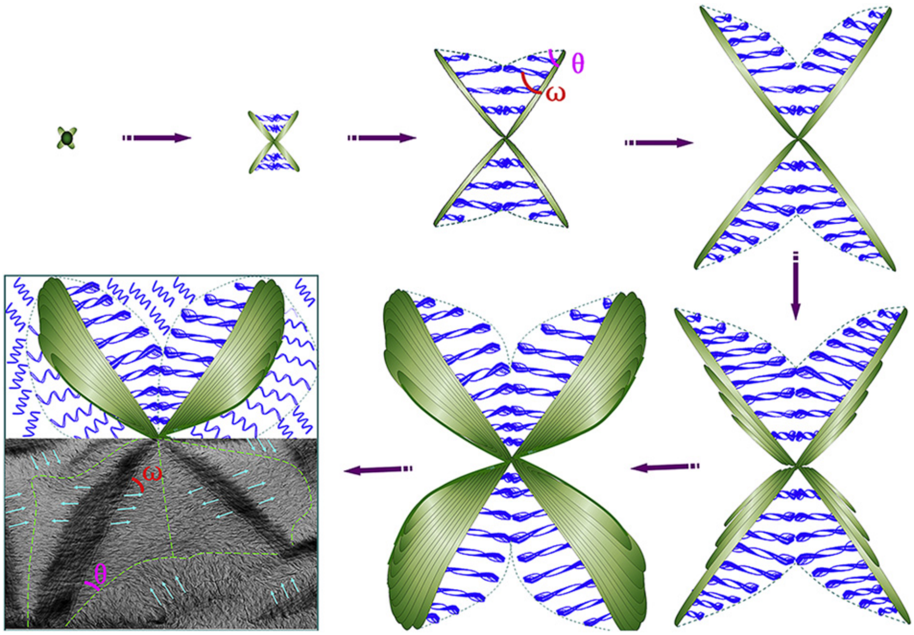

Fig. 3. Schematic illustrations demonstrating the different growth stages of the windmill crystals and the associated twisted lamellar overgrowths.

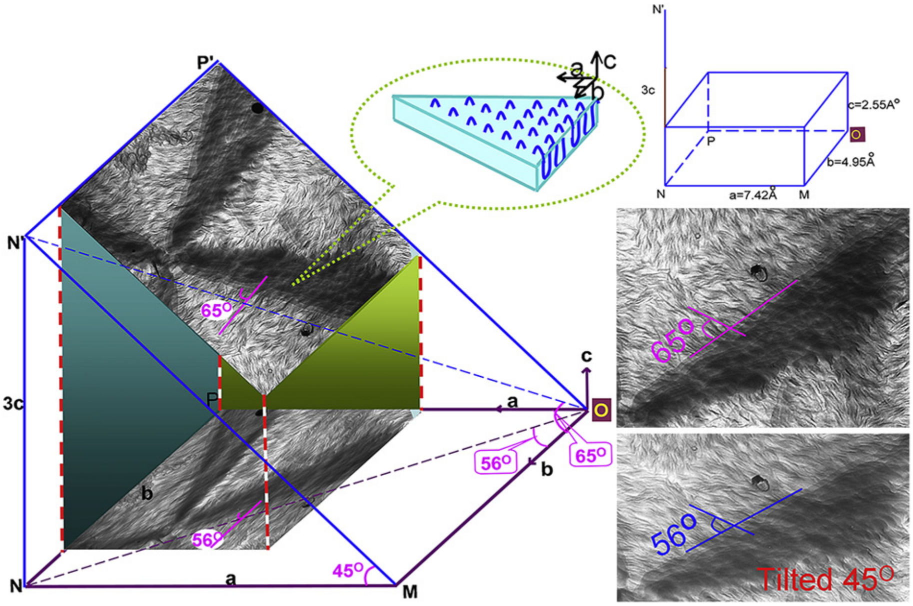

Fig. 4. The schematic illustrations of the angles between the twist lamellae overgrowths and its straight edge changed from 65° to 56° upon a 45° tilting of the specimen around *b*-axis. This relation confirms the preferential growth direction of the petals is along [113] axis.

constant growth rate with time at given crystallization temperature together with a decreased growth rate at elevated temperature, we can conclude that the crystallization of the straight edge of petals is a thermodynamically determined process by the degree of super cooling rather than a kinetically controlled process by either chains diffusion or incorporation rate during packing.

Avrami equation is the most frequently used model to describe the isothermal crystallization kinetics of semi-crystalline polymer, where Avrami exponent is a crucial parameter to determine the nucleation mode and growth dimensions of the crystals [19]. Experimentally, DSC measurements are usually performed to obtain serial time-dependent fractional crystallinities for the kinetic analysis by using Avrami equation. However, if the crystallization of a sample is not suitable for DSC experiment, e.g. thin films which couldn't provide enough crystal volume for measurement, or crystallization occurs under special environment, the morphological methods could be employed if feasible. In such case, the morphology of the crystals in terms of volume should be measured in the real time. For the crystallization kinetics of the twisted lamellar overgrowths associated to the petals, the relative degree of crystallinity $[x(t)]$ with growth time (t) could be evaluated by the areas calculated from the optical micrographs assuming that they have the comparable thickness. Correspondingly, the plots of $\ln\{-\ln[1-x(t)]\}$ versus $\ln t$ for the samples isothermally crystallized at 114 °C, 115 °C and 117 °C, respectively, are obtained and given in Fig. 6. As is shown, all these plots could be linearly fitted, resulting in corresponding Avrami exponents of 2, 2, and 2.15, respectively. This result has already demonstrated that the crystallization of these twisted lamellar overgrowths is heterogeneously nucleated, which is consistent with the observations in the growth process

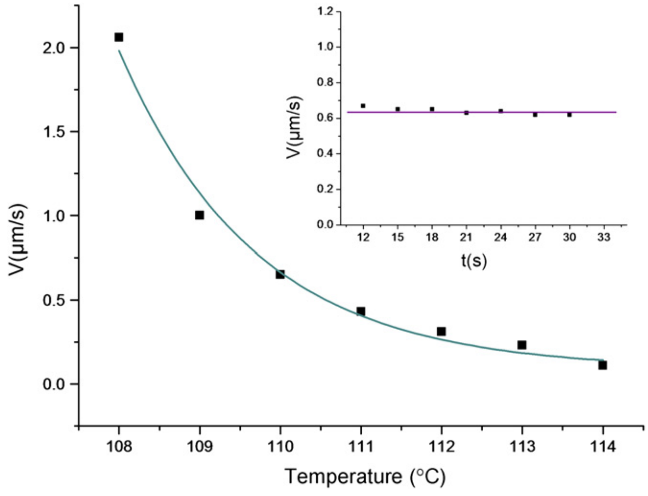

Fig. 5. The plot of linear growth rates of straight edge of the petal versus isothermal crystallization temperatures. The inset shows the constant growth rate with time at a given crystallization temperature (110 °C) before meet others. The solid curve and line serve to guide the eye.

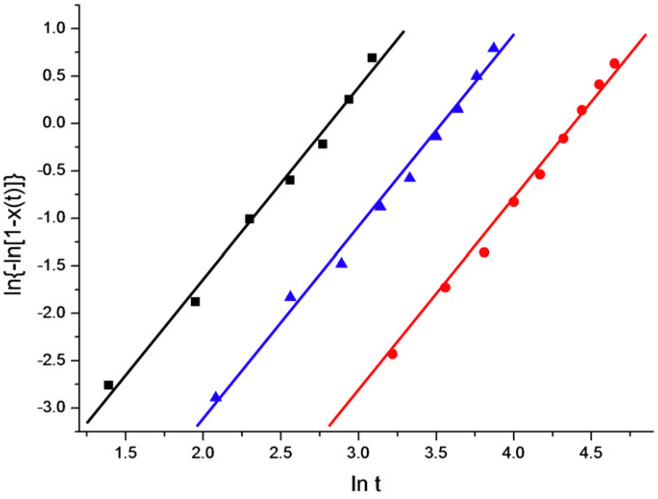

Fig. 6. The plots of ln{-ln[1-x(*t*)]} against ln*t* at different crystallization temperatures of 114 °C (■), 115 °C (▲), 117 °C (●), and linearly fitted lines. The slopes of these lines are 2.0, 2.0 and 2.15 for 114 °C, 115 °C and 117 °C, respectively.

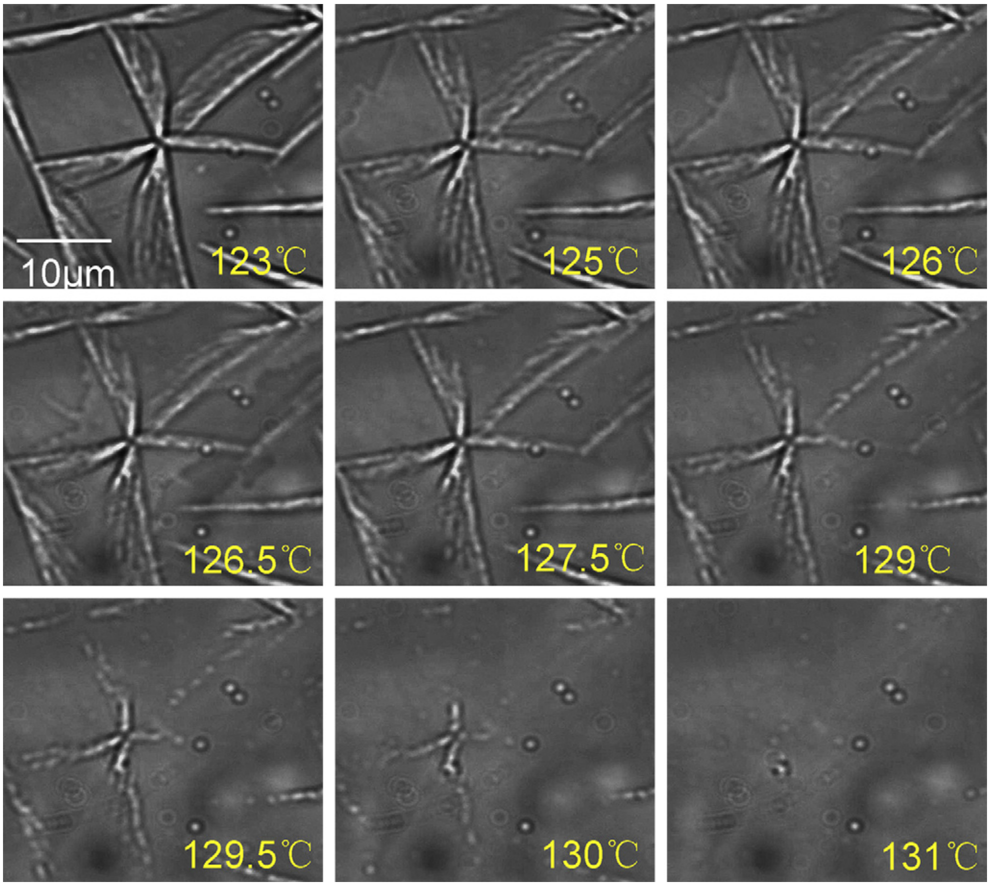

Fig. 7. A series of OM snapshots showing melting process of the windmill crystals and the twisted lamellar overgrowths at different temperatures upon heating at 10 °C/min. The curves serve to guide the eye for the easy reorganization of the sketch of the petals.

that their growth is nucleated by the straight edge of the petals, as observed by optical microscopy.

A video showing the detailed melting process of the windmill crystals and associated twisted lamellar overgrowths upon heating has been recorded (Supporting Information), which is the reverse process of that in crystals growth. As shown in Fig. 7, the melting process of the twisted lamellar overgrowths associated to the petals almost simultaneously starts at 123 °C. Only after these crystals have been completely melted at ca. 127.5 °C the straight edge of the petal starts to melt from outside to the center, which is also reversed to that observed in crystal growth during crystallization. Eventually, all the crystals fade out from the field at ca. 131 °C upon further heating. It should be noted that although no morphological feature could be distinguished above this temperature (131 °C), the core of windmill crystal might not be destroyed completely. Moreover, the central junctions could still survive after being heated to a temperature even higher than 200 °C. The preservation of this hardly dissolvable core is mainly responsible for the acquisition of this novel morphology of polyethylene.

Based on the sequential crystallization and reverse melting processes of the straight edge of the petal, twisted lamellar overgrowths together with the latterly grown curved edge of the petal, we are able to get deeper insight into the formation details of this novel morphology of polyethylene. We could further infer that the firstly grown lamellae, i.e. the straight edges of the petals, might be composed of polyethylene chains with longer sequence of ethylene segments, which are able to crystallize at relatively higher temperature (lower super cooling rate) and results in thick lamellae. While the other polyethylene chains can only crystallize at low temperatures, which contribute to the remaining parts of the crystals.

4. Conclusions

The detailed morphology of windmill crystals of polyethylene has been extensively investigated by various morphological characterization tools, e.g. BF-TEM, SEM, OM, POM and AFM. In particular the AFM topography confirms that the central junction of the windmill is the thickest part compared with all the other parts in the novel crystal. This center correspondingly becomes the most difficultly dissolvable part which is responsible, if not all, but at least partially for the formation of this novel morphology of polyethylene via nucleation control.

The real time investigation on the crystallization process shows that the straight edge of the petal grows radically in pair from the center firstly, which acts as the nucleus for the melting polyethylene in between the petals to develop into twisted lamellar overgrowths. The terrace lamellae contribute to the curved edge of the petals form lastly and thus the integrated petals are obtained. It is confirmed that the petals of the windmill crystals takes preferential growth direction along crystallographic [113] axis instead of conventional *b*-axis for melt crystallization of polyethylene in a thin film. The linear growth rate of the lamellae of the petals is constant with time, demonstrating a thermodynamically determined crystallization process. According to the Avrami equation, the crystallization kinetics of the twisted lamellar overgrowths shows heterogeneous nucleation and two-dimensional growth, which is consistent with crystallization details observed morphologically.

The melting experiment of these crystals gives largely the reverse process as that of crystallization. We infer that the formation of this novel morphology and sequential crystallization process for each part might be relevant to the different sequence lengths of ethylene segments, which results in the various fractions with slightly different crystallizabilities.

Acknowledgment

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Appendix. Supplementary data

Videos showing the growth and melting details for the windmill crystals and associated twisted overgrowths. It should be noted that in order to obtain an acceptable file size for convenient transmission, the time scale for both videos has been adjusted. This material is available free of charge via the Internet at http://www.sciencedirect.com.

The supplementary data associated with this article can be found in the on-line version, at doi:10.1016/j.polymer.2009.08.008.

References

[1] Wang J, Lu GH, Li LG, Lu ZH, Yang XN, Zhou EL. Macromolecules 2008; 41:1273.
[2] Mellbring O, Kihlman Øiseth S, Krozer A, Lausmaa J, Hjerberg T. Macromolecules 2001;34:7496.
[3] Hartman P, Perdok WG. Acta Crystallogr 1955;8:49.
[4] Hartman P, Perdok WG. Acta Crystallogr 1955;8:521.
[5] Bassett DC, Frank FC, Keller A. Philos Mag 1963;8:1739.
[6] Keller A. Philos Mag 1957;2:1171.
[7] Burbank RD. Bell System Tech J 1960;39:1627.
[8] Bassett DC, Keller A. Philos Mag 1962;7:1553.
[9] Bassett DC, Olley RH, Raheil LAM. Polymer 1988;29:1539.
[10] Lauritzen Jr JI, Hoffman JD. In: Hannay NB, editor. Crystalline and non-crystalline solids, 3. New York: Plenum Press; 1976. p. 497.
[11] Strobl G. Eur Phys J E 2000;3:165.
[12] Hoffman JD, Frolen LJ, Ross GS, Lauritzen JI. J Res Nat Bur Stand Sect A Phys Chem 1975;79A:671.
[13] Wunderlich B. Macromolecular physics. New York: Academic Press; 1976.
[14] Bassett DC. Principles of polymer morphology. New York: Cambridge University Press; 1981.
[15] Cheng SZD, Lotz B. Polymer 2005;46:8662.
[16] Yamamoto T. Polymer 2009;50:1975.
[17] Barham PJ, Keller A, Otun EL, Holmes PA. J Mater Sci 1984;19:2781.
[18] Phillips PJ, Vatansever N. Macromolecules 1987;20:2138.
[19] Avrami M. J Chem Phys 1939;7:1103.