Shear-Induced Crystallization at Polymer−Substrate Interface: The Slippage Hypothesis

Bo Shen,[†,‡] Yongri Liang,[†] Chenggui Zhang,[†] and Charles C. Han[*,†]

[†]State Key Laboratory of Polymer Physics and Chemistry, Joint Laboratory of Polymer Science and Materials, Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

[‡]Graduate School of Chinese Academy of Sciences, Beijing 100190, China

ABSTRACT: When a shear-induced crystallization of polymers was formed between a pair of rotating plates, there existed two possibilities in forming this shear-induced crystal: one is that the shish-kebab formed is uniformly distributed in the bulk polymer melt, and the other is that it appears only on both sides of polymer−substrate interfaces. Since the mechanism of each scenario depends on the boundary conditions of the experiment, we mainly focus on the second scenario in this study and will discuss why and when the shish-kebab grows on the polymer−substrate interfaces. Through the ex-situ polarized optical images of flow−velocity gradient plane, velocity gradient−vorticity plane, and flow−vorticity plane combined with in situ phase contrast optical images and attenuated total reflection (ATR) Fourier transformed infrared spectrum, we are able to infer how shish-kebab is distributed in the bulk. We conjectured that wall slip might be the most possible and reasonable origin for the formation of the shish-kebab on the interface which leads to the two different scenarios mentioned above. This is confirmed by the results from the shear rate dependence experiment. Shear time dependence experiment is also made to study the long shear time effect. By carefully cleaning the quartz plate used for shear experiment and comparing with the results obtained from uncleaned quartz plate, we further testified our point of view and led to some physical understanding for the formation of the shish-kebab as well as the wall slip mechanism.
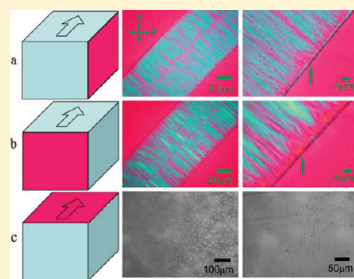
■ INTRODUCTION

The discussion on the fundamental problems of polymer crystallization behavior under flow field is not only scientifically significant but also valuable for guiding polymer processing due to its dramatic influence on the crystallization kinetics and morphology of semicrystalline polymers. Among the many problems in flow-induced crystallization, the shish-kebab, which is a very interesting structure formation in flow field, drew considerable attention in past decades.[1−7] Researches on this superstructure can roughly be categorized into two parts. One is how the nucleus of shish-kebab is formed under shear; the other is what are the critical parameters for the shish-kebab formation.[8,9] The first part is the core of shear-induced crystallization which receives the most attention. But after many years of research, the mechanism of shish-kebab formation is still controversial. Many models and mechanisms have been developed to describe this phenomenon. In early studies, the most popular concept to explain the shear induced shish-kebab morphology was the coil−stretch transition. This concept was first proposed by De Gennes[10] and was used to interpret the shish-kebab formation in the polymer solution. Keller also believed that the reason why the shish-kebab structure is formed in polymer melt is that the polymer chain undergoes the coil to stretch transition under the external field—the same reason why shish-kebab structure is formed in polymer solution.[2] But this theory was not widely accepted because there was no clear evidence that coil−stretch transition can happen in entangled polymer melt.[11] Another concept deduced from the coil−stretch transition is critical orientation molecular weight

introduced by Keller.[2] He believed that, due to their long relaxation time, long polymer chains were more easily deformed under flow field compared with the short ones. So the primary nuclei are mainly composed of long chains. Many experiments have been aimed to verify whether this point of view is correct or not.[12−17] Although supported by some experiments,[5,12,13] this point of view was challenged by the neutron scattering experiment done by Kornfield and her co-workers, who reported that the concentration of long chain species in the shish matches that in the bulk.[15] Although many researchers may still believe that long chain enhances the formation of shish-kebab, but we do not know exactly what role it plays. Recently more and more people tend to accept the view that primary nucleus comes from the deformed network under flow field.[5,18] As for the second part of research, up to now, there is no consensus on the critical conditions under which shish-kebab forms. Some people believed that there exist a critical shear rate,[8] and it should be greater than the inverse Rouse time,[1,19] while Janeschitz-Kriegl argued that the parameter which controls the shear-induced crystallization is mechanical work.[20] Extending this point of view, Mykhaylyk believed that the shear rate should be greater than inverse Rouse time of the longest polymer chain,[9,21] but Li believed strain is the controlling parameter.[18]

Most experiments have focused on various problems related to crystallization under flow field. However, this process not only includes crystallization but also contains a wide variety of hydrodynamic problems such as wall slip, shear banding, and hydrodynamic instability under high shear rate. Neglecting these problems could lead to a misinterpretation of the experimental data. Almost all the experiments associated with shear-induced crystallization assumed that there was no slip on the boundary. It is correct for small molecular weight liquid because the viscosity ratio of bulk to near the substrate interface is almost one, while for polymer, that ratio strongly depends on the boundary conditions, i.e., the interaction between polymers and the substrate, and is usually larger than one due to the entanglement.[22] So it is much easier for polymer to slip on the boundary, especially for polyolefin.

There are many different models to explain the origin of wall slip, and Joshi gave a detailed summary and classification.[23] Two models are widely accepted in recent years.[24−27] The first view holds that the wall slip occurs because polymer chains which adsorb on the wall disentangle from those in the bulk. It is a kind of cohesive failure.[28] The second view explains the wall slip by dynamic detachment and reattachment process of polymer chains from the wall, and this type of slip is a kind of adhesive failure.[29] Large slip occurs because of a sudden desorption of polymer chains from the wall. The disentanglement theory originates from the scaling model which was proposed by De Gennes and Brochard-Wyart.[30−32] They believed that when the polymer melt passes a wall with low grafting density where the adsorbed chains do not overlap, and then the graft chains slightly deform but still entangle with bulk chains if the velocity at the wall is low; but when the velocity increases, the polymer chains attached to the wall elongate due to the entanglement with neighboring bulk chains. The diameter of the trajectory of the elongated polymer chain decreases gradually, and when it is smaller than the length between the entanglements, the graft chain disentangles with bulk chain completely and slip occurs. The graft polymer chain is forbidden to reptate in its tube because its "head" is fixed at the surface, so it can only follow the relaxation process of arm retraction and constraint release.[30,33] This process is called coil−stretch transition, the same concept used by Keller to explain the cause of shish-kebab. Besides these two theoretical models, another model based on the experimental results proposed by Joseph which can be considered as a modified disentanglement model believes that there is a lubrication layer next to the wall.[34,35] Both the lubrication model and disentanglement model believe slip is a cohesive failure, and their difference is the thickness of the boundary layer (slip layer). In De Gennes' disentanglement model, the thickness of boundary layer is on the order of radius of gyration of graft chain, while in the lubrication model, the boundary layer is on the order of 100 nm or more based on the result from ATR-FTIR experiment.[36] The slip that takes place in a thicker region was also mentioned by De Gennes.[37]

Our group has studied the behavior of single component crystallizable system[38] and two components with liquid−liquid phase separation system which involves one crystallizable component and the other noncrystallizable component as well as both crystallizable components under flow field,[39,40] and we have concluded that the primary cause of nucleation comes from the deformation of entangled network. In this paper we focus on the polymer−substrate interface, using in situ rheo-optical, ex situ optical microscopy, and ATR-Fourier transformed infrared spectroscopy (FTIR). We discuss why and when the shish-kebab
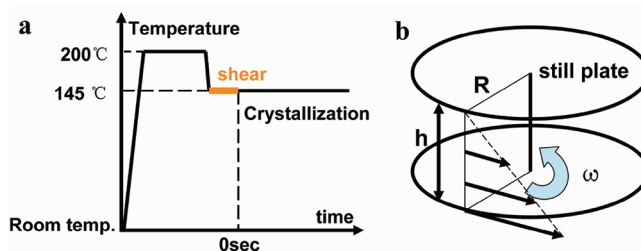

Figure 1. (a) Temperature and shear protocol for shear-induced crystallization experiment. The iPP samples was heated to the temperature above the equilibrium melting temperature, held for 8 min, and then cooled to the crystallization temperature and shear at given shear rate for an indicated shear time. (b) Schematic diagram of linear flow field assumed for the bulk part in a parallel plate shearing device.

appears on the interface and give some new insight into the formation of the primary nuclei of shish-kebab near the interface.

■ EXPERIMENTAL SECTION

Materials. Isotactic polypropylene (iPP) (M_w = 3.4 × 10^5, polydispersity M_w/M_n = 3.7) was provided by Yanshan Petrochemical Corp., Inc.

Instruments. The commercial parallel plate shearing hot stage Linkam CSS-450 with optical microscopy (Nikon E600POL) was used to study the in situ shear-induced crystallization, which provides precision control of shear flow and temperature. The sample unloaded from shear-induced crystallization experiment was studied by FTIR (Bruker Equinox-55) with Multi-Reflection ATR accessory (PIKE Technology).

Experimental Details. The iPP sample was heated to 200 °C, held for 8 min to eliminate thermal history, and then quenched to 145 °C at the cooling rate of 30 °C/min. Just after reaching the crystallization temperature, the sample was subjected to the shear at the given shear rate for an indicated shear time.

To make the surface of the quartz plates for shear experiment clean enough to completely wetted by demineralized water, the surface was cleaned carefully with the following three-step procedure: first, each of quartz plates for shear experiment was immersed and sonicated in acetone and demineralized water in sequence for 15 min, respectively; after that, the plates were treated with a fresh piranha solution which is the mixture of sulfuric acid and hydrogen peroxide (in the volume ratio of 7:3) at 120 °C for 8 h, and then they were rinsed and ultrasonically cleaned in demineralized water. Finally, the silica plates were dried in a high-purity nitrogen flow.[41,42]

■ RESULTS AND DISCUSSION

In our experiment, we find that under the assumption of uniform shear field two scenarios occur. One is that shish-kebab uniformly disperses in the bulk as it normally happens (Figure 2). The other is that shish-kebab appears on the polymer melt−substrate interface (as depicted in Figure 3a,b). In order to distinguish the surface of polymer melt from the bulk, we marked the inside of upper quartz plate with oil ink which is still (the geometry of shearing devices is shown in Figure1b) and then repeated the experiment. When the oil ink was in focus, the shish-kebab could be seen clearly at the same time as shown in Figure 4. Besides, the oil ink was surrounded by the shish-kebab (Figure 4b), further suggesting that shish-kebab and oil ink were on the same plane which is the inside surface of the upper quartz plate.
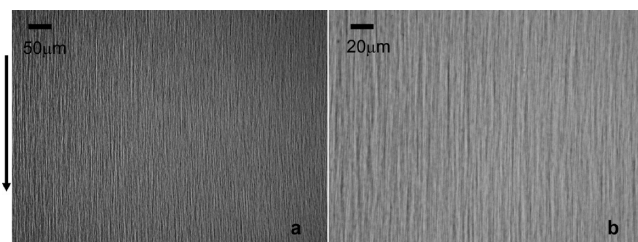
Figure 2. In situ phase contrast microscope (PCOM) image of iPP sheared at 145 °C with the shear rate 46 s^{-1} and shear time 5 s; surface treatment was made to prevent the formation of shish-kebab on the surface. (b) is the magnified view of (a). The shish-kebab was uniformly distributed in the bulk, so we could not make all the shish-kebab in focus. The black arrow indicates the flow direction.
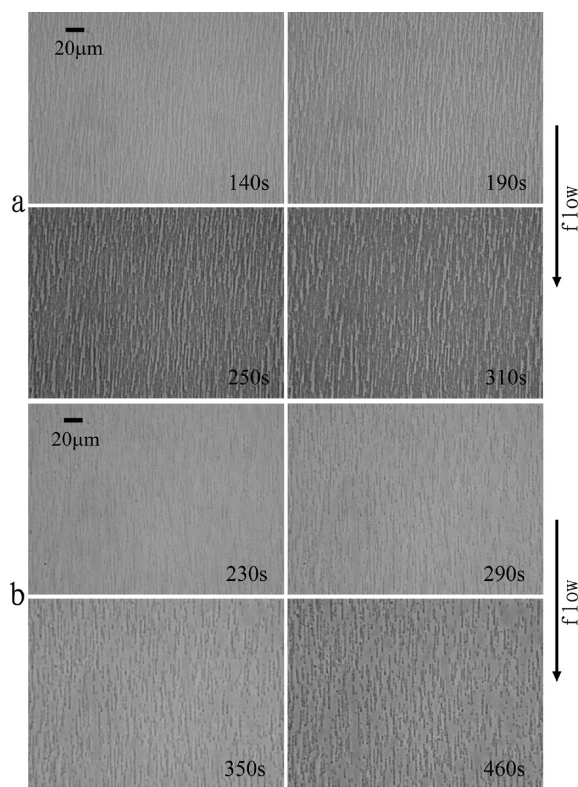

Figure 3. Time evolution of PCOM image during crystallization process of iPP after the cessation of shear. The sample was sheared at 145 °C with apparent shear rate 5 s^{-1} and shear time 5 s. The top polymer—substrate interface (a); the bottom polymer—substrate interface (b). The quartz plates were not specifically cleaned.

It can also be seen from the transmission IR and ATR-FTIR spectra that when the polarizer changed from parallel to the shear direction to perpendicular to the shear direction (the experiment procedure for ATR-FTIR experiment is a little different, we rotated the sample instead), the absorbance of transmission spectrum due to the vibration of transition moment did not changed much, whether it is parallel (998 cm^{-1} assigned to CH$_3$ rocking and C—C chain stretching, 841 cm^{-1} assigned to CH$_2$ rocking and C—CH$_3$ stretching) or perpendicular (900 cm^{-1} assigned to CH$_3$ rocking, CH$_2$ rocking and CH bending, 809 cm^{-1} assigned to CH$_2$ rocking, C—C chain stretching and C—CH stretching)[43] to the polymer chain axis. Meanwhile, the
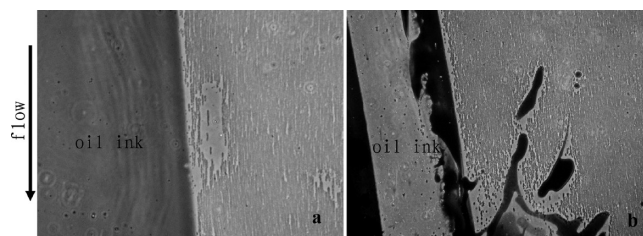

Figure 4. PCOM image of shish-kebab formed on the interface of the upper plate which was labeled with oil ink using a black marker to draw a line along the flow direction on the upper plate. The black regions are smeared ink. The sample was sheared at 145 °C with apparent shear rate 8 s^{-1} and shear time 5 s.

relative absorbance of the ATR-FTIR spectrum from the plate—polymer interface, which is the ratio of parallel and perpendicular to the polymer chain such as A_{998}/A_{900} or A_{841}/A_{809}, in the same spectrum changed dramatically. The orientation function was used to quantitatively characterize the average degree of orientation of the whole sample and sample surface. It defines as the coefficient of $P_2(\cos \theta)$ which is the spherical harmonic functions used to expand the orientation distribution function and equals to the average of $\langle (3 \cos^2 \theta - 1)/2 \rangle$, where θ is the angle between the chain axis and the deformation direction. The orientation function can be related to the dichroic ratio D in IR spectroscopy by the expression[43,44]

$$\langle P_2(\cos \theta) \rangle = \left\langle \frac{3 \cos^2 \theta - 1}{2} \right\rangle = \frac{D - 1}{D + 2} \frac{D_0 + 2}{D_0 - 1}$$

where D_0 is given by $D_0 = 2 \cot^2 \alpha$, α is the angle between the transition moment and chain axis, and D is given by $D = A_{\parallel}/A_{\perp}$, the ratio of the FTIR absorbance for polarized light parallel and perpendicular to the deformation direction. Using the 998 cm^{-1} band which is ascribed to the absorption in the crystalline region as the reference peak, we calculated that the average degree of orientation P_2 of the whole sample is only 1.5% from the transmission spectrum and the degree of orientation P_2 of the sample at the quartz plate interface is as high as 30% and 36% from the ATR-FTIR spectrum.[45] Combining results from the optical microscopy, we know that shish-kebab grows indeed on both sides of polymer melts, and there is almost no orientated iPP crystalline structure with this shearing condition in the bulk. The important question for this shear condition is that if the shear rate and shear stress are indeed the same along the direction of thickness, then shish-kebab should have distributed uniformly in the bulk. Instead, what we have observed in this experiment is that the anisotropic growth of shish-kebab is dominated on the two polymer melt—substrate interfaces, at least for the low shear rate and short shear time (5 s^{-1} shear rate and 5 s shear time).

In order to correctly interpret the mechanism of shish-kebab formation, it is necessary to know how far away from the interface the shish-kebab can extend to. Considering the depth of field of microscopy, we carried out a more detailed experiment to find out the distribution of shish-kebab in the bulk. The sample sheared in the rheo-optical experiment was allowed to isothermally crystallized at 145 °C. When the sample was fully crystallized, we cooled the sample to room temperature and then used a microtome to cut it in the flow—velocity gradient plane and velocity gradient—vorticity plane for polarized optical microscopy studies. Since the crystalline polymers are optically anisotropic,
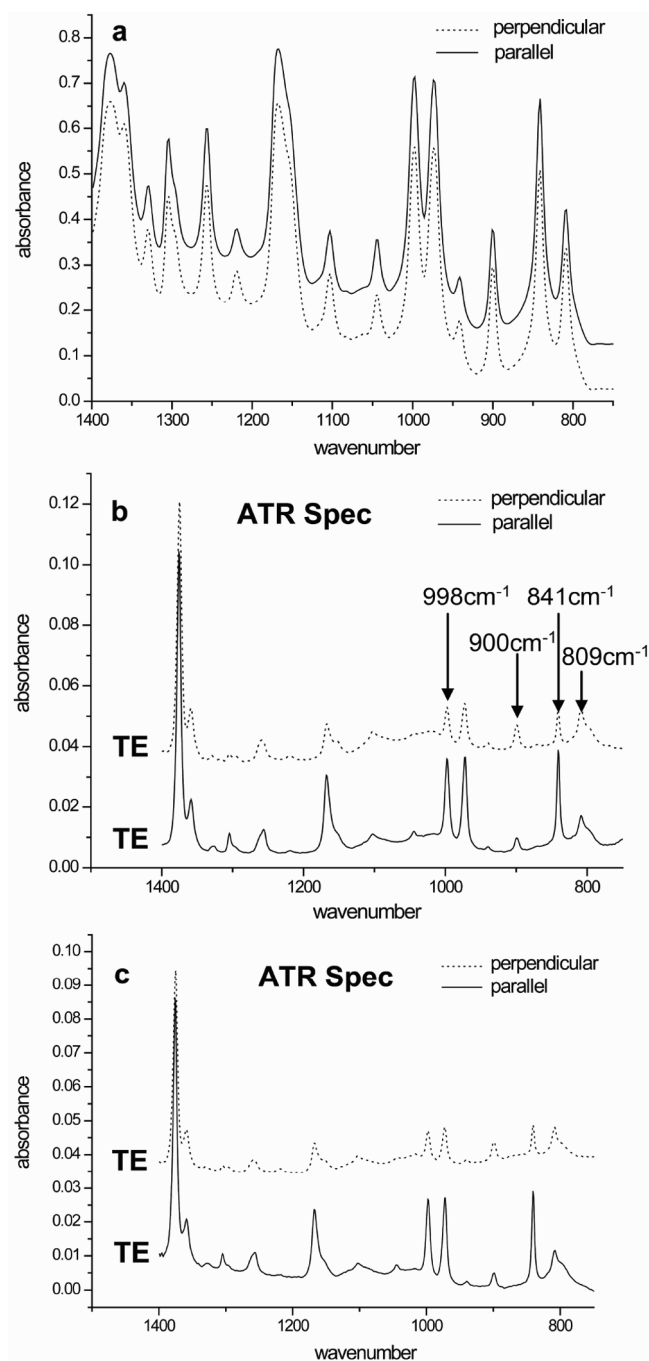
Figure 5. Polarized Fourier transformed infrared spectrum of sheared iPP sample with the polarization direction parallel and perpendicular to the shear direction: transmission spectrum (a), ATR-FTIR spectrum of upper surface (b), and lower surface (c). The depth of penetration is about 7.7 μm. TE here denotes transverse electrical wave.

Figure 6. Ex-situ optical image of the cross section of iPP sample sheared at 145 °C with shear rate 5 s^{-1} and shear time 5 s. Polarized light image in flow—velocity gradient plane (a) and velocity gradient—vorticity plane (b) viewed through the crossed polarizers (orientated as indicated) with λ plate (the slow axis aligns from the top right to the bottom left); reflecting light image of iPP sample surface (c). The left column is the three-dimensional schematic diagram showing the cross section where we cut from the sample (represent by red color) and the arrow indicates the flow direction.

the cross section in the flow—velocity gradient plane; the lamellar grows obviously normal to the two lateral facets toward the middle, so the location of initial nucleus must be on the boundary of polymer melt. Taken together with the fact mentioned above that the shish-kebab grows very near the surface, as well as the directions of the cutting cross section, we can tell the blue light on the boundary as pointed out by green arrow is the location of original shish-kebab. Figure 6b shows the cross section of velocity gradient—vorticity plane which means the direction of chain orientation is normal to the plane of this figure because the shish is along the flow direction, so there will be no orientation on the boundary, as shown in the image. Figure 6c is the surface of the sample; after shear the sample was placed directly under the microscope with the reflection mode. Therefore, the shish-kebab as well as spherulite on the sample surface can be seen clearly. Through these three sectioned views in different directions; a three-dimensional scenograph can be obtained. It is quite clear to understand how shish-kebabs are distributed in space: shish-kebab orientates along the flow direction and is located on both sides of the melt—plate interfaces at this low shear rate condition. Its distribution is like a step function normal to the plate surface. This experimental fact can not be explained by any mechanism proposed before, and it leads to some questions worth considering: the important issue is the boundary condition. For a perfect Couette flow, the velocity gradient is uniform; both sides of polymer melts has finite shear rate which is the same as in the bulk, and then it is obvious that this flow and boundary condition cannot explain the phenomenon we have observed in this experiment. So what actually happened on the melt—plate interface is the key question which needs to be answered.

Almost all reported studies on the shear-induced crystallization concentrated on the condition that no slip condition was satisfied at the melt—substrate boundary. Reconsidering the results of our experiment, it was natural for us to believe that

the refractive index along the chain axis is slightly larger than that perpendicular to it.[46] If the chain axis is parallel with slow axis of the first-order red plate that align from the top right to the bottom left of the image, it increases the order of interference color and the image should be blue; otherwise, if it is perpendicular to it, the image should be orange. Thereafter, we can extract orientation information of polymer chains from the images viewed through the polarized optical microscope. Figure 6a is
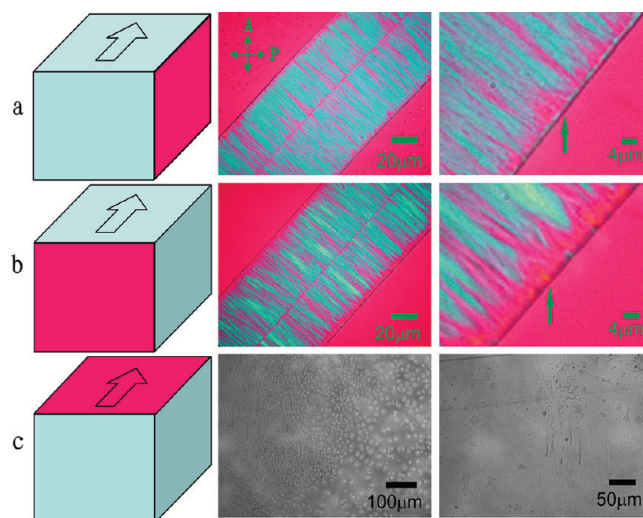
at least in this reported conditions the Couette flow which we assumed was not consistent with the actual flow field, and the boundary conditions in our experiment must have changed. Most likely some form of wall slip had occurred. It is interesting to point out that one of the molecular mechanisms to explain the origin of wall slip is the coil—stretch transition theory. Keller once pointed out that the formation of shish-kebab is a manifestation of coil—stretch transition, but this view was challenged by some rheological scientists who argued that coil—stretch transition could not occur in the entangled polymer melt. However, the coil—stretch transition can be introduced near the melt—wall interface through a completely different mechanism, i.e., a wall slip mechanism with a partial absorption. If we put the molecular mechanism for wall slip proposed by De Gennes and the shish-kebab formation proposed by Keller together, then it is natural and intuitive to interpret our experimental observation of shish-kebab formation from a wall slip mechanism with a partial adsorption.

Indeed, the shear rate dependence with constant shear time of 5 s gives us supporting data for what we believed as shown in Figure 7. When the external applied shear rate was low, only spherulites formed on the interface, and the induction time was long compared with other higher shear rate results. When the external shear rate was increased, the morphology formed on the interface changed from spherulite to the shish-kebab structure, and there was no shish-kebab in the bulk at short time. Until the shear rate reached 33 s^{-1}, the shish-kebab formed not only on the interface which exhibited wavelike morphology but also in the bulk, however, with less number density and shorter length compared with that on the interface. With further increased shear rate, the whole sample was filled with shish-kebab and with increased number density, but the flat surface of the sample although full of shish-kebab was completely distorted. The morphology formed on the interface changed from spherulite to shish-kebab which indicated that there existed a local flow field, and it changed with external applied shear field. The necessary condition for shish-kebab formation is that the shear rate should be above a critical value. Therefore, there are definitely shear rates with large difference on the interface and in the interior. The former is larger than the latter, so the shish-kebab first appeared on the interface, and then the shear rate in the bulk reached critical value. The shear rate near the interface is much higher than that in the bulk, so the number density and length of the shish-kebab formed at the interface are always higher and longer than that in the bulk. The most possible and reasonable answer for these phenomena is wall slip (maybe a stick and slip) appeared on the polymer—substrate interface.

We believe that the wall slip is the key to find out how the shish-kebab is formed, and it is easy to test our ideas by verifying whether wall slip happens or not. According to the result of Mhetar and Archer, for uncleaned silica surface, there are surface-adsorbed polymer chains; therefore, stick—slip motion could happen at the surface when under the shear flow, also when the shear stress increases, the inhomogeneous adsorption of polymer chain on the substrate will lead to surface voids; while for the cleaned silica surface (the cleaning procedure was similar as we described in the Experimental Section), maybe due to the elimination of all the organic debris and contaminants, the voids was not observed and the measured slip length was lower than that of the uncleaned one and wall slip was suppressed.[47] On the basis of the strong dependence of wall slip on the surface treatment, we carefully cleaned the quartz plate used in our

experiment (the cleaning procedure is described in the Experimental Section) which can be completely wetted by water and compared the result with uncleaned quartz plate (without doing the cleaning procedure) with the water contact angle about 80°. We designed the following three comparative experiments, all done in the same experimental conditions except for the surface property of quartz plate: In the first experiment, both quartz plates were uncleaned and was a little hydrophobic. In the second experiment, the upper surface was carefully cleaned and the lower surface was uncleaned. In the third experiment, both quartz plates were carefully cleaned. As we expected, in the first experiment when the surface of quartz plates for shear was not cleaned, the adsorbed polymer chains on the wall do not give sufficient friction, wall slip can happen on both sides of the interface, so we can see shish-kebab grow on the upper surface as well as on the lower surface (Figure 8a). If the two interfaces were made one cleaned and the other uncleaned, as we did in the second experiment, shish-kebab disappeared on the cleaned interface where wall slip was suppressed compared with the uncleaned one based on Archer's results. While on the uncleaned interface where wall slip was easy to happen, shish-kebab can be seen (Figure 8b). In the last experiment when both interfaces were carefully cleaned, wall slip was suppressed, and there was no shish-kebab on either side of the interface (Figure 8c). Only in this case the no slip boundary condition was totally satisfied. So we increased the shear rate to see if the shish-kebab can be seen in the bulk. When the shear rate reached 46 s^{-1}, shish-kebab is full of entire field of vision and was uniformly distributed in the bulk, which was the first scenario we pointed out at the beginning of this part and was also shown in Figure 2. These three experiments were consistent with our point of view and also showed the complexity of the relationship between the interfacial conditions and wall slip as well as the shish-kebab formation.

The shear time dependence of shish-kebab with the same shear rate 3.5 s^{-1} in the case the quartz plate did not subject to the surface treatment was also made to see if the shish-kebab formed on the interface can induce other shish-kebab formation or crystallization growth in the bulk after sufficient shear time. As we can see from Figure 9, when the shear time was 5 s, we can clearly observe shish-kebab on both interfaces but not in the bulk of the sample at 130 s after the shear. When the shear time was increased to 10 s, shish-kebab formed on the interface become longer. Actually, just about 7 s after the start of shear, shish-kebab can already be seen on the interface (not shown in Figure 9), although the external applied shear did not stop at that time. Then the sustained shear could make the shish-kebab aggregate and distort on the interface and also made them longer and longer. After the shear motion stopped, we waited for more time to see if the bulk can be filled with shish-kebab, but we only observed the blurred image of shish-kebab in the middle frame of shear time of 20, 40, and 80 s. Although it looks different from the shish-kebab formed inside of the bulk as shown in the shear rate dependence experiment (Figure 7) with the shear rate of 40 s^{-1} and shear time of 5 s, it might be the shish-kebab grown toward the interior of the sample induced by the shish-kebab already formed on the interface because of the long shear time or an interior image which included the defocused image of shish-kebab readily growing toward and into the interior direction from the interface due to the depth of field of microscope. As expected, the shish-kebab became longer with increasing shear time on the interface was because there does exist a local field caused by wall slip.
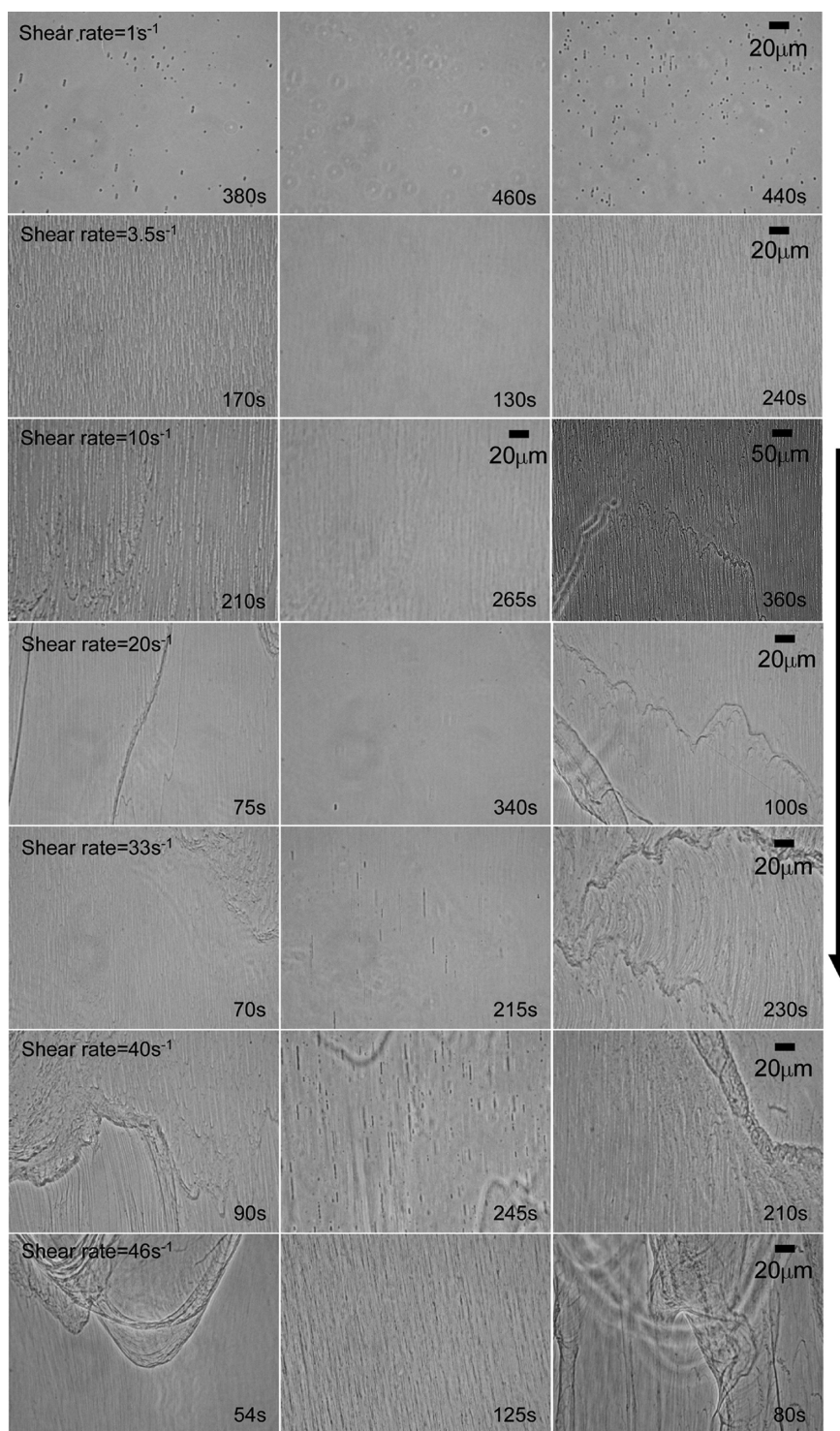
Figure 7. In-situ PCOM image of shish-kebab formed on the polymer—substrate interfaces (the left column is morphology at the upper surface and the right is that at lower surface) and inside of the bulk (the middle column) in the case the quartz plates did not subject to surface treatment. The sample was sheared at 145 °C with different apparent shear rate but the same shear time of 5 s. The crystallization time is shown at the bottom right. The black arrow indicates the flow direction.

We tried to analyze the molecular mechanisms of wall slip proposed by those pioneers to extract some useful information, so as to provide a physical interpretation of this type of shish-kebab formation. Considering the three main explanations for wall slip, it seems that the disentanglement model proposed by De Gennes and the lubricated layer model proposed by Joseph were more consistent with our experiments. But meanwhile we also need to take into account the experimental facts that the boundary layer is about hundreds of nanometers thick as shown in Figure 6a (as point out by the green arrow) and is much thicker than that in De Gennes's model. The length of shish-kebab is at least on the order of micron, which we can see obviously from
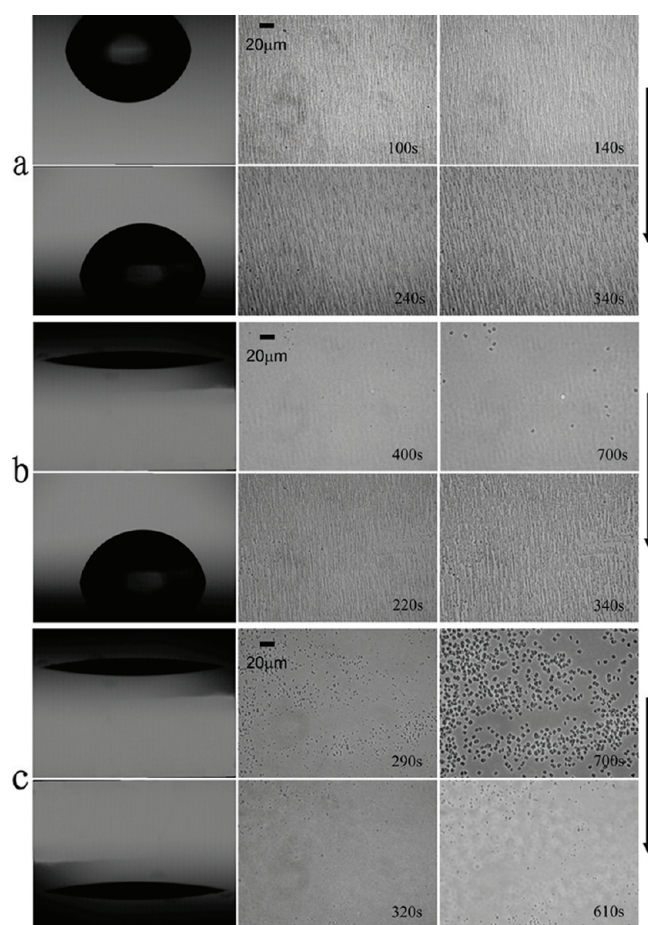
Figure 8. In-situ PCOM image of shish-kebab formed on the polymer—substrate interface with different surface property. The left column of this picture is the wettability test of upper surface and lower surface. Both quartz plates were uncleaned (a); the upper surface was carefully cleaned and the lower surface was uncleaned (b); both the quartz plates were carefully cleaned (c). The sample was sheared at 145 °C with apparent shear rate 5 s^{-1} and shear time 5 s. The black arrow indicates the flow direction. The crystallization time is indicated in the picture.

Figure 9. In-situ PCOM image of shish-kebab formed on the polymer—substrate interfaces (the left column is morphology at the upper surface and the right is that at lower surface) and inside of the bulk (the middle column). In this case the quartz plates did not subject to surface treatment. The sample was sheared at 145 °C with the same shear rate 3.5 s^{-1} but different shear time. The crystallization time is shown at the bottom right. The black arrow indicates the flow direction.

optical images (Figure 3), and is much longer than a fully extended polymer chain. So the single chain with its "head" adsorbed on the wall was pull through the entangle polymer melt to undergo the coil—stretch transition and form the primary nucleus cannot be the complete process, if the wall slip model proposed by De Gennes was used to interpret our experiment result. The nucleation process of polymer must have generated some cooperated "alignment", "packing", or "association" for the nucleus formation in the process. Meanwhile, Joseph's lubricated layer model may be more phenomenological but does give the correct length scale for the wall slip. Since the only difference between these two models is the thickness of the boundary layer, the molecular mechanism proposed by De Gennes is still an inspiration to us. So we imagine that the whole physical picture could be something like the following: if the polymer—substrate interaction is weak or the interfacial friction is not sufficient to suppress the wall slip, the whole flow field can be divided into two different regions: one is very close to the wall which is called boundary layer or slip layer, and the other is outside the boundary layer called the main flow region. Within the boundary layer, the variance of velocity normal to the surface changed much more
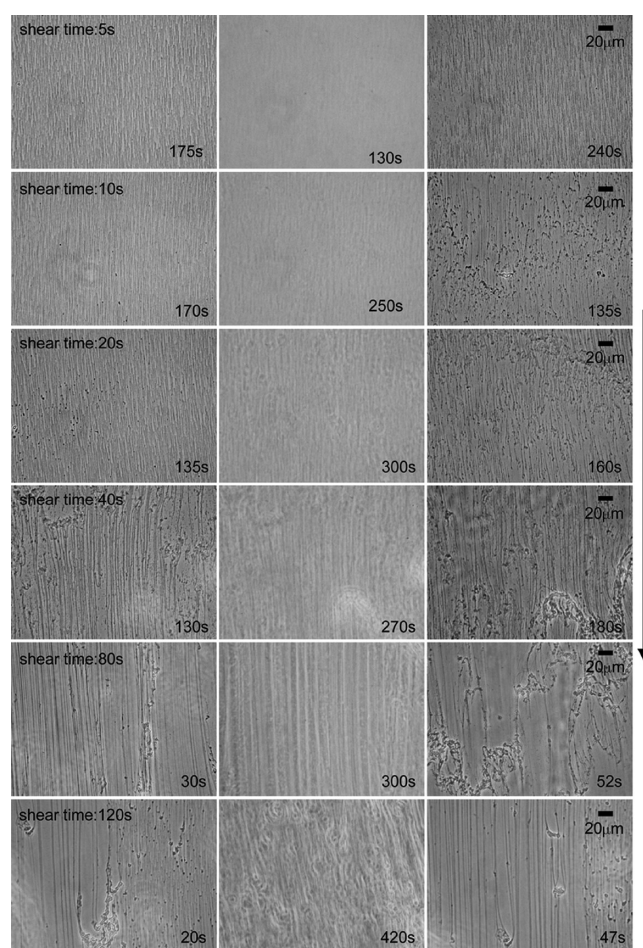
rapidly than in the bulk; this may be caused by the reason that the relative velocity of polymer chain attached to the wall equals zero, and on the other hand, when the polymer fluid goes a very short distance away from the wall to the interface between the boundary layer and the main flow region, its velocity takes a finite value of main flow region. Therefore, within this narrow region, the velocity changes dramatically and makes its gradient much higher compared with the main flow region. Under such a flow field, the polymer chains are locally orientated and form the small nuclei first, and then the continued shearing transforms these small nuclei into the primary nuclei of shish. While in the bulk, the actual shear rate which is even smaller than the apparent shear rate will not cause enough chain orientation, so we cannot see any shish-kebab in the bulk. This type of stick—slip motion does exist which can be found in the literature[41,48] and has been suggested by Klein in his study on the small molecular motion confined to thin layer.[49,50] Then it is reasonable for the interpretation of our experiment data and intuitive for our explanation on the shish-kebab formation at partially surface slip conditions. This definitely needs to have a critical shear rate at the surface layer with its time constant (inverse shear rate) shorter than the

relaxation time of orientated chain in order to form this surface shish-kebab crystallization. At much higher shear rate when the shear rate in the bulk part reaches this critical value, the bulk part of the polymer melt will also be filled with shish-kebab.

CONCLUSION

There exist two possibilities in shear-induced crystallization: one is that the shish-kebab formed is uniformly distributed in the bulk; the other is that it orientates along the flow direction and locates only on the interface of polymer melts and substrate, and its distribution is like a step function normal to the substrate surface. Distinguishing these two scenarios helps us correctly interpret the experimental data and understand the shish-kebab formation. Especially in the latter case, the macroscopic shear rate needed for the formation of shish-kebab is much lower than that in the former case. Unless we change the boundary condition, shish-kebab will prefer to form on the interface than in the bulk first. We conjectured that the most possible and plausible reason why shish-kebab forms on the interface might be the occurrence of wall slip due to the low interfacial friction at uncleaned surface. Wall slip leads to the discontinuity of the shear rate between the boundary layer and the main flow region. The shear field in the boundary layer, a very narrow region compared with the whole flow field, is larger than that of the bulk and makes it possible to form the shish-kebab on the interface under the low apparent shear rate, when the shear rate in the main flow region reaches the critical value, shish-kebab formed in the bulk of polymer melt as well. The mechanism we proposed can be further supported by the results of shear rate dependence of the shish-kebab formation as we have observed. By changing the surface condition, shish-kebab can form in the bulk and not on the interface. All the phenomena are interpreted by the stick—slip motion on melt substrate interface which is intuitive and reasonable. The formation of the shish-kebab on the interface which correlates the two different and apparently not related phenomena, the shear induced crystallization and wall slip, will give us better understanding of the shish-kebab formation as well as the wall slip mechanisms.

AUTHOR INFORMATION

Corresponding Author

*Phone: +86 10 82618089. Fax: +86 10 62521519. E-mail: c.c. han@iccas.ac.cn.

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