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Morphology and structure of micro-fibrillar crystal of nylon 10 10

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Abstract

The nanoscale and microscale fibrillar crystals of nylon 10 10 were obtained by atomizing the very dilute formic acid solution. The length–diameter ratio of these fibrillar crystals increases as the concentration of the atomizing solution increases. Electron diffraction (ED) analysis showed that the hydrogen-bonded sheet in these solution-grown fibrillar crystals was imperfect and had a lower order.

Both electron diffraction and characteristic morphology show that melt-crystallized fibrillar crystals always possess perfect packing order and stable structure. A rather perfect ED pattern of the triclinic form of nylon 10 10 along the [001] zone was obtained by tilting the specimen 41° along the elongated direction of the crystal.

Fibrillar crystals from bulk have a great tendency to aggregate with parallel packing to form crystal clusters, which look like shish kebabs in morphology. Spherulite is observed occasionally in the domains with very rich sample.

Keywords: Nylon 10 10; Fibrillar crystal; Polymer morphology

1. Introduction

Fibril structure extensively exists both naturally and synthetically. Fibroin takes up more than 70% of the ingredient in the silks of *Bombyx mori* and the fibroin is composed of ca. 100 fibrils, which is packed by thousands of microfibrils. Specifically, all these fibrils have the similar basic structure, the so-called the anti-parallel β-sheet. The hair and feature of animals are also fundamentally assembled by protofibril 2 nm in diameter. Each protofibril is composed of three entangled α-helix(D) peptide chains. Specifically, the α-helix protofibril would transform to β-sheet structure if the hydrogen bonds within the chain were destroyed by heating or external stress exerted on them. In the synthetic polymers, polyamides with high molecular weight, which are also practically called as "nylon" fibers, easily give fibril structure [1].

Definitely, β-sheet structure is dependent on the hydrogen-bonding interactions between individual strands [2,3]. β-Sheet, which can provide key element in protein–DNA [4], protein–RNA [5], and protein–protein [6] recognition, has recently been regarded to play an especially important role in the protein structure. Some nylons, such as nylon 6 [7], 46 and 8 [8], also have a scheme closely analogous to β-sheet. Typically, the packing spacing of the molecular chains has a similar distance of 4.5 Å in the various proteins and nylons. Some writers believe that hydrogen bonds are responsible for this type of packing.

The morphology and structure of fibril is commonly investigated by small-angle X-ray scattering (SAXS) and small-angle neutron scattering (SANS) in the bulk state. However, nanoscale fibrillar crystals can only be revealed by transmission electron microscopy (TEM) [2] and atomic force microscopy (AFM) [9]. Both tools can give the morphology of separated or slightly aggregated fibrillar crystals. Nevertheless, for the analysis of chain packing, one can only resort to TEM although AFM is free from effects of electron beam radiation.

Nylons easily form spherulitic crystals or lamellar crystals while crystallized from molten film or dilute solution [10–15]. The fibrillar structure of nylons extensively exists in the drawing bulk samples, but the morphology and structure of separated fibrillar crystals is rarely observed. As a synthetic polymer, nylon has many similarities to natural fibrous protein, both structurally and functionally. Fibrillar structure is a fundamental element in these fibrous materials. Any information on molecular packing gained from a detailed study of fibrillar nylon may be useful in dealing with the far more complex problems presented by fibrous proteins. In this work, we developed a new method to

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prepare the nanoscale and microscale fibrillar crystals of nylon 10 10.

Nylon 10 10, which has the crystal structure analogous to nylon 66, is another important commercial polyamide. Mo and co-workers [16] report the crystal structure and thermodynamic parameters of nylon 10 10, which crystallizes in the triclinic system, with cell dimensions: $a = 0.49$ nm, $b = 0.54$ nm, $c = 2.78$ nm, $\alpha = 49°$, $\beta = 77°$ and $\gamma = 63.5°$. Nylon 10 10 crystal only contains one monomeric unit in its unit cell and belongs to the $P_{\bar{1}}$ space group.

2. Experimental part

The sample used in this study was a granular commercial product of Shanghai Cellulose Works, Shanghai City. The M_n determined by dissolving in *m*-cresol was approximately 13,000. The granular sample was dissolved in *m*-cresol and the solution was poured into large amount of methanol. This process was repeated for several times to remove the possible impurities. The finally purified powder sample was thus obtained by drying the precipitate in the vacuum oven overnight.

2.1. Sample preparation

A method called "atomizing very dilute solution" was introduced to prepare the fibrillar sample of nylon 10 10. As a polar polymer, nylon can slightly dissolve in strong polar solvent such as hot glycerin, 1,4-butanediol, formic acid and *m*-cresol. However, only formic acid is suitable for this method for its relatively higher evaporability than others. In our work, 0.0025% (g/ml) and 0.01% (g/ml) formic acid solution of nylon 10 10 were prepared. The microdroplets of solution generated by a self-made atomizer were sprayed onto the new cleaved mica coated with carbon film. For some specimens, the precipitator of ethanol was occasionally cast on the substrate and thus the carbon film was fully wetted by ethanol before the nylon solution was atomized. In order to avoid the severe aggregation of microdroplets on a domain, there was a suitable intermediate time between the certain times of atomizing operations, which allows the solvent to evaporate.

The melt-crystallized specimens were prepared by heating the atomized specimen to 250°C and keeping at this temperature for 5 min, then quickly cooled to 175°C and annealing at this temperature for 36 h. All the melting and annealing operations were carried out in an environment filled with oxygen-free dried nitrogen.

2.2. Transmission electron microscopy

The samples for morphology observations and structure analysis were prepared as following: the films on mica were floated off on the distilled water surface and picked up onto 400-mesh electron microscope copper grids. Afterwards, the films were shadowed with Pt/C in a high-vacuum evaporator to improve contrast in the morphological observations and then coated with a thin layer of carbon. Calibration substance (Au) was also occasionally evaporated as inner calibrating substance for electron diffraction spacing after carbon coating. The TEM observations were conducted on JEOL JEM-2010EX Transmission Electron Microscope operated at 200 kV. The spacings of diffraction spots on the electron diffraction patterns were calibrated by the Debye–Scherrer rings generated from the thin layer of gold occasionally evaporated on the same specimen.

3. Results and discussion

3.1. Nanoscale and microscale fibrillar crystals from very dilute solution

Fig. 1 shows the transmission electron micrographs of nylon 10 10 fibrillar crystals obtained by atomizing its 0.0025% solution. The fibrillar crystals prepared by atomizing the sample on the substrate without precipitator is shown in Fig. 1a. The diameter of these fibrils is only 5–8 nm and their length reaches 50–300 nm. All the dimensional values are very similar to those of nylon-6 fibrils [1] obtained by drawing and annealing, which were determined by using two-dimensional SAXS to be 100–300 nm in length and 5–10 nm in diameter. Fig. 1b gives the morphology of specimen atomized on the substrate filled with ethanol. Obviously, the length of these rod-like nanoscale fibrillar crystals is less than 100 nm, while their diameter reaches 12–18 nm. Additionally, some small fibrillar crystals are aggregated to form fibrillar crystal cluster. The difference of morphology between these two specimens is obvious and mainly is dependent on the length–diameter ratio. Generally, ethanol is a poor solvent for nylon 10 10. Therefore, the dropping of microdroplets on it will result in the immediate precipitation of nylon samples. This means the free and well-extended nylon chains in the very dilute formic solution must be coiled while they are dissolved a poor solvent. As a consequence, the precipitated fibrillar crystals will possess a shorter length. Furthermore, due to the evaporation of formic acid and ethanol, microdroplets or precipitated fibrillar crystals, especially those small ones, will slightly move on the surface, just like the drifting of powerless boat on the ocean. This must cause the aggregation of fibrillar crystals and thus forming the cluster.

Electron diffraction (ED) analysis was carefully performed on these fibrillar crystals. In order to avoid the influence of electron beam radiation on their packing order, selected-area electron diffraction (SAED) operations were carried out on those crystals that were not exposed to the beam. However, the diffraction signals were still especially weak. We did not record the electron diffraction pattern. Another reason is from the fact that diffraction signals contributed by the fibrillar crystals on the selected area

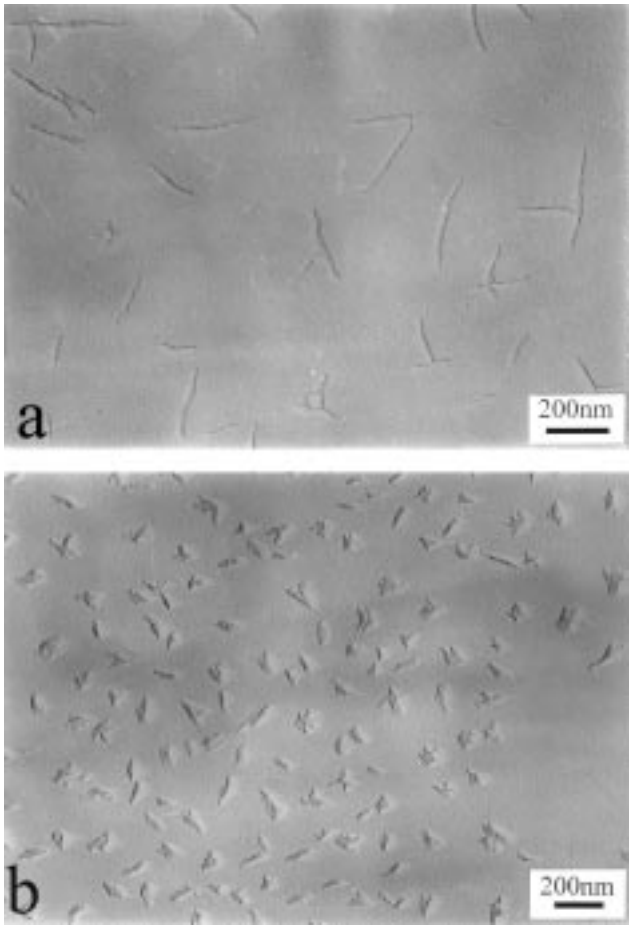

Fig. 1. Transmission electron micrographs of nylon 10 10 fibrillar crystals obtained by atomizing its 0.0025% solution on the substrate (a) without ethanol and (b) with ethanol.

were dispersive and there was no prevailing orientation because of their multi-orientation on the substrate.

The morphology of fibrillar crystals obtained by atomizing 0.01% formic solution is shown in Fig. 2. The length of them is mainly between 500 nm and 1 μm, but some reach

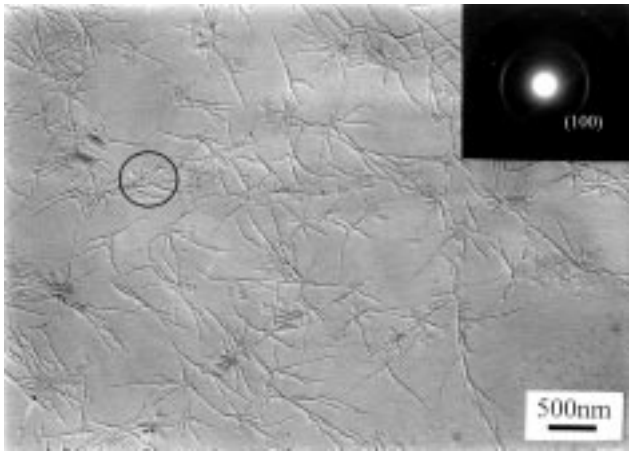

Fig. 2. Bright-field morphology of nylon 10 10 fibrillar crystals obtained by atomizing its 0.01% solution.

several microns. Their diameter is determined to be 8–20 nm. Most of them have branches and aggregate to give the floria-like morphology. Higher concentration of polymer in solution must give rise to more number of polymer chains in each atomized microdroplets. As a result, the diameter of fibrillar crystals slightly increases from 5–10 to 8–20 nm. However, the increasing rate of length is very high compared to the rate of increase of diameter. This means the length–diameter ratio of the fibrillar crystals increases as their dimensions become larger.

For these relatively larger fibrillar crystals, electron diffraction analysis is also carefully carried out by using the similar method mentioned above. In fact, the packing order of these crystals is a little better than those shown in Fig. 1a. However, their ED pattern is still difficult to record. Fortunately, we obtained some arced ED pattern on the selected field. One of them is shown in the insert of Fig. 2. The distance of diffraction arc is determined to be 4.5 Å, which corresponds to the reflection of (100) plane. This suggests that the hydrogen-bonded sheet is along the elongated direction of the fibrillar crystals.

The hydrogen bond is the main component in the nylon crystals and it always leads to the formation of connected sheet in the materials. The hydrogen-bonded sheets then pack to form crystals via the action of van der Waals forces. Without any exception, hydrogen bonds also extensively exist in the nylon 10 10, even in the melt-quenched sample [17]. However, the strong organic acid, such as the formic acid, can severely destroy the hydrogen bond. Therefore, no hydrogen bonds can survive after the nylon is dissolved in formic acid and it is also difficult to re-construct perfect hydrogen-bonded sheet as the solvent evaporates in a rapid speed. As a consequence, the hydrogen-bonded sheets in these solution-grown fibrillar crystals must be especially imperfect and unstable. This can be proved by their weak and rapidly disappearing electron diffraction signals as shown in the insert of Fig. 2, which represents the interchain distance within hydrogen-bond sheet. Nevertheless, the developing speed of hydrogen-bonded sheet is much faster than the packing rate of sheets. This gives rise to the fibrillar structure of atomized sample. The fact that the growing rate along the hydrogen bond direction faster than the other directions has also been found on the lamellar single crystals grown in dilute solution. As a result, the lamellae possessed the elongated morphology with long dimension in the (100) direction.

Fig. 3 represents the specimen obtained by atomizing excess amount of solution and shorter interval time during the atomizing operations. The fibrils connected and severely overlapped. It should be noted here that their width was larger than height in these fibrils. This suggests that the fibrillar crystals here no longer have the traditional round profile. Instead, their width reaches 40–60 nm, while their height still is approximately 10 nm. In fact, the height of fibrils shown in Fig. 2 is also roughly of this value.

The height of the fibrillar crystals is slightly varied

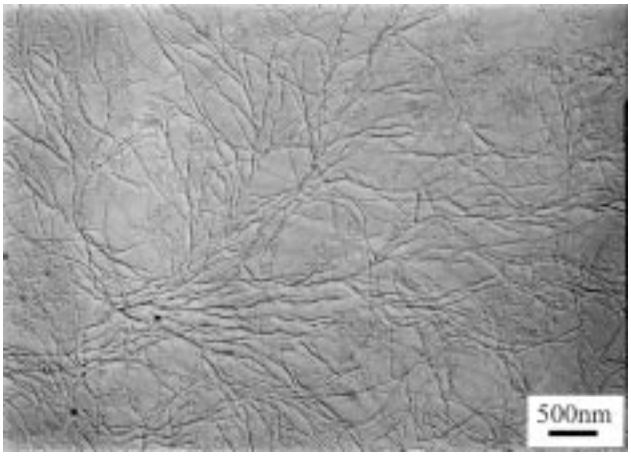

Fig. 3. Bright-field morphology of nylon 10 10 fibrillar crystals with long length obtained by atomizing excess amount of solution sample.

irrespective of the severe increase of length and width. According to the specific morphology of different fibrillar crystals obtained in this work, we can regard the formation process of fibrillar structure as following. At the very early stage of crystallization, the nylon chains fold with almost constant folded period and hydrogen bonds formed between the neighbor stems. The hydrogen-bonded sheet is thus constructed, although having many defects and therefore unstable in packing. Then, the sheet increasingly expands along the inherent direction, while the packing process between the sheets is extremely slow. This gives rise to greatly different growing rate in the two dimensions and, finally, the fibril structure is formed. Moreover, as the amount of polymer in microdroplets increases, more sheets will pack on a fibril and this must contribute to the larger dimension in the width.

3.2. Fibrillar crystals obtained from molten sample

The typical morphology of melt-crystallized fibrillar crystals is shown in Fig. 4. The length of these fibrillar crystals reaches several microns, while their width is approximately 20 nm and their height is similar to those of fibrillar crystals from dilute solution in the former section. By comparing that shown in Figs. 3 and 4, we can find that the difference in the morphology of a single fibrillar crystal is not obvious. However, the packing manner of inter-fibril and crystallinity of two crystals are greatly different, which can be observed by their electron diffraction and morphology. Even at the same TEM operation condition, the ED signal of the fibrillar crystals from solution was far weaker than that of the crystals from bulk. On the contrary, the ED pattern from melt-crystallized fibrillar crystals was strong and clear. Not only the fibrillar crystals from the dilute solution possessed low orientation and packing order within each fibril, but also all of these fibrils disorderly disperse on the substrate while melt-crystallized fibrillar crystals have a great tendency to parallelly pack each other. Fig. 5 shows the SAED patterns. Fig. 5a was obtained when the incident electron beam was normal to the substrate. Only a single diffraction dot (observed as a pair) was observed, which is attributed to the reflection from (100) plane. By tilting the specimen along the axis of elongated direction of fibrillar crystals, a new ED pattern as

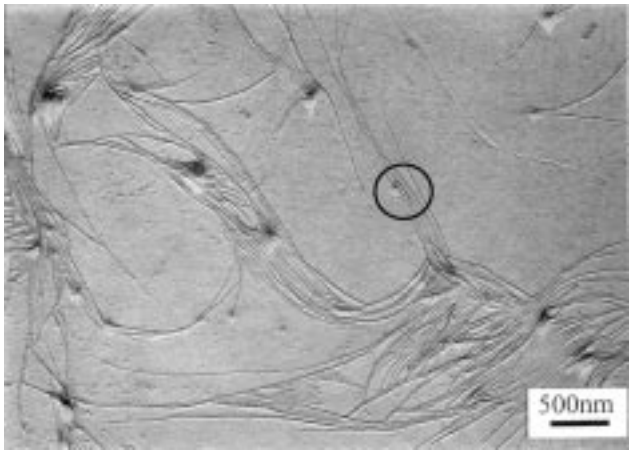

Fig. 4. TEM morphology of melt-crystallized nylon 10 10 fibrillar crystals.

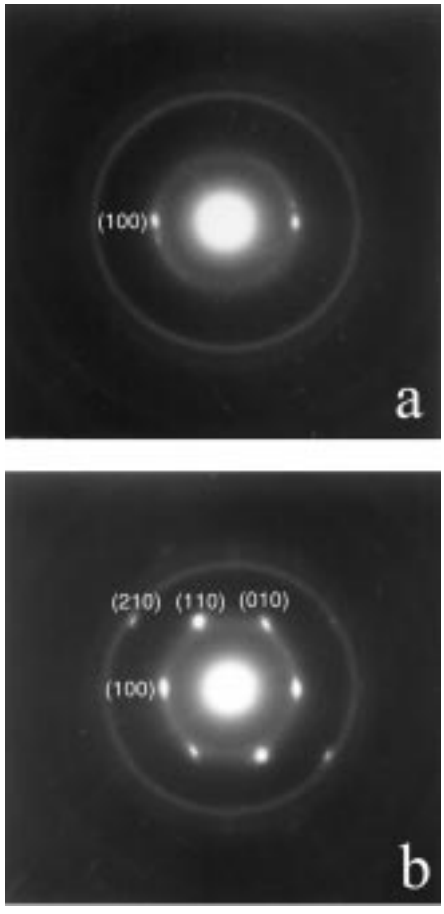

Fig. 5. Selected-area electron diffraction of fibrillar crystals shown in Fig. 4a electron beam normal to the substrate; (b) tilted 41° along the elongated axis of fibrillar crystal so as electron beam paralleling to the chain axis.

shown in Fig. 5b was observed when the tilting angle reached 41°, which gives rise to the electron beam parallel to the chain axis. All the diffraction dots can be indexed by using the cell dimensions proposed by Mo et al. [16] for nylon 10 10. Bunn and Garner [18] proposed a chain conformation model for nylon 66, in which the polymer chains have 13° tilt in the (100) plane and 41° in the (010) plane to the *a*–*b* substrate. The results of the tilted electron diffraction pattern suggest the packing manner in the fibrillar crystals of nylon 10 10 also possessed the similar chain packing mode to that of nylon 66. Due to the slightly tilted angle (only 13°), the (100) plane can capture the electron beam and give diffraction signals when the beam was normal to *a*–*b* plane. However, the more tilted (010) plane will not present any diffraction signals unless the fibrillar crystals are tilted to certain angle so as to minimize or eliminate the titled angle between incident beam and orientation of polymer chains in the (010) plane. Fig. 6 schematically represents the cell model of nylon 10 10 crystals and the mechanism of tilting operations to determine the chain orientation in the unit cell.

Fig. 7 shows another morphology of melt-crystallized fibrillar crystals. The crystals in the field are mainly oriented in two directions. These two kinds of crystals connected by a relatively larger fibrillar crystal, looked like a double-faced comb. The insert shows the SAED of the marked area. Two pairs of diffraction dots appeared on the ED pattern, which were contributed by the respective oriented fibrillar crystals. We are much interested in the transitional packing manner of the crystals in the connected region. Both the morphology and ED pattern give the evidence that there is no gradient transitional region between the two oriented crystals. This suggests the transition of crystal packing is sudden from one to another.

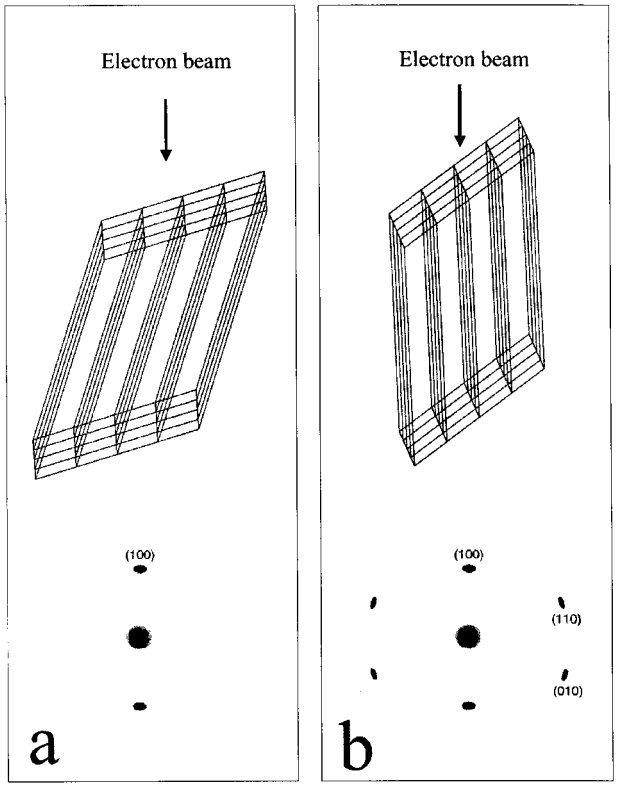

Fig. 6. Schematic representation of the relationship between the incident electron beam and orientation of polymer chain in the unit cell of crystals. (a) Electron beam normal to the substrate and thus there is approximately 41° inclination angle between them; (b) tilted 41° along *a*-axis so that electron beam is parallel to the chain axis.

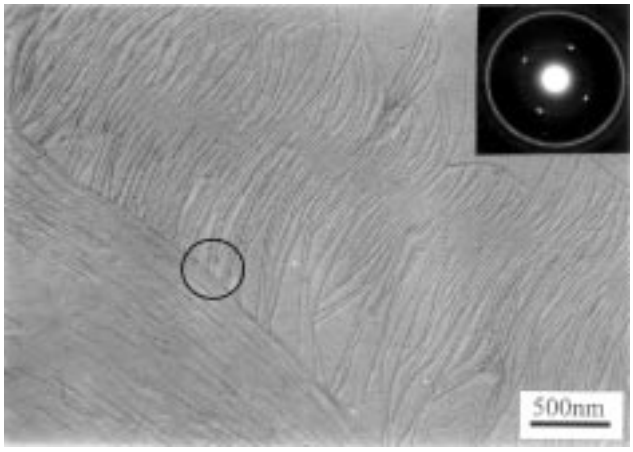

Fig. 7. Another TEM morphology of melt-crystallized nylon 10 10 fibrillar crystals. All the fibrillar crystals are oriented in two directions and have clearly connected part. The insert shows the ED pattern of marked area.

The melt-crystallized fibrillar crystals are easy to aggregate and their aggregation characteristics are dependent on the richness and dispersion of samples on the substrate. Frequently, they easily aggregate to form the crystal cluster like shish kebabs in morphology and all these crystal clusters are always connected by the thin fibers. Fig. 8 shows the morphology of such crystal clusters. This kind of morphology will appear when it crystallizes from limited amount of sample. However, it has never been observed in the common bulk sample, even in the early stages of crystallization. It is believed that in an environment where there is

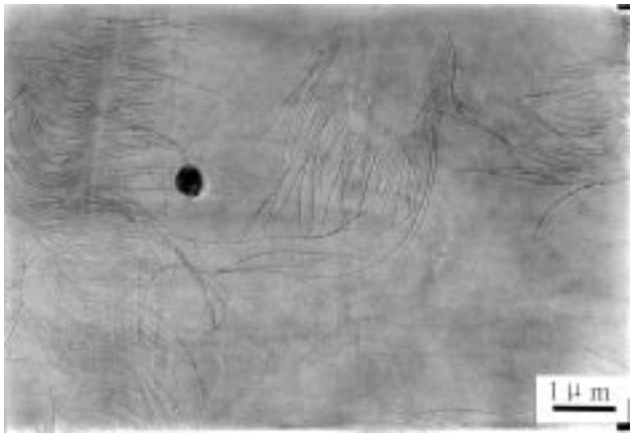

Fig. 8. Transmission electron micrographs of nylon 10 10 fibrillar crystals looked like shish kebabs in morphology.

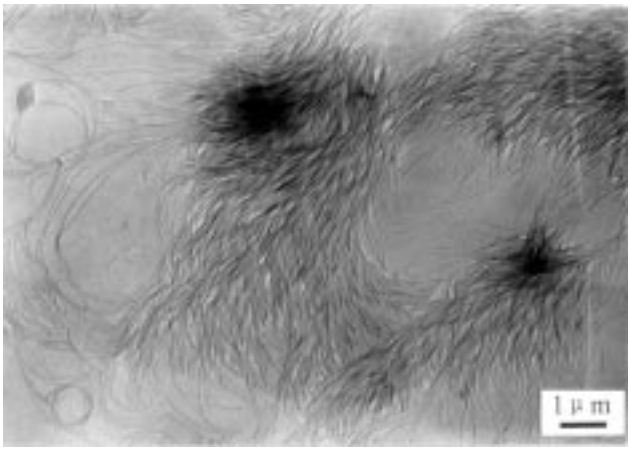

Fig. 9. Spherulitic morphology of melt-crystallized nylon 10 10 in the domains with rich sample.

extremely limited sample in a domain, such as single chain or pauci chains, nylon 10 10 will form fibrillar crystals. The crystal clusters like shish kebabs will then be formed by the parallel packed and partly connected fibrillar crystals. In fact, the central part of the crystal clusters has been connected into the lamellar crystals due to the tight packing of fibrillar crystals. Specifically, the spherulitic morphology as shown in Fig. 9 will be observed on a field where excess sample was aggregated even though there are the fibrillar crystals in some regions. This suggests the morphology of melt-crystallized nylon 10 10 is solely dependent on the richness of the sample on the domain.

4. Conclusions

The nanoscale and microscale fibrillar crystals of nylon 10 10 were prepared by atomizing the very dilute formic acid solution. Their morphology and structure were investigated by TEM and electron diffraction. The length–diameter ratio of the fibrillar crystals is elevated as the concentration of atomizing solution increases. hydrogen-bonded sheets do exist in these crystals. However, the ED pattern revealed that the hydrogen-bonded sheet was imperfect and thus unstable.

Melt-crystallized fibrillar crystals possess higher crystallinity and packing perfection than those from dilute solution. The stable structure allows the determination of the orientation of polymer chains in the crystals by using tilt electron diffraction technique. Only one strong reflection at 4.5 Å was obtained when the electron beam was normal to the substrate. We recorded a rather perfect ED pattern of nylon 10 10 from [001] zone by tilting the specimen 41° along the *a*-axis of crystal so that the electron beam is parallel to chain direction. This suggests that the polymer chains in the *b*–*c* plane have 41° tilt with the substrate.

Fibrillar crystals have a great tendency to aggregate with parallel packing to form crystal cluster, which looks like shish kebabs in morphology. An excess amount of the sample will eventually lead to the formation of spherulite.

Acknowledgements

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