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Shear-induced crystallization of poly(phenylene sulfide)

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ABSTRACT

The crystalline morphology of poly(phenylene sulfide) (PPS) isothermally crystallized from the melt under shear has been observed by polarized optical microscope (POM) equipped with a CSS450 hot-stage. The shish–kebab-like fibrillar crystal structure is formed at a higher shear rate or for a longer shear time, which is ascribed to the tight aggregation of numerous oriented nuclei in the direction of shear. The crystallization induction time of PPS decreases with the shear time, indicating that the shear accelerates the formation of stable crystal nuclei. Under shear, the increase of spherulite growth rate results from highly oriented chains. The melting behavior of shear-induced crystallized PPS performed by differential scanning calorimetry (DSC) shows multiple melting peaks. The lower melting peak corresponds to melting of imperfect crystal, and the degree of crystal perfection decreases as the shear rate increases. The higher melting peak is related to the orientation of molecular chains. These oriented molecular chains form the orientation nuclei which have higher thermal stability than the kebab-like lamellae that are developed later. A new model based on the above observation has been proposed to explain the mechanism of shish–kebab-like fibrillar crystal formation under shear flow.

1. Introduction

Shear-induced crystallization of polymers is a major subject of the current polymer studies since shear can produce molecular orientation, which leads to the morphological change of semi-crystalline polymers, and thus is relative to properties of the polymer parts [1–3]. In most processing operations, polymer melt is subjected to flow prior to crystallization, thus, it is of importance to investigate the effect of shear field on the crystallization of polymers. Previous studies [4–10] have shown that shear can accelerate the crystallization kinetics of polymer and change the crystalline morphology from spherulites to crystallites oriented in the direction of flow. The enhancement of crystallization kinetics is attributed to the increase of the nucleation rate on the basis of studies of the nucleation density, the crystallization induction time and the spherulite growth rate.

However, most works of shear-induced crystallization are focused on the polyolefins, especially isotactic polypropylene [4–46]. Few works [47,48] are devoted to the engineering polymers which are as important as the commodity plastics in practical applications. It is maybe because of the difficulty in handling the in situ experiments of most engineering polymers such as poly(ethylene terephthalate) (PET) and poly(phenylene sulfide) (PPS) due to their high melting temperatures and the associated possibility of degradation. Unfortunately, knowledge from polyolefins cannot be directly applied to engineering polymers. One reason is the difference in rigidity of chains, which can strongly influence the relaxation process. Generally, the molecular chains of engineering polymers have higher rigidity which, unlike the flexible chain polymer like iPP, are not easy to orient under shear condition but difficult to relax once oriented. Therefore, it is of high significance to understand the shear-induced crystallization of engineering polymers, accordingly, in this work, PPS was studied.

In this work, we will elucidate shear-induced crystallization of PPS by use of polarized optical microscope (POM) equipped with a CSS450 hot-stage, differential scanning calorimeter (DSC) and atomic force microscope (AFM). PPS is a typical engineering polymer with semi-rigid chains, and exhibits good thermal stability, chemical resistance, flame resistance and precision moldability [49,50]. Nevertheless, these superior properties of PPS are greatly influenced by its crystallization behavior, crystallinity and superstructure. So far, some literatures have been focused on the crystallization behavior of PPS under quiescence condition [51–55]. However, very little attention is paid to the shear-induced crystallization of PPS. In the processing operations, the crystallization behavior and final morphology of PPS are, to a greater degree, dictated by the applied flow conditions. Thus, it is crucial to

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investigate the crystallization behavior of PPS under shear flow condition, especially the crystalline morphological change of PPS induced by shear flow. In this paper, we show from the polarized micrographs that the shish–kebab-like fibrillar crystal structure can be produced by a steady shear in a supercooling PPS melt. A new schematic of shish–kebab-like fibrillar crystal structure is proposed in which fibrillar crystal consists of numerous stable nuclei that align tightly in the direction of shear.

2. Experimental

2.1. Materials and sample preparation

The PPS resin powder obtained from Deyang Science and Technology Limited Corp. (China) was employed in the present experiments. Its molecular weight is $M_w = 48{,}000$, $M_n = 21{,}000$. The thin film of PPS sample was molded between two glass slips by heating the PPS resin to the melting state.

2.2. Shear apparatus

A CSS450 high-temperature shear hot-stage (Linkam Scientific Instruments Ltd., UK) was used to control the shear rate and thermal history of the PPS sample.

2.3. Morphological observation

The morphology of PPS was observed by polarized optical microscope (POM) with video attachment, which is connected to a shear flow cell (CSS450). Temperature calibration of the shear hot-stage was performed with naphthalene, indium, anthraquinone and sodium nitrate. Briefly, the temperature protocol for shear experiments was as follows: (1) heat the polymer sample from room temperature to 340 °C at a rate of 30 °C/min; (2) hold the temperature at 340 °C for 5 min to allow the sample to melt completely; (3) cool the sample to 260 °C for isothermal crystallization at a rate of 30 °C/min; (4) shear the PPS melt at a shear rate of 15, 30 and 45 s^{-1}; (5) hold the temperature at 260 °C until the crystallization was completed. The images of PPS crystal growth were taken at a given time during this period.

2.4. Atomic force microscopic measurement

The shear-induced crystallized PPS sample at 260 °C for 80 min was quenched to the room temperature for AFM measurement. The measurement was performed in the tapping model with an SPA300HV AFM (Seiko, Japan), and both the height and phase images were recorded simultaneously. The Si tips with a resonance frequency of approximately 120 kHz and a spring constant of about 20 N m^{-1} were used.

2.5. Differential scanning calorimetric (DSC) measurement

After crystallized completely at 260 °C, the shear-induced crystallized PPS samples were used to perform the heating scan in a nitrogen atmosphere by a Diamond DSC (Perkin–Elmer Corp., USA). The melting endotherm was recorded when the samples (ca. 4 mg) were heated to 340 °C at a rate of 10 °C/min.

3. Results and discussion

3.1. Crystalline morphology of PPS after shear

3.1.1. Crystalline morphology observed by POM

The spherulite superstructure of PPS can be observed clearly by the polarized optical microscope, as shown in Fig. 1. Under the

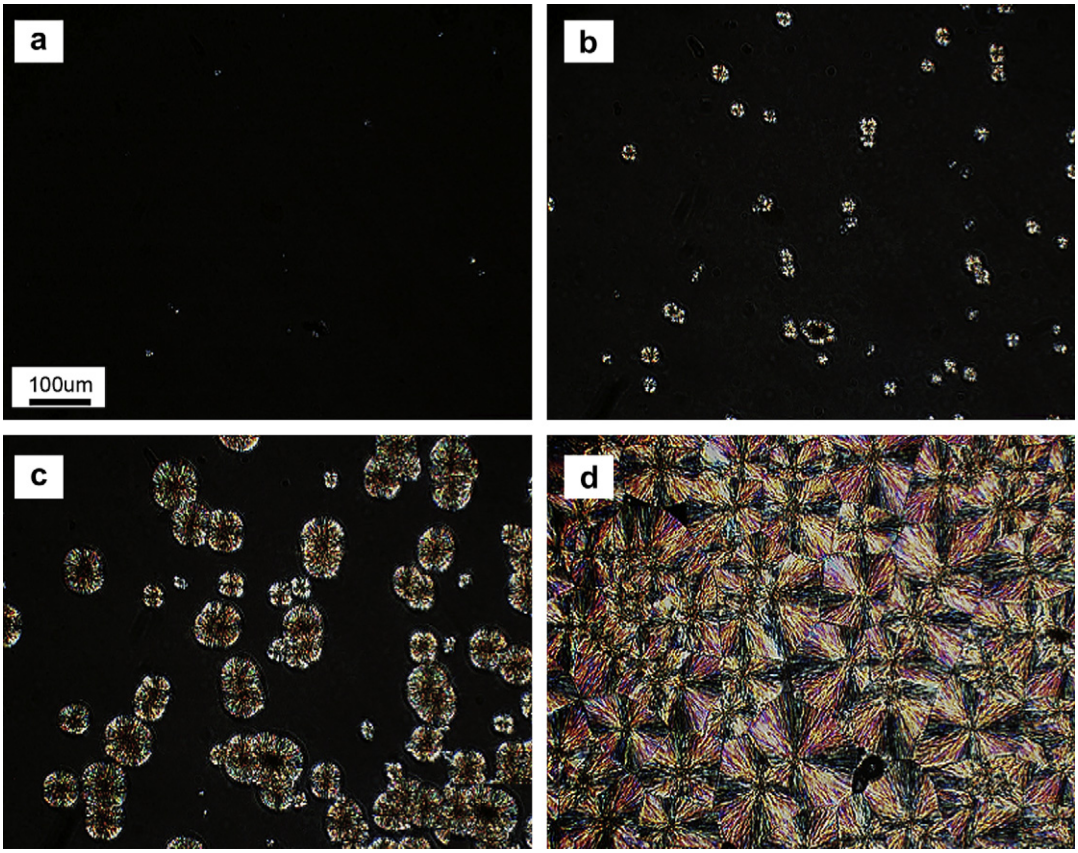

Fig. 1. Optical micrographs of PPS. PPS melted at 340 °C for 5 min, then quenched to 260 °C for isothermal crystallization: (a) 6, (b) 14, (c) 30, and (d) 86 min.

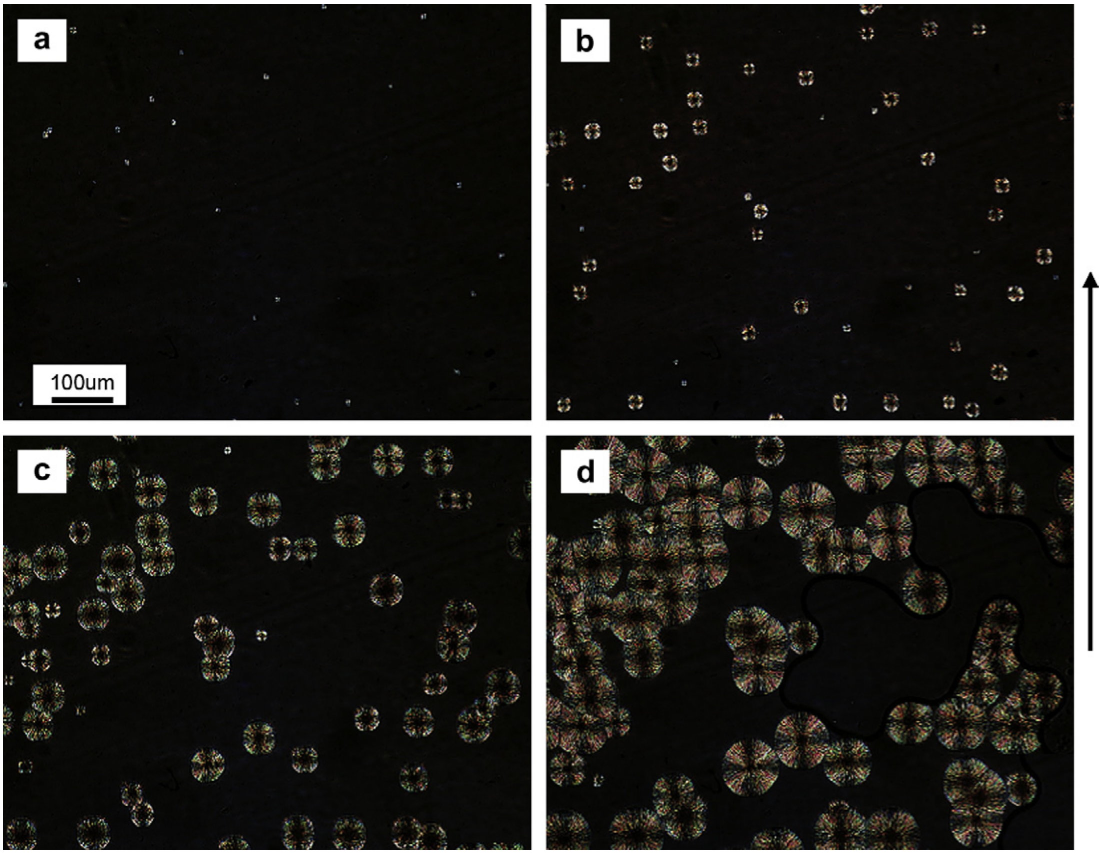

Fig. 2. Optical micrographs of PPS. PPS melted at 340 °C for 5 min, then quenched to 260 °C and then sheared for 30 s at the shear rate of 15 s^{-1}. After shear cessation, samples were isothermally crystallized at 260 °C for (a) 6, (b) 15, (c) 30, and (d) 48 min. The black arrow indicates the flow direction.

quiescent condition, the crystalline morphology of PPS isothermally crystallized from the melt is always spherulite. With increasing the crystallization time, the nuclei increase, indicating the occurrence of thermal nucleation during the isothermal crystallization. And at the late stage, the spherulites of PPS impinged into each other due to the space confine.

After being sheared for 30 s at a rate of 15, 30 and 45 s^{-1} at 260 °C, the crystalline morphology of PPS is presented in Figs. 2–4, respectively. As seen from Fig. 2, PPS is mainly spherulite after sheared at the rate of 15 s^{-1}, while from Figs. 3 and 4, the fiber-like textures are being clearly observed after sheared at the rate of 30 and 45 s^{-1}, which are actually shish-like core structures. This phenomenon shows that there exists a critical shear rate above which PPS can form the shish–kebab-like fibrillar crystals, while below which it cannot. In Fig. 3, one can see that the kebab-like structure begins to grow epitaxially around the shish-like core. As the time prolongs, the kebab-like lamellae impinge with each other due to the space confination. The most interesting phenomenon is that, as shown in Fig. 4, the shish–kebab-like fibrillar crystals are composed of numerous oriented spherulites aligning in the direction of shear flow. With the crystallization time increasing, these oriented spherulites grow and impinge with each other in the longitude.

Fig. 5 shows the typical crystalline morphology of PPS isothermally crystallized at 260 °C after sheared for 40 s at the shear rate of 15 s^{-1}. This image exhibits a long shish-like fibrillar structure in the core and the kebab-like lamellae around it. However, the long shish-like fibrillar structure is not a consecutive integer but divided into two parts (red arrow in Fig. 5). (For interpretation of the references to colour in this figure, the reader is referred to the web version of this article.) The deviation of shish-like structure directly leads to the formation of dislocation for the whole shish–kebab-like fibrillar crystal. This phenomenon shows that the core of shish–kebab-like fibrillar crystal is not consonant of the extended molecular chains. We suggest that it consists of numerous nuclei which align tightly in the direction of shear flow. This result can be verified by the observation of melting process of fibrillar crystals, just as shown in Fig. 6. With the temperature increasing, the fibrillar crystals (white box in Fig. 6a–c) melt slowly. When the temperature reaches its melting temperature, the fibrillar crystal core melts completely together with the spherulites in the bulk.

Moreover, one can find in Fig. 5 that the spherulites grown from the fibrillar core have no Maltese cross. This interesting phenomenon means that lamellar rotation within such spherulites is restricted. Namely, they are grown in 2-dimensional directions. This is quite different from the usual 3-dimentional growth of the usual Maltese-crossing spherulites.

3.1.2. *Fibrillar crystal morphology observed by AFM*

In order to study the shish-like fibrillar skeleton structure on a smaller size scale, the shear-induced crystallized PPS sample was observed by AFM. Figs. 7 and 8 represent the typical height and phase images of the shear-induced PPS sample crystallized at 260 °C for 80 min before quenching to the room temperature. It can be seen from the height images of Figs. 7a and 8a (Fig. 8 represents the white box part of Fig. 7) that there exhibit many impingement lines (red arrows in Fig. 8a) for the adjacent crystals in the fibrillar crystal, which show again that the fibrillar crystal consists of many uniform small crystals aligning in the direction of shear flow. (For interpretation of the references to colour in this figure, the reader is referred to the web version of this article.) Interestingly, we can find the long shish–kebab-like fibrillar crystal and in the center of the fibrillar crystal there exists a fibrillar crystal core. In addition, it can be seen from Fig. 8a that the height of shish-like fibrillar crystal core

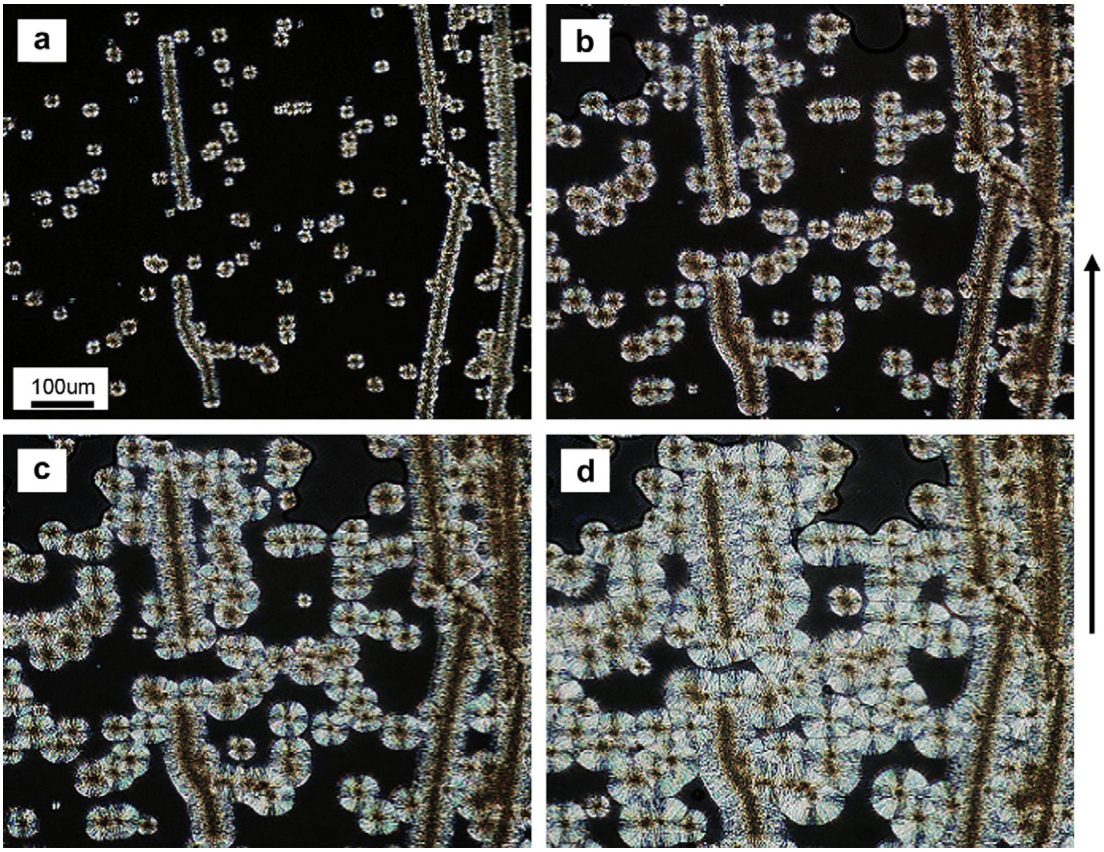

Fig. 3. Optical micrographs of PPS. PPS melted at 340 °C for 5 min, then quenched to 260 °C and sheared for 30 s at the shear rate of 30 s^{-1}. After shear cessation, samples were isothermally crystallized at 260 °C for (a) 13, (b) 23, (c) 30, and (d) 42 min. The black arrow indicates the flow direction.

is lower than that of the kebab-like lamellae around them, and this structure looks like a ditch which is caused by the growth process of spherulite. The same phenomenon can be obtained from the height image of PPS spherulite by AFM after cessation of shear, just as shown in Fig. 9. The height image of PPS spherulite structure indicates that there exists a concave in the center of spherulite. This phenomenon shows that the formation of fibrillar crystal channel (shish-like structure) is relevant to the presence of concave in the spherulite center. The 2-dimensional growth of numerous spherulites in the direction of shear flow leads to the formation of fibrillar crystal channel which looks like a shish-like structure under POM. This result shows again that the fibrillar crystal consists of many spherulites which align in the direction of shear flow. However, according to Li et al.'s results [56–58] observed by AFM, the height of the whole spherulite did not change greatly. This difference can be ascribed to the influence of shear flow. It is well known that shear flow can cause the molecular chain orientation. These oriented molecular chains will greatly affect the growth process of crystals, especially the growth of crystal nucleus. Thus, the concave in the center of spherulite is quite possibly caused by shear flow.

3.2. *Analysis of fibrillar-like crystal morphology*

In the case of shear-induced crystallization, many groups have paid much attention to the polyolefins [4–46]. About the shish–kebab structures, these groups hold the same ideas that the shish consists of (defective) extended-chain crystals and the kebab grows epitaxially around it. The total length of shish–kebab entity is on the order of μm (some were even 10 μm). Even for the cylindrite proposed by Han et al. [44], its length is not more than 200 μm. However, in Figs. 3 and 4 the length of fibrillar-like crystal can reach approximately 1 mm. The total length of the fibrillar-like crystal is so large that it is impossible for PPS with middle molecular weight ($M_w = 48{,}000$) to form the fibrillar-like crystal by stretched molecular chains. Thus, we believe that in our experiment the fibrillar-like structure is formed from the numerous nuclei which align tightly in the direction of shear flow; otherwise, the fibrillar-like structure observed in our experiment should have a similar length to or a little longer than Han's and others' observation. The phenomenon of spherulites' orientation has also been observed by Han et al. [43,44]. However, they suggested that the formation of aligned spherulites is caused by the presence of cylindrite structure.

It should be stressed here that the formation of fibrillar-like crystal is greatly dependent on the nuclei density in the direction of shear flow in the crystal growth process. In Fig. 4 the nuclei density in the shear direction is unsymmetrical, which leads to 3-dimensional growth of crystals for lower nuclei density (white box 1 in Fig. 4b), while 2-dimensional growth for the higher one due to the space limitation (white box 2 in Fig. 4b). We believe that the higher nuclei density in the shear direction is relevant with the higher stiffness of PPS molecular chains. After shear cessation, PPS molecular chains are easier to maintain their orientation due to its higher rigidity. In the direction of shear flow there exist numerous oriented chains. These oriented molecular chains form crystal nuclei that align tightly in the shear direction. The final result is the formation of fibrillar-like crystal.

The most intriguing is that the fibrillar crystal core observed under POM is actually a channel (Figs. 7a and 8a) which is formed from numerous spherulite concaves in the shear direction. The different heights between the fibrillar crystal core and its outer lamellae lead to the formation of different colorful parts under optical microscope (Figs. 4 and 5), which is attributed to the different light spaces when the light goes through the fibrillar crystal.

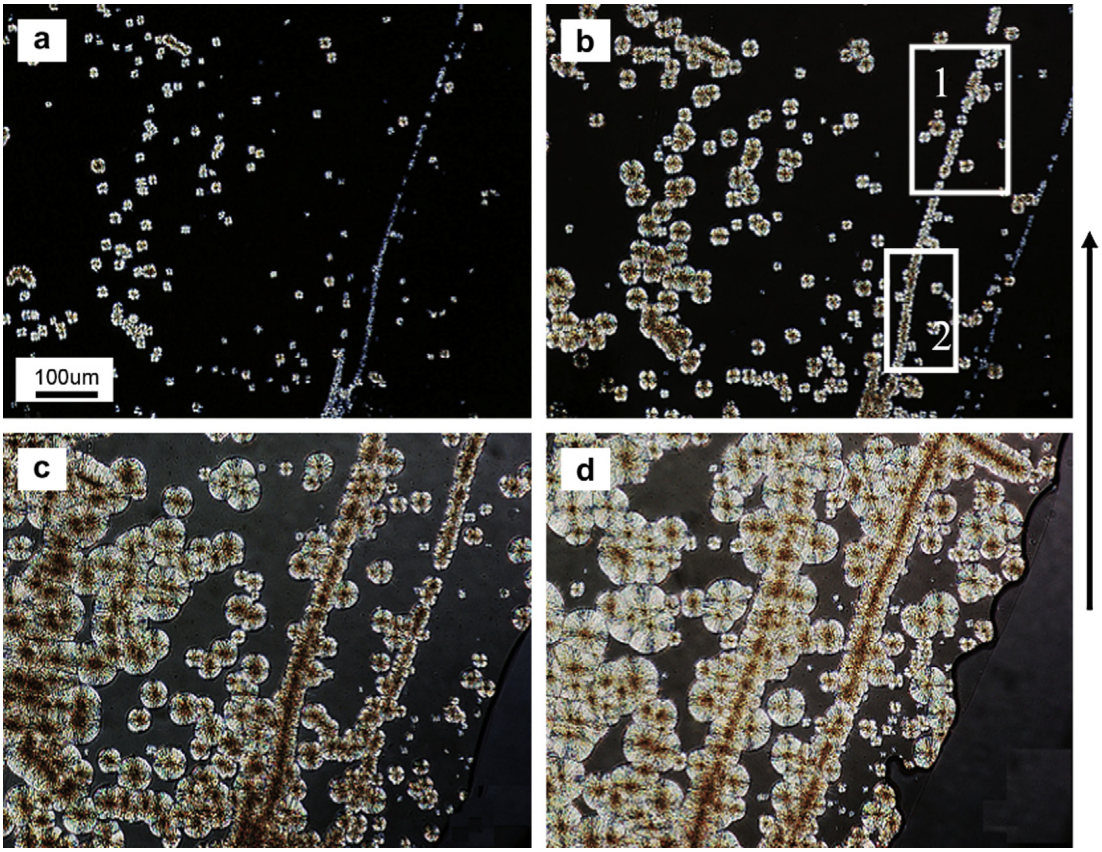

Fig. 4. Optical micrographs of PPS. PPS melted at 340 °C for 5 min, then quenched to 260 °C and sheared for 30 s at the shear rate of 45 s^{-1}. After shear cessation, samples were crystallized isothermally at 260 °C for (a) 18, (b) 29, (c) 55, and (d) 80 min. The black arrow indicates the flow direction.

Thus, we believe that this shish-like fibrillar crystal core is different from the conventional shish structure.

3.3. Crystallization induction time of PPS after shear

Fig. 10 represents the relationship of shear time with the crystallization induction time at the shear rate of 15, 30 and 45 s^{-1}. The crystallization induction time is defined as the time needed for the occurrence of first PPS crystal nucleus. It can be seen from Fig. 10 that the crystallization induction time of PPS decreases after the PPS melt is subjected to shear flow, again showing that the shear can accelerate the crystallization nucleation of PPS. In addition, the crystallization induction time of PPS decreases as the shear time increases, which shows that the longer the shear time is, the faster the crystallization nucleation rate of PPS is. It can also be found that the higher shear rate can cause the decrease of the crystallization induction time after sheared for the same time. For example, after being sheared for 20 s, the crystallization induction time of PPS is 3, 2.6 and 2 min, respectively, at the shear rate of 15, 30 and 45 s^{-1}. On the basis of these results, it appears that the shear plays an important role in the crystallization process. The longer the shear time is and the more the shear rate is, the less the crystallization induction time is. It is well known that the shear flow causes the molecular chains to stretch, and these stretched molecular chains are higher order than those unstretched ones. Also, prior to crystallization the stretched chains are aligned to form the bundles whose size is approaching to the critical size of nucleus, which need less time to form the stable nucleus. Thus the crystallization induction time decreases. This phenomenon is consistent with that investigated by Imai et al. [59–62], Takeuchi [63] and Cebe and Hong [64] who found that the orientation fluctuation of polymer segments occurs before the density fluctuation and concluded that this corresponds to parallel ordering of polymer chains prior to crystallization.

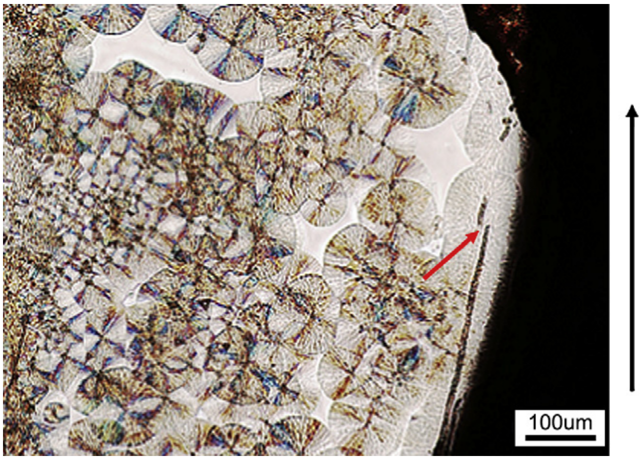

Fig. 5. Optical micrographs of PPS. PPS melted at 340 °C for 5 min, then quenched to 260 °C and sheared for 40 s at the shear rate of 15 s^{-1}. After shear cessation, samples were crystallized isothermally at 260 °C for 108 min. The black arrow indicates the flow direction.

3.4. Nucleation rate of PPS after shear

It is well known that the shear can greatly influence the crystallization kinetics of a polymer due to the high orientation of polymer molecular chains under shear flow. These shear-induced

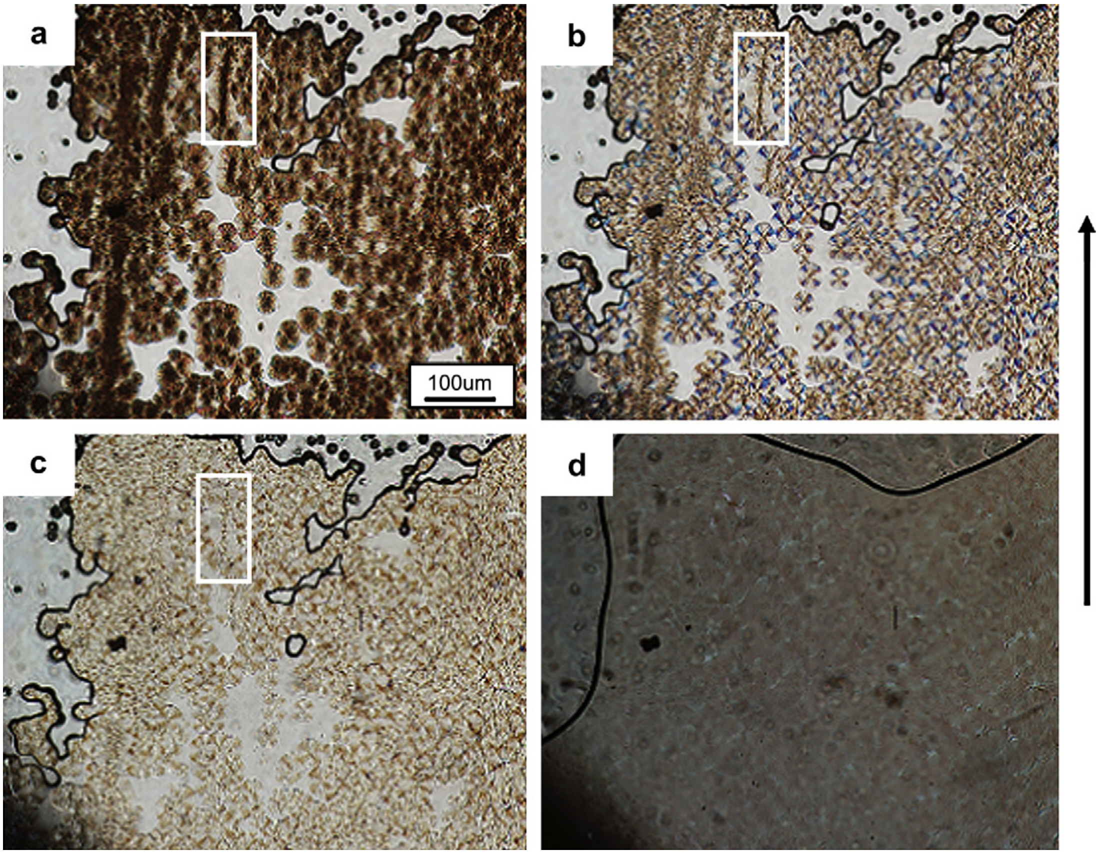

Fig. 6. Optical micrographs of PPS. PPS melted at 340 °C for 5 min, then quenched to 260 °C and sheared for 30 s at the shear rate of 45 s^{-1}. After shear cessation, samples were crystallized isothermally at 260 °C for 30 min. Then heated to 291 °C at a rate of 5 °C/min to observe its melting process. (a) 260, (b) 287, (c) 289, and (d) 291 °C. The black arrow indicates the flow direction.

oriented molecular chains markedly change the nucleation rate and the crystal growth rate of the polymer.

The nucleation rate, characterized by the density of crystal nuclei, of PPS increases after the PPS melt is subjected to shear flow (Figs. 1a and 2a). It appears that the shear can induce crystallization nucleation of PPS. And the decrease of crystallization induction time and spherulite growth rate of PPS also indicates that the shear flow can play an important role in the crystallization kinetics of PPS. These phenomena can be ascribed to the high orientation of molecular chains caused by shear which decreases the free energy of crystal nucleation. On the basis of theory of crystallization nucleation, the nucleation rate is determined by the formation of a crystal nucleus of the critical size. At the constant temperature and pressure, the more the order of molecular chains is, the easier the formation of stable nuclei is. As is well known, the shear can cause the molecular chain to orient, which decreases the entropy of system. These oriented molecular chains have more order than those unoriented ones. Thus, less time is needed to form the stable

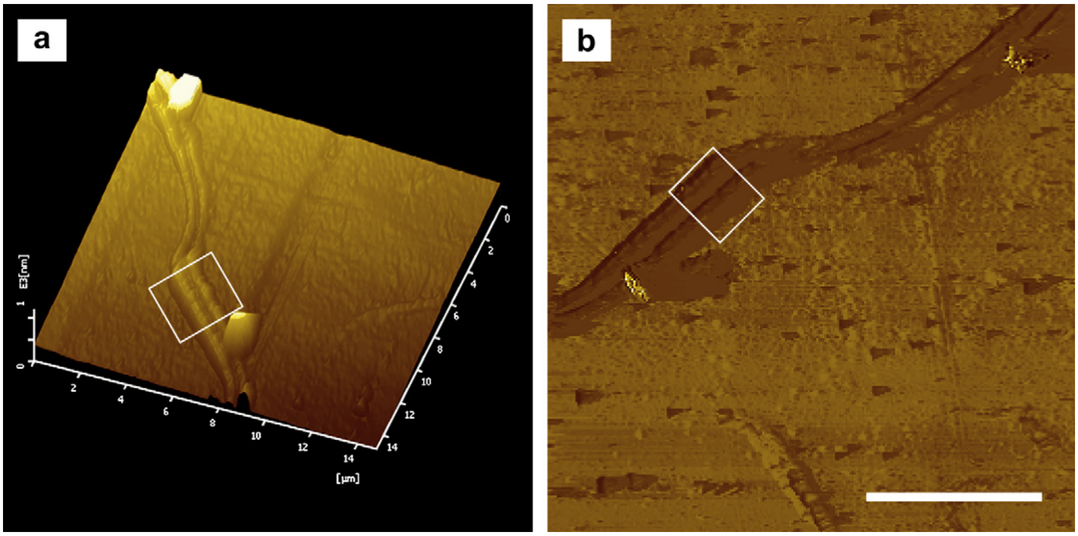

Fig. 7. (a) Height and (b) phase images of shear-induced crystallized PPS sample by AFM. The scale bar represents 5 μm.

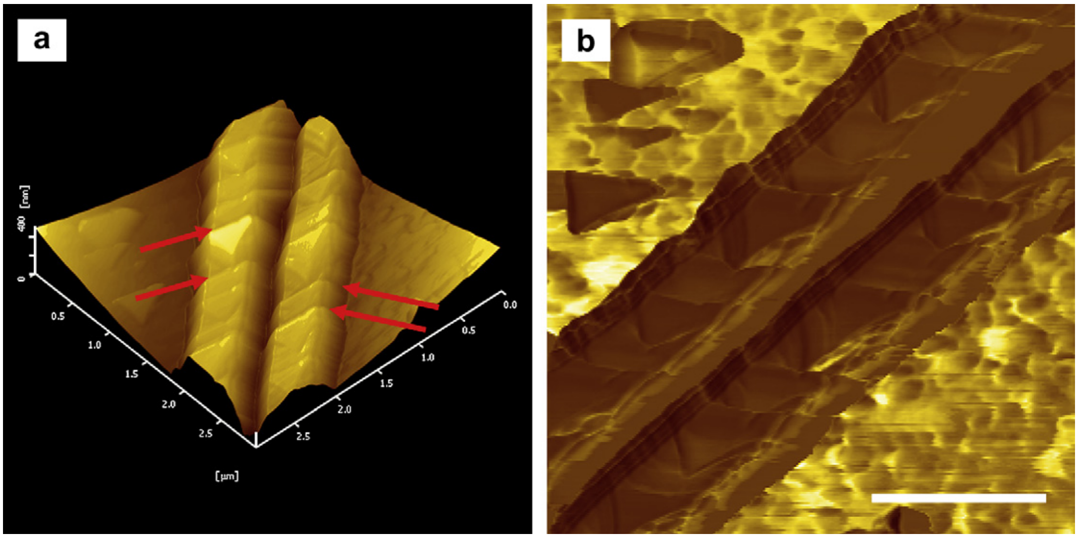

Fig. 8. (a) Height and (b) phase images of shear-induced crystallized PPS sample by AFM. The scale bar represents 1 μm.

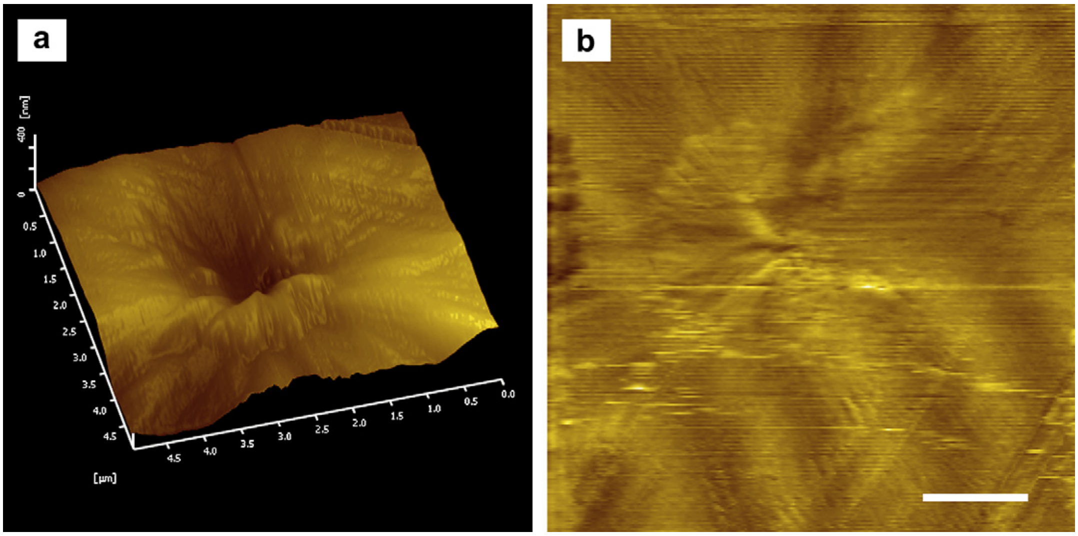

Fig. 9. (a) Height and (b) phase images of the shear-induced crystallized PPS spherulite observed by AFM. The scale bar represents 1 μm.

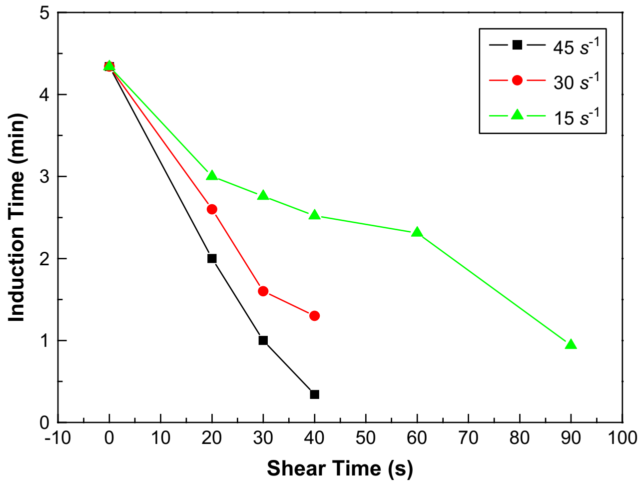

Fig. 10. The relationship of crystallization induction time with shear time at the shear rate of 15, 30 and 45 s^{-1} (crystallized isothermally at 260 °C).

nuclei for oriented chains, which leads to the increase of the density of crystal nuclei and decrease of crystallization induction time.

3.5. *Spherulite growth rate of PPS after shear*

The dependence of spherulite growth rate of PPS on the shear time at the shear rate of 15, 30 and 45 s^{-1} is represented in Fig. 11. As it can be seen, the spherulite growth rate of PPS increases after the PPS melt is subjected to shear flow. For the shear rates of 15 and 30 s^{-1}, the spherulite growth rate increases with the shear time and shear rate. The higher the shear rate is and the longer the shear time is, the higher the spherulite growth rate is. Nevertheless, after the PPS melt is subjected to shear flow at the shear rate of 45 s^{-1} for 20 s, it appears that the spherulite growth rate has a trend to reach maximum, then with the shear time increasing the growth rate decreases. The results are not consonant with that obtained by Huo et al. [65] and Avila-Ortaa et al. [66]. These investigators suggested that the spherulite growth rate had been little influenced by shear flow.

Generally speaking, the crystal growth is a process that the molecular chains transport from the melt to the surface of crystal,

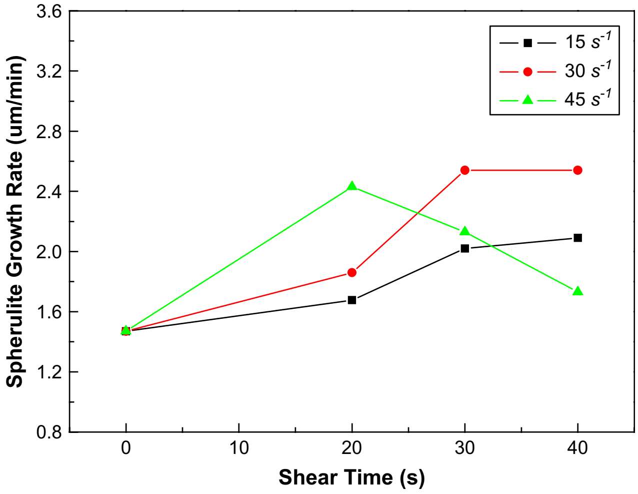

Fig. 11. The relationship of spherulite growth rate for PPS crystallized isothermally at 260 °C with shear time at the shear rate of 15, 30 and 45 s^{-1}.

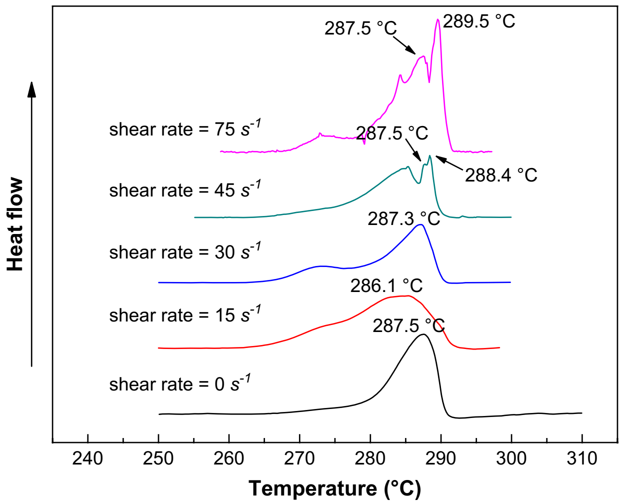

Fig. 12. The DSC heating scan curves of PPS under the quiescent and shear conditions (shear time = 30 s).

and the spherulite growth rate is greatly depended on the velocity of chains' transportation which is determined by the configuration of molecular chains in the melt. PPS molecular chains are always stretched and oriented after being subjected to shear flow. These stretched molecular chains have higher order and form appropriate configuration which accelerates the chains to enter the growth front of crystal. That is, the shear-induced oriented chains need less time to go from the melt to the growth front of crystal compared to those unoriented ones. Thus, spherulite growth rate increases.

Also, the fibrillar crystal growth rate and spherulite growth rate of PPS crystallized at 260 °C after sheared at 45 s^{-1} for different times are shown in Table 1. As can be seen, the growth rate for fibrillar crystal is similar with that for the spherulite, which indicates that the growth process for lamellae in fibrillar crystal is the same as that in spherulites except for different growth dimensions.

3.6. *Melting behavior of fibrillar crystals*

The melting behavior of PPS crystallized isothermally under quiescent condition has been thoroughly investigated by Chung and Cebe [67–69] and Cheng et al. [70]. These researchers found that PPS usually displays multiple melting peaks and attributed it to the degree of crystal perfection and the degree of supercooling. As far as the melting behavior of PPS subjected to shear flow, few reports are available.

The DSC curves of PPS crystallized completely at 260 °C after being sheared at different shear rates are presented in Fig. 12. It can be seen that the endotherm peak of PPS crystallized under quiescent condition is monomodal. However, this result is different from that obtained by Chung and Cebe [67–69]. They investigated the cause of double melting behavior of melt-crystallized PPS over a wide range of undercoolings and found that the double melting peaks' behavior is relevant with the degree of crystal perfection. The difference suggested that the PPS crystal perfection is higher than that obtained by Chung and Cebe, which causes the presence of monomodel melting peak. In contrast, there occur double melting peaks for the shear-induced crystallized PPS at the shear rate of 15 and 30 s^{-1}. In particular, three higher melting peaks are obtained when the shear rate is over 45 s^{-1}, that is, a lower melting peak, a medium melting peak and a higher main melting peak. The lower melting peak corresponds to the melting of imperfect crystals which arise from the faster deposited ratio of molecular chain in the growth front of crystal caused by shear. Here we consider that it is not caused by the secondary crystallization since only one melting peak appears in the melting curve of PPS crystallized under quiescent condition. In addition, one can see that the lower melting peak intensity increases as the shear rate increases, indicating that the increase of shear rate greatly deteriorates the crystal perfection of PPS. The medium melting peak temperature remains constant and is similar to that of PPS crystallized under quiescent condition. However, it is worthy of noting that the higher main melting peak temperature of the shear-induced crystallized PPS samples at the shear rate of 45 and 75 s^{-1} is higher than that of PPS crystallized under quiescent condition. It can be ascribed to the occurrence of shear-induced shish–kebab-like fibrillar crystal structure. Moreover, the higher main melting peak intensity increases with the shear rate, which shows that higher shear rate causes more molecular chains' orientation and increases the amount of shish–kebab-like fibrillar crystal. This phenomenon was also observed by Gahleitner et al. [71] and Hsiao et al. [46] in other semicrystalline polymers like PE when subjected to shear flow. They proposed that the shear-induced shish–kebab precursor consisted of macrokebabs and microkebabs, and the outer macrokebabs melt first and then the inner microkebabs when the temperature was increased. However, from the AFM and POM results, we suggest that the higher melting peak is related to the orientation of molecular chains. Generally, the longer molecular chains form higher order bundles which nucleate prior to the shorter ones after shear cessation. Numerous order bundles align tightly in the direction of shear flow to form the fibrillar crystal core. These fibrillar crystal cores have higher thermal stability than the kebab-like lamellae that developed later.

Table 1
The growth rate of spherulite and fibrillar crystal for PPS crystallized at 260 °C after sheared at 45 s^{-1}

Shear time (s)	Spherulites' growth rate ($\mu m\ s^{-1}$)	Fibrillar crystals' growth rate ($\mu m\ s^{-1}$)
20	0.0405	0.041
30	0.0355	0.0361
40	0.027	0.025

3.7. *Mechanism of shish–kebab-like fibrillar crystal formation*

The polymer crystal growth process after being sheared has been extensively reported by many groups [1,34,38–44,72–76]. Keller and Kolnaar [1] first proposed the idea of elongational flow-induced crystallization in solution. Somani et al. [34] extended this idea to shear flow in the melt and suggested that only molecules

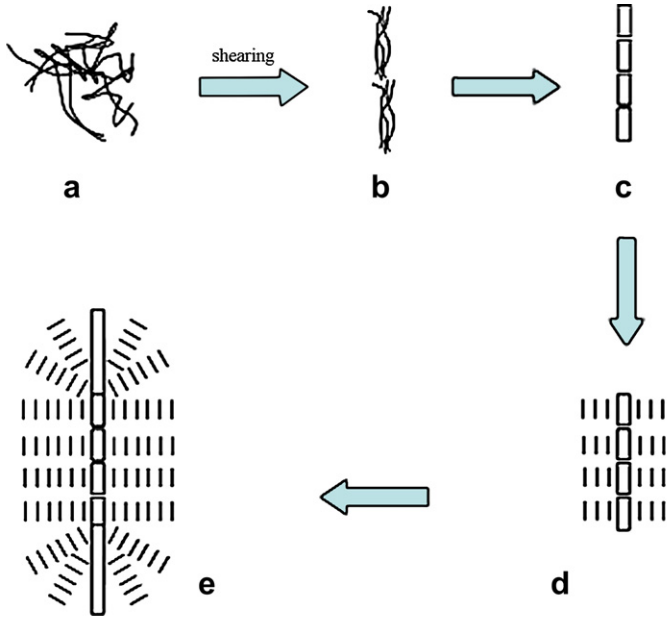

Fig. 13. Schematic picture of shear-induced crystallization in PPS: (a) amorphous molecular chains in melt, (b) shear-induced molecular chain orientation, (c) formation of oriented crystal nuclei, and (d and e) 2-dimensional growth of crystal.

with a chain length above a critical value M^* were supposed to be oriented at a given shear rate and the oriented molecules served as the precursor or primary nuclei. Although these models interpret different mechanisms of crystal growth after shear, they have the same pictures assuming that the shish consists of (defective) extended-chain crystals. Particularly, Han et al. [44] proposed a definitely different idea about the mechanism of shish–kebab-like cylindrite formation at low temperature and low shear rate. They suggested that the cylindrite core comes from the stretched bundles of the entangled network strands but not from the extended crystals of stretched single chains. Although these models can clearly expound the formation of shear-induced oriented structure for polyolefins, no models can successfully illuminate the mechanism of oriented crystal formation for the rigid or half-rigid molecular chain engineering polymers, e.g., PPS. It is because the PPS chains are hard to relax after shear cessation.

According to the above results, the fibrillar crystal core comes from the numerous stable nuclei that align tightly in the direction of shear. Hence, we proposed a new model about the mechanism of shear-induced crystallization of PPS. In Fig. 13, a schematic is given to describe this process. Initially, the molecular chains of PPS are presented as random coils in the melt (Fig. 13a). After application of steady shear the chains are somewhat stretched (Fig. 13b). These stretched chains aggregate each other to form bundle structure which promotes the formation of stable nuclei, and these stable nuclei align tightly in the direction of shear to form the fibrillar-like skeleton structure, which means the formation of oriented crystal nuclei (Fig. 13c). Subsequently, these aligned nuclei grow by absorbing the neighboring molecular chains. Because not enough melt and space support the nuclei to continuously grow toward the longitude, the nuclei grow perpendicular to the direction of shear flow, which leads to the 2-dimensional growth of PPS crystal (Fig. 13d and e). The final result is the shish–kebab-like fibrillar crystal structure: the oriented nuclei aggregate tightly and form the shish-like fibrillar crystal skeleton, while the lamellae grow epitaxially around it. Throughout this article, we have used the "shish–kebab-like fibrillar crystal", "shish-like fibrillar" and "fibriallar crystal", just because we could not consider a better way to describe the structures developed in our experiments and make a comparison with other studies. We suggest that the fibrillar crystal structure occurring in the rigid or half-rigid chain polymers is definitely different from the ones in polyolefins.

4. Conclusions

The isothermal crystalline morphology of PPS under shear condition has been investigated by POM equipped with a shearing hot-stage. The shear has an important influence on the crystalline morphology, crystallization induction time and spherulite growth of PPS. The shish–kebab-like fibrillar crystals were observed after the PPS melt was subjected to shear flow at higher rates or for longer duration. The induction time reduces as the shear time and/or the shear rate increases. In addition, the melting behavior of PPS shows that the degree of crystal imperfection increases with the shear rate. And the higher melting peak is related to the orientation of molecular chains. These oriented molecular chains form the initial lamellae which are thicker than the kebab-like lamellae developed later due to the chain relaxation. The results of optical microscopic and AFM observation indicate that the shish-like fibrillar crystals are consisted of numerous stable nuclei in the direction of shear flow.

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