

Effect of Molecular Weight on Crystallization of Semirigid Poly(phenylene sulfide) Under Shear Flow

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ABSTRACT: Isothermal crystallization of poly(phenylene sulfide) with three molecular weights ($M_w = 22k, 48k, \text{ and } 52k$, respectively) under shear condition has been investigated. It appears that shear can induce all these three PPS samples to form a thread-like crystal structure which consists of the numerous stable nuclei that align tightly in the direction of shear. Crystallization kinetics of PPS has been greatly influenced by shear flow. Higher shear rate and long shear time can lead to decrease of spherulite growth rate of PPS. Also, the spherulite growth rate of PPS is affected by supercoolings and molecular weight. For the lower molecular weight ($M_w = 22k$), the spherulite growth rate is independent on the shear rate and shear time; while

for the higher ones ($M_w = 48k \text{ and } 52k$), with the increasing of shear rate, the spherulite growth rate of PPS increases to reach maximum at first, and then decreases. The lower the crystallization temperature is, the more the spherulite growth rate changes, showing that higher orientation of molecular chains can be obtained more easily with increased supercooling. A model has been proposed to explain the mechanism of thread-like crystal formation under shear flow. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 1562–1569, 2012

Key words: thread-like crystal; molecular weight; spherulite growth rate; chains

INTRODUCTION

Shear-induced polymer crystallization is one of the most interesting subjects of the past four decades since shear flow can cause molecular chain orientation which results in a change of crystalline structure and morphology, thus changing the properties of final product.^{1,2} Generally speaking, most polymers are subjected to shear flow during processing operations prior to crystallization. Hence, it is of great importance to study the effect of shear flow on the crystallization of polymers. Previous studies^{3–14} have shown that shear flow can change the crystalline morphology of spherulites producing oriented crystallites in the shear flow direction and enhancing the crystallization kinetics of polymers. However, most studies^{15–20} were mainly focused on the crystalline

nucleation density and kinetics of polymers under shear. As for the effect of shear on the spherulite growth rate of polymers, only Huo et al.¹⁸ and Avila-Ortaa et al.¹⁹ were actively involved in it and suggested that spherulite growth rate is little influenced by the shear. Nevertheless, our previous work²⁰ shows that spherulite growth rate of PPS increases when lower shear rate is applied. Generally, the macromolecular chains will stretch under shear flow. It will take more time for the stretched chains to relax and add to the crystal growth front. Thus, the spherulite growth rate depends on the orientation degree of the polymer chains. Our question is: what happens for the spherulite growth rate of PPS if the shear time is longer and/or shear rate is higher; will the spherulite growth rate and crystalline morphology of PPS be affected by its molecular weight when subjected to shear flow?

In this article, we will briefly introduce the isothermal crystallization of PPS with three different molecular weights under shear flow. On the basis of previous studies,^{1,7,21–24} the shear-induced oriented structure of polymers is greatly influenced by its molecular weight. During the crystallization of the polymer under shear, the stretch of polymer chains, ε_0 , is proportional to its critical molecular weight, M^* , only those polymer chains with molecular weight greater than M^* could stretch and retain

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orientation. The longer polymer chains greatly enhance the formation of stretch structures. Nevertheless, little attention has been paid to the crystal growth rate of polymers under shear, especially to crystallization of the rigid PPS. In this work, the spherulite growth rate and the crystal morphology of PPS with three molecular weights under shear condition have been reported by use of a polarized optical microscope (POM) equipped with a CSS450 hot-stage, differential scanning calorimeter (DSC), and atomic force microscope (AFM).

EXPERIMENTAL

Materials and sample preparation

Three PPS resin powders with different molecular weights obtained from Deyang Science and Technology Limited Corp. (China) were employed in the present experiments. The molecular weight of PPSHC is $M_w = 52\text{k}$, $M_n = 26\text{k}$; $M_w = 48\text{k}$, $M_n = 21\text{k}$ for PPSHB, and $M_w = 22\text{k}$, $M_n = 11\text{k}$ for PPSHA. The thin film of PPS sample was molded between two glass slips by heating the PPS resin to melting point.

Shear apparatus

A CSS 450 high-temperature shear hot stage (Linkam Scientific Instruments Ltd., UK) was used to control the shear rate and thermal history of the PPS sample. The gap width between two glass slips was set to 30 μm .

Morphology observation and spherulite growth rate determination

The morphology of PPS was observed by POM which is equipped with 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 PPS film 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 250, 255, 260, and 265°C respectively, 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} respectively; and (5) hold the sample at crystallization temperature until the crystallization was completed. The images of PPS crystal growth were taken at given times during this period. The radius of PPS spherulite at different crystallization temperature was also determined as a function of the crystallization time.

Atomic force microscope measurement

The shear-induced PPS sample crystallized completely at 250, 255, 260, and 265°C, respectively, was quenched to room temperature for AFM measurement. The measurement was performed in a tapping model with a SPA300HV AFM (Seiko, Japan), and both the height and phase images were recorded simultaneously. Si tips with a resonance frequency of approximately 120 kHz and a spring constant of about 20 N m^{-1} were used.

Differential scanning calorimeter measurement

After complete crystallization 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., Massachusetts). The melting endotherm was recorded when the samples (~ 4 mg) were heated to 340°C at a rate of 10 °C/min.

RESULTS AND DISCUSSION

Spherulite growth rate of PPS after shear

The spherulite growth rate of PPSHB under quiescence has been studied extensively. However, no report has been found about the effect of shear on its spherulite growth rate. Generally, shear flow can induce the orientation of the molecular chains which changes the packing time of chains from the amorphous state to the ordered state, thus changing its crystallization rate, as shown in Figure 1. From Figure 1, we can see that the spherulite growth rate of PPS is markedly influenced by shear rate and/or shear time. At a certain shear rate, (for example, shear rate = 45 s^{-1}) the spherulite growth rate

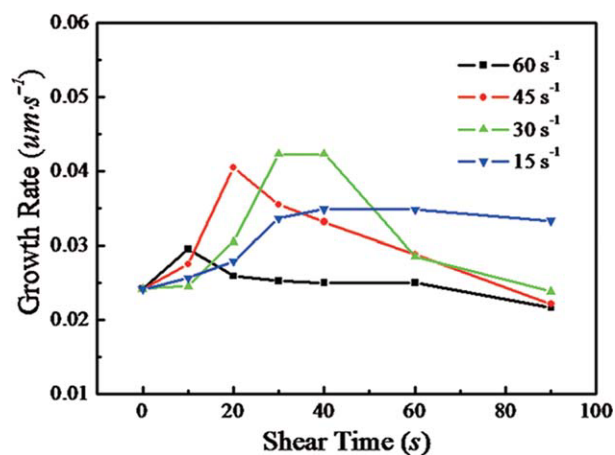


Figure 1 Dependence of spherulite growth rate of PPSHB crystallized at 260°C on the shear time rate at different shear rate. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

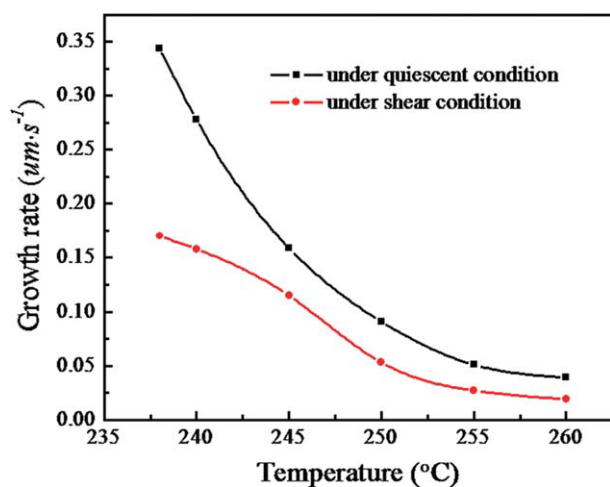


Figure 2 Dependence of growth rate of PPSHB on crystallization temperature under quiescent and shear condition respectively, (shear rate = 60 s^{-1} , shear time = 150 s). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

increases with shear time and then reaches a maximum, as the shear time increases further, the spherulite growth rate decreases. Additionally, the same change trend has been observed with the dependence of maximum spherulite growth rate on shear rate during the range of shear time. Moreover, it appears that the shear time needed for reaching the maximum spherulite growth rate is greatly dependent on the shear rate. That is, the higher the shear rate is, the lower the shear time is needed to reach the maximum spherulite growth rate.

More interesting is that the spherulite growth rate of PPS after being subjected to shear flow at a higher shear rate for 90 s is almost less than that without shear flow. To understand the effect of higher shear rate and/or longer shear time on the spherulite growth rate of PPS, we recorded the spherulite growth rate for PPS crystallized at different crystallization temperatures after being subjected to shear flow at a shear rate of 60 s^{-1} for 150 s, just as seen in Figure 2. It seems that the spherulite growth rate of PPS markedly decreases after being subjected to shear flow. The higher the crystallization temperature, the more the spherulite growth rate decreases. For example, the spherulite growth rate of PPS crystallized at 238°C under quiescent conditions is almost twice more than that after being subjected to shear flow. This is because that at higher supercooling the stretch molecular chains induced by shear flow need more time to adjust their configuration to add to the crystal growth front, thus decreasing the growth rate.

Generally speaking, crystal growth is a process that the molecular chains transport from the melt to the crystal growth front, and the spherulite growth rate is greatly dependent on the velocity of chain

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. On the basis of our results, it appears that spherulite growth rate increases under certain shear conditions, indicating that shear flow can induce the molecular chains to form an appropriate configuration state which accelerate the chains entering the growth front of the 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. Nevertheless, the spherulite growth rate decreases after higher shear rate and/or a long shear time is applied, which means that a higher shear rate can induce the PPS molecular chains to be highly stretched. As is well known, PPS contains many rigid molecular chains. It is hard for these rigid chains to relax once stretched. Hence, these highly stretched molecular chains need more time to relax to form an appropriate configuration for joining the crystal growth front. Thus the spherulite growth rate decreases.

Effect of M_w on spherulite growth rate of PPS after shear

Figure 3 represents the spherulite growth rate of PPSHA, PPSHB, and PPSHC, respectively, isothermally crystallized at different temperatures after shear at different shear rates for 30 s. It can be seen from Figure 3 that the influence of shear rate on spherulite growth rate of PPS is greatly dependent on its molecular weight. For the lower molecular weight, PPSHA [Fig. 3(a)], although the spherulite growth rate increases with supercooling, it is little affected by shear rate at the same crystallization temperature. However, from Figure 3(b,c) it can be found that spherulite growth rate of PPS with a higher molecular weight is not only influenced by shear rate, but also by supercooling. The higher the supercooling, the greater the effect of shear rate on spherulite growth rate. For example, the spherulite growth rate is almost the same in the research range of shear rate at lower supercooling (265°C), while at higher supercooling the spherulite growth rate increases to reach a maximum, first with shear rate, then it decreases as the shear rate increases further. This result can be attributed to the stretching process of rigid chains of PPS with different molecular weights under shear flow.

According to the Keller's "stretching-coil" theory, we suggest that the short molecular chain sample, PPSHA, is unable to form the stretch chains induced by shear flow, or shear can induce PPSHA chains to become stretched, but they relax fast due to thermal fluctuation. Hence, the spherulite growth rate of

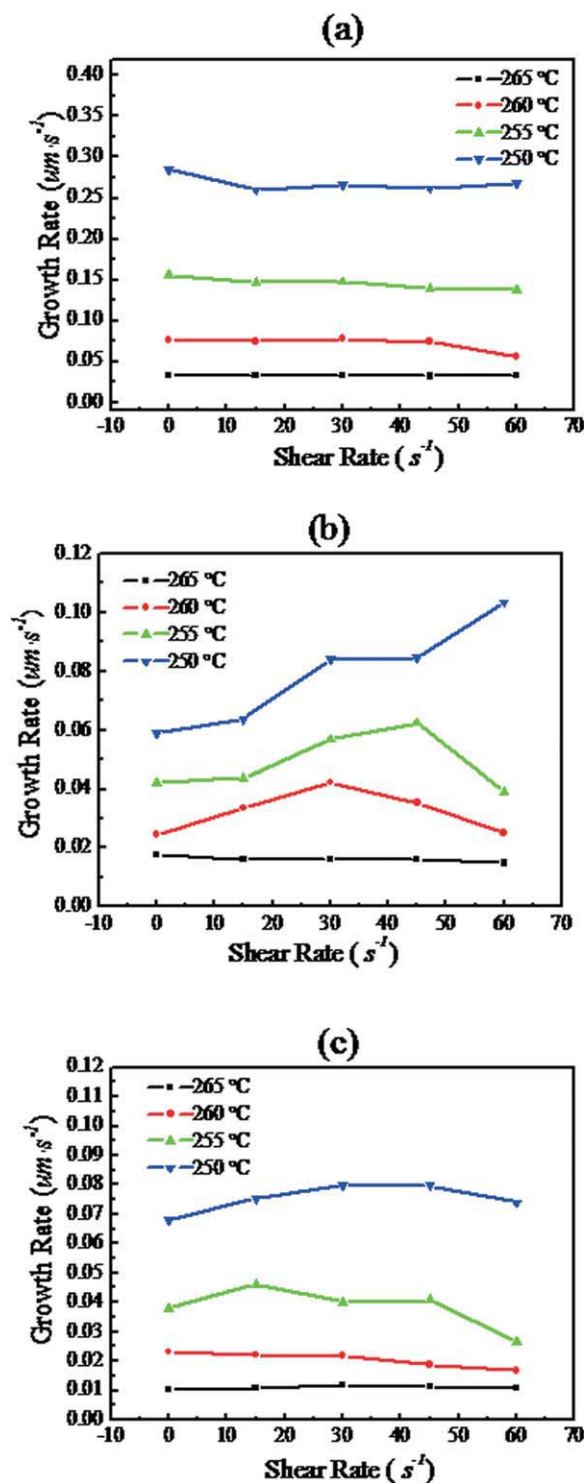


Figure 3 Dependence of spherulite growth rate of (a): PPSHA; (b): PPSHB; and (c): PPSHC on the shear rate at different crystallization temperature (shear time = 30 s). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

PPSHA is little influenced by shear flow. Nevertheless, for the long molecular chains, PPSHB and PPSHC, shear can induce molecular chain stretching depending on shear strength. Compared to those

without shear, molecular chains subjected to a lower strength of shear have more order and form an appropriate configuration which accelerates the growth of crystal, resulting in an increased spherulite growth rate. Whereas, at higher shear strengths, the molecular chains are highly stretched; these highly stretched chains need a longer time to relax and form an appropriate configuration to add to the growth front due to its high rigidity, this leads to a decrease in spherulite growth rate.

Morphology of PPS with different M_w after shear

After being sheared for 20 s at a rate of 45 s^{-1} , the crystalline morphologies of PPSHB isothermally crystallized at 260°C are presented in Figure 4. Besides the spherulite, several thread-like crystalline textures can be clearly observed under POM, which are actually shish-like core structures. With crystallization time being prolonged, the thread-like crystalline structure began to grow perpendicular to the shear flow until they impinged on each other or the spherulite around them. Interestingly, one can find from Figure 4 that the thread-like crystalline structure is composed of numerous spherulite nuclei aligning tightly in the direction of shear flow [see the red arrows in Fig. 4(a)]. With longer crystallization time, these aligned spherulite nuclei grow and impinge with each other in longitude due to a limitation of space, which results in a 2-dimensional growth of thread-like structures perpendicular to the direction of shear.

Figure 5 shows the typical crystalline morphology of PPSHA, PPSHB, and PPSHC, respectively, isothermally crystallized at 260°C after being sheared for 30 s at the shear rate of 45 s^{-1} . It appears from Figure 5 that all three samples can form thread-like textures under shear condition. For the short molecular chain PPSHA, it can be clearly observed that the thread-like crystal is formed by the spherulite nuclei being aligned tightly in the direction of shear due to the lower nucleation density. On the basis of the results regarding the spherulite growth rate of PPSHA under shear, it shows that unlike the shish-kebab structure, the thread-like crystal structure does not consist of stretched molecular chains. To observe the thread-like structures on a smaller scale, we used AFM to study the thread-like structure. Figure 6 represents the typical height and phase images of the shear-induced PPS sample crystallized completely at 260°C before being quenched to room temperature. It can be seen from the height image of Figure 6(a) that they exhibit many impingement lines from the adjacent crystals in the thread-like crystal, which again shows that the thread-like crystal consists of many small crystals aligned tightly along the direction of shear.

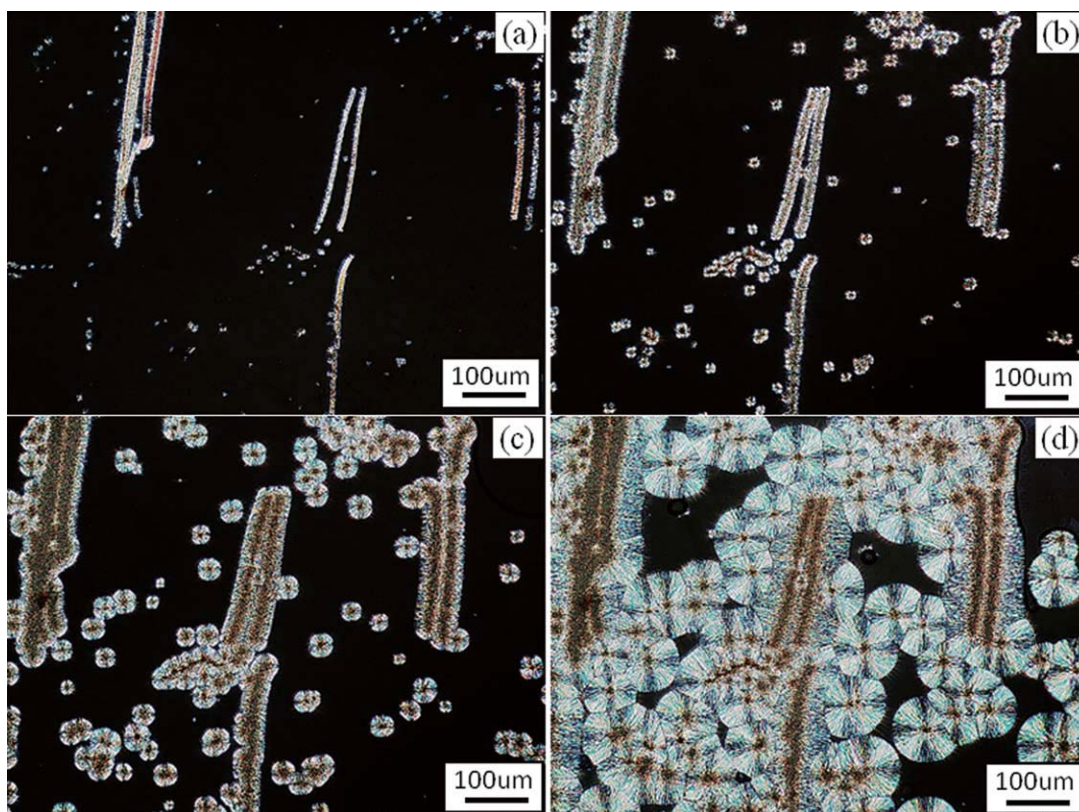


Figure 4 The polarized optical micrographs of PPSHB crystallized isothermally at 260°C after sheared at a rate of 45 s⁻¹ for 20 s. (a) 300 s; (b) 600 s; (c) 1200 s; (d) 3000 s. The black arrow represents the direction of shear. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Thermal melting behavior of PPS after shear

The DSC melting curves of PPSHA, PPSHB, and PPSHC, respectively, crystallized completely at 260°C after being sheared at different shear rates for 30 s are shown in Figure 7. It can be seen that the endotherm peaks of these three PPS samples crystallized under quiescent conditions are monomodal. For the lower molecular weight, PPSHA, its melting peak temperature is about 3°C lower than that of PPSHB and PPSHC. This can be ascribed to the fast nucleation and transportation ability of short molecular chains in the supercooling melt results in the formation of thinner lamellae. Generally, shear-induced orientated structures have higher melting temperatures. The same results can be obtained for the shear-induced crystallization of PPS. One can find that all of these three PPS samples have two melting peak temperatures after being subjected to shear at the rate of 45 s⁻¹. It appears that higher melting peak intensity is dependent on the molecular weight of PPS. Obviously the higher melting peak intensity of PPSHA is weaker than that of PPSHB, indicating the formation of less content of thread-like crystal structures in the PPSHA sample. Moreover, the higher melting peak intensity increases as the shear rate increases [Fig. 7(b)],

which shows that higher shear rate causes more molecular chain orientation and increases the amount of thread-like crystal. This phenomenon was also observed by Gahleitner et al.²⁵ and Wang et al.²⁶ in other semicrystalline polymers like PE when subjected to shear flow. Based on our results, we suggest that the higher melting peak is correlated with the formation of thread-like structures.

Mechanism of thread-like crystal formation

A great effort^{1,7,21-29} has been made to study the role of higher molecular weight or longer molecular chains in the shear induced crystallization of polymers, and has suggested that the longer molecular chains can greatly accelerate the formation of shish-kebab structures under shear. More recently, Kimata et al.,³⁰ Housmans et al.³¹ and Zhao and co-workers^{32,33} suggested that the shish structure consists of both long- and short molecular chains. According to our results, we suggest that the thread-like crystal comes from the numerous stable nuclei that align tightly in the direction of shear. A model about the mechanism of thread-like crystal formation has been proposed, just as shown in Figure 8. Initially, the molecular chains of PPS are presented as random coils in the melt [Fig. 8(a)]. After shear flow

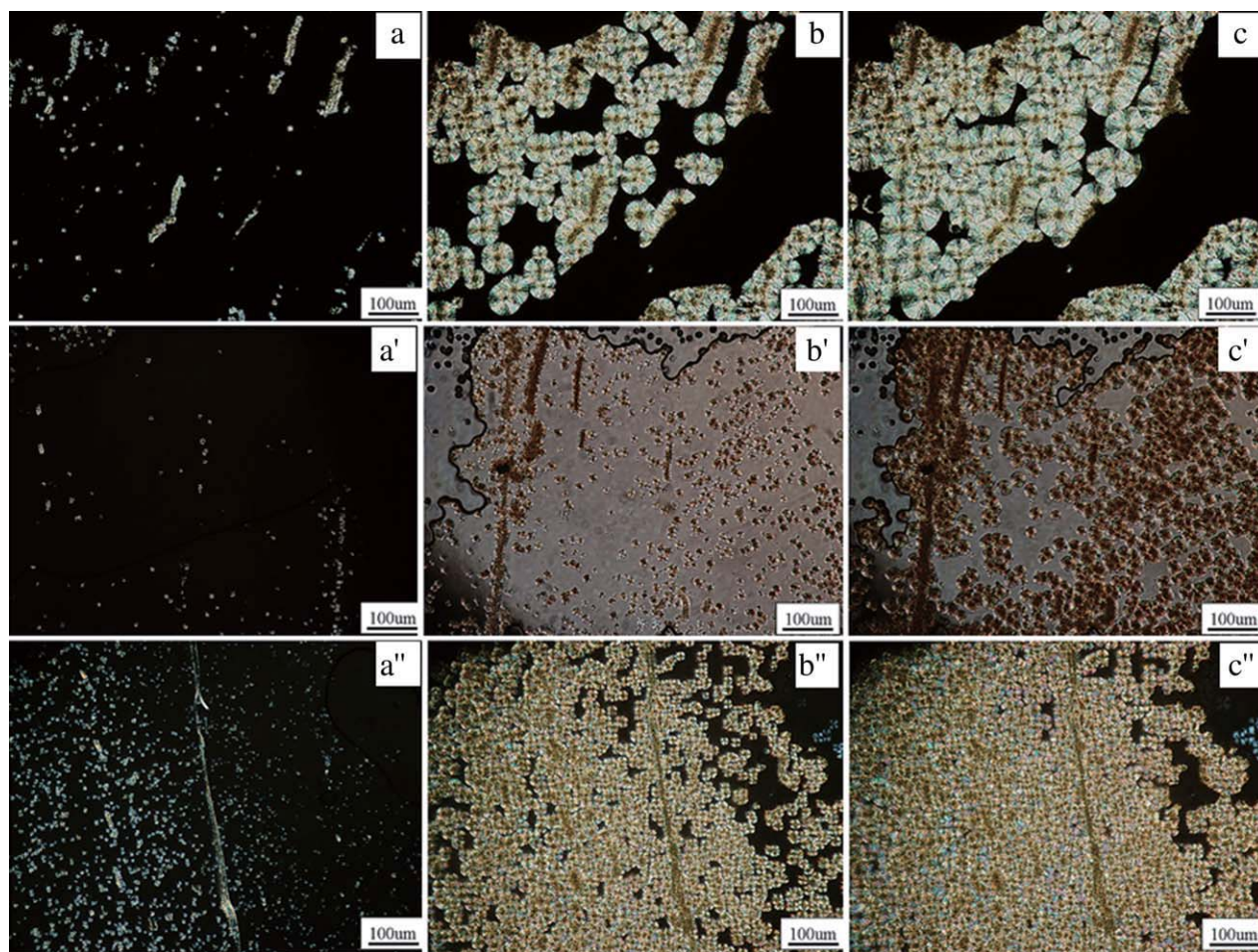


Figure 5 The polarized optical micrographs after crystallized isothermally at 260°C at shear rate of 45 s^{-1} for shear time of 30 s. PPSHA: (a) 120 s; (b) 480 s; (c) 720 s. PPSHB: (a') 240 s; (b'), 540 s; (c'), 1020 s. PPSHC: (a'') 300 s; (b'') 780 s; (c'') 1080 s. The black arrow represents the direction of shear. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

is applied the chains are somewhat stretched. These stretched chains aggregate each other to form bundle structures which promote the formation of stable

nuclei, and these stable nuclei align tightly in the direction of shear [Fig. 8(a)]. Subsequently, these aligned nuclei grow perpendicular to the direction

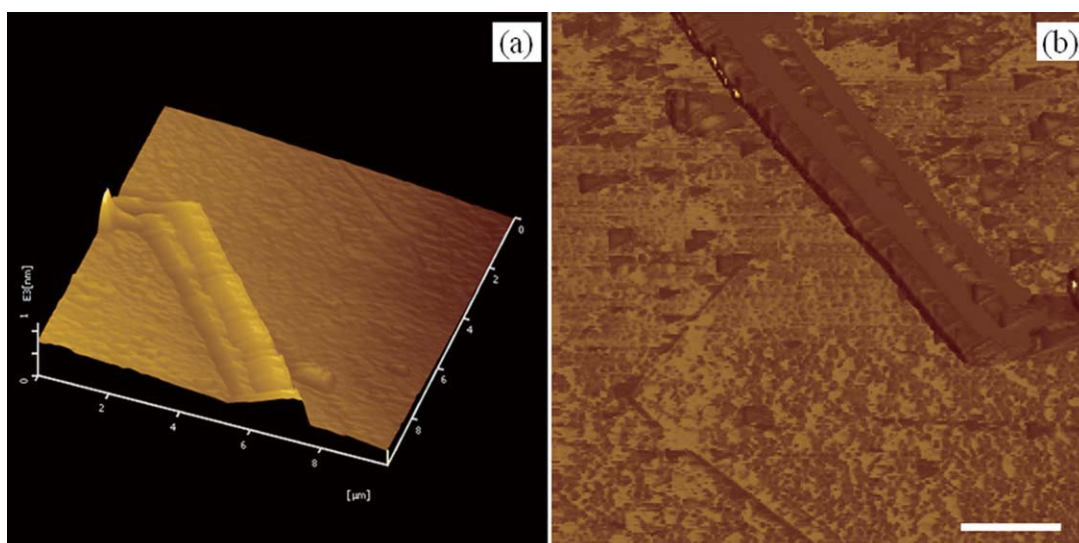


Figure 6 Height (a) and phase (b) images of shear-induced crystallized PPSHB sample by AFM. The scale bar represents 2 μm . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of shear flow by absorbing the neighboring molecular chains, resulting in a 2-dimensional growth of PPS crystal due to the space limitation in the direction of shear.

CONCLUSIONS

The isothermal crystalline morphology of PPS with three different molecular weights under shear condi-

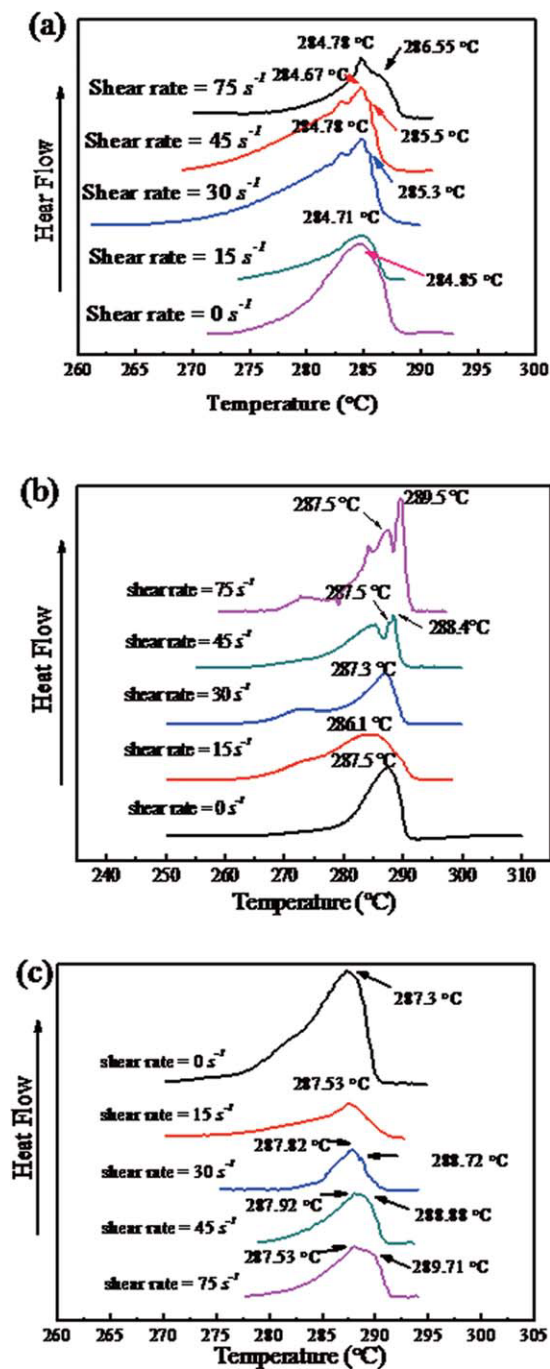


Figure 7 The DSC heating scan curves of (a): PPSHA; (b): PPSHB; and (c): PPSHC isothermally crystallized at 260°C under the quiescent and shear condition respectively, (shear time = 30 s). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

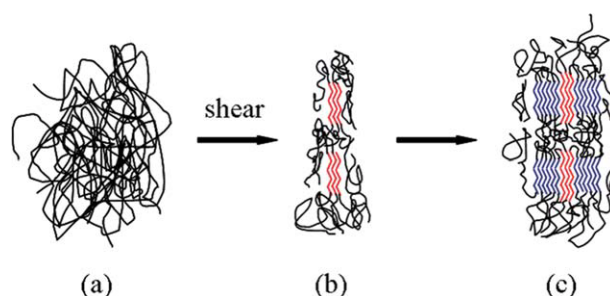


Figure 8 Schematic picture of shear-induced crystallization in PPS: (a) amorphous molecular chains in melt, (b) formation of thread-like oriented crystal nuclei, and (c) 2-dimensional growth of thread-like crystal. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

tion has been investigated by POM equipped with a shearing hot-stage. It appears that all these three PPS samples can form thread-like structures after sheared. The melting behavior of PPS after shear shows that only higher shear strength can induce low molecular weight PPS to form orientation structure due to the fast relaxation of chains. These results indicate that the thread-like structure crystals are consisted of numerous stable nuclei aligned tightly in the direction of shear flow. The dependence of spherulite growth rate on shear strength, molecular weight, and supercooling shows that shear plays an important role in crystallization of PPS. The higher the supercooling is, and the higher the molecular weight is, the more easily the chains stretch.

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