The Influence of Ethyl Branch on Formation of Shish-Kebab Crystals in Bimodal Polyethylene under Shear at Low Temperature

Zong-Bao Wang*a, Yi-Min Mao*b,c, Xu-Ke Li*†, Yi-Guo Li*, Chatuchai Jarumaneeroj*d, Boonyakeat Thitisak*d, Piyawan Tiyapiboonchaiya*d, Wonchalerm Rungswang*d,† and Benjamin S. Hsiao*†

a Ningbo Key Laboratory of Specialty Polymers, School of Materials Science and Chemical Engineering, Ningbo University, Ningbo 315211, China
b Department of Materials Science and Engineering, University of Maryland, College Park, Maryland 20742, USA
c NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA
d SCG Chemicals Co., Ltd., Siam Cement Group (SCG). 1 Siam Cement Rd., Bangsue, Bangkok 10800, Thailand
e USA Department of Chemistry, Stony Brook University, Stony Brook, NY 11794-3400, USA

Abstract  Formation of shish-kebab crystals using a bimodal polyethylene system containing high molecular weight (HMW) component with different ethyl branch contents was investigated. In situ small-angle X-ray scattering (SAXS) and wide-angle X-ray diffraction (WAXD) techniques were used to monitor the formation and evolution of shish-kebab structure sheared at low temperature in simple shear mode and low rate. Only the bimodal PE with no branch formed shish-kebab crystals at the shear temperature of 129 °C, and the shish length increased with the crystallization time, while bimodal PE with branch has no observable shish under the same conditions. The degree of crystallization for bimodal PE with no branch increased with time up to above 7%, while those with ethyl branch increased continually up to above 23%. Furthermore, bimodal PE’s Hermans orientation factor with no branch increased to 0.60, while those with ethyl branch only increased to a value below 0.15. This study indicated that the shish-kebab crystal formed at the low temperature of 129 °C is due to the stretch of entangled chains under shear for the bimodal PE with no branch. Only partly oriented lamellar crystals were formed for the bimodal PE with ethyl branch. All the results at the shear temperatures higher, closed to, and lower than the melting point, the modulation of shish crystals formation owing to different mechanisms of the coil-stretch transition and the stretched network by changing shear temperature was achieved in the bimodal PE samples.

Keywords  Bimodal polyethylene; Shish-kebab; Ethyl branch; Shear

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INTRODUCTION

Flow-induced crystallization has long been an inevitable concept in semi-crystalline polymer processing because any polymeric final products' properties are directly related to their internal morphology. Compared with the typical spherulites formed at static crystallization, shish-kebab crystals, formed in shear and extension fields, can significantly increase the strength, thermal stability and other properties of final products.[1–11] Therefore, shish-kebab crystals are critical in polymer processing, such as fiber spinning, film blowing, injection molding. Despite the extensive studies over the past decades, the formation mechanism of flow-induced shish-kebab crystals, which is essential for tailoring property of the final product, is still elusive. The desire of the high-performance product demands further in-depth explorations.[9,10,12–24]

The shish-kebab crystals were first obtained in dilute polymer solutions under shear.[8] Researchers often used the concept of coil-stretch transition (CST) initiated by de Gennes to interpret the formation of shish-kebab crystals in dilute polymer solutions under shear.[25] Keller et al. further extended the CST concept to polymer melts and proposed a concept of a “critical molecular weight” under flow.[26–30] According to the CST concept, the long polymer chains play an essential role in forming shish-kebab crystals in polymer melts under flow.[31,32] Using polyethylene blend systems and in situ X-ray scattering and diffraction techniques, Hsiao et al. carried out a series of experimental work to study the effect of the high molecular weight (HMW) component in the formation process of shish and kebabs.[10,33,34] They found that the existence of a small amount (2%) of HMW chains significantly altered the crystallization kinetics of the entire system, where shish-kebab crystals formed thereof when compared with the crystallization of base polyethylene (PE) without the HMW component under the same flow field. They further confirmed this behavior by using different polymer systems, such
as isotactic polypropylene (iPP) under shear.\textsuperscript{[35]} Actually, different material systems investigated by Hsiao et al. were all inconsistent with the CST mechanism.

Kornfield et al. focused on the role of low molar mass fraction in the shish formation of shear-induced crystallization of iPP blend at a temperature lower than the melting point.\textsuperscript{[36]} In contrast, they drew a different conclusion that the HMW component did not participate in the shish component and the HMW ones only accelerated the formation and growth of shish by advancing the order of local short chains. More shish-kebab crystals found in a highly entangled melt system seem to lead the shish formation to the other mechanism, i.e., a stretched network model, which is accepted by more and more researchers. They think it is quite tricky to disentangle the highly entangled chains to extended chains and form shish. Han et al. found shear-induced shish-kebab-like cylinder of iPP sheared at a low rate and a temperature lower than the melting point.\textsuperscript{[37,38]} They thought that the shear force could not drive the molecular chains to disentangle and form extended chains under such conditions, and to deform the entangled network composed of the fibrillar crystals, and in final to develop into the shish. They further extended the shish generation mechanism and proposed that the point nuclei firstly generated under shear flow upon the entangled network’s deformation and subsequently grow in the shish shape.\textsuperscript{[39]} Moreover, by combining the extensional rheological and in situ small-angle X-ray scattering (SAXS) technique, Li et al. explored the formation mechanism of the shish in high-density polyethylene (HDPE) melt at a low temperature of 125 °C.\textsuperscript{[40]} They illustrated a critical strain for inducing shish and shish-kebab generation from the stretched network in polymer melt. To uncover the correlation between shish formation and strains, they examined the extension-induced crystallization of lightly cross-linked HDPE melt at a temperature of 132 °C.\textsuperscript{[41]} They observed four types of nucleus morphologies in the strain range, which excellently coincided with the four regions defined by the stress-strain curve, i.e., from the uncorrelated oriented point nuclei, scaffold-network, and micro-shish to shish. The shish formation should be attributed to the stretched network, as the sample they measured was permanently cross-linked. They further studied the strain-temperature equivalence on nucleation with a similar lightly cross-linked system. They defined four regions in the strain-temperature space, i.e., orthorhombic lamellar crystal, orthorhombic shish crystal, hexagonal shish crystal and oriented shish precursor. They found that the estimated critical nucleus thickness is determined by the transition from lamellar to shish nuclei.\textsuperscript{[42]} Recently, Li et al. performed a real-time investigation on flow-induced crystallization of PE blends with a different molecular weight in high entanglement at temperatures lower than the melting point.\textsuperscript{[43]} It has clearly illustrated that the stretched network plays a significant role in forming shish and supports a kinetic process for shish formation from initial chain conformation to final stable nuclei. Similarly, a four-stage model, i.e., stretching of molecular segments, nucleation, alignment of shish nuclei, and fibrillation, was also proposed by Mykhal’ylyk et al. for explaining the formation of shish crystals in the shear-induced crystallization of monodisperse hydrogenated polybutadienes.\textsuperscript{[44]} In summary, scientists have done much research and proposed two different notions on the formation of a shish-kebab crystal, but the formation mechanism is still an open question.

According to past studies, it is not hard to discover that the two models were proposed based on the observations under different crystallization conditions. The CST model explains the shish formation at a high shear temperature above the melting point, while the stretched network proposes the situations of shearing or stretching below the melting temperature. In other words, the chosen shear or stretch temperature may be the critical factor in controlling the crystallization mechanism in the constraint studied system since shish formation is positively related to the change of chain entanglement. In the polymer melt with low entanglements, polymer chains move flexibly, particularly at a high temperature. Once a particular strength of flow field is exerted, chains with a molecular weight larger than the critical value in polymer melt may be pulled out from entanglement and undergo the coil-stretch transition and form shish with extended-chain crystal.

In contrast, disentangling the long chains at low temperatures is much more difficult, and consequently, only point crystal nuclei can be formed. Therefore, it is reasonable to expect that the shish formation from the two proposed mechanisms of CST and stretched network can be modulated by adjusting the temperature of flow fields in the dedicated studied system.

By choosing the bimodal PE system containing an HMW fraction with different ethyl branch contents, we recently found that the presence of short-chain branch favored the generation of shish-kebabs at shear temperatures higher than melting point (139 and 136 °C) and low shear rates of 1 and 3 s\textsuperscript{-1}, which supported the CST mechanism.\textsuperscript{[45,46]} In our recent study, the same bimodal PE system was used to investigate the formation of shear-induced shish-kebab crystals at shear temperatures.\textsuperscript{[47]} The results illustrated that shish-kebab crystals were also formed at the shear temperatures of 127 and 124 °C and a low shear rate of 3 s\textsuperscript{-1}, which supported the stretched network mechanism. Herein, to further confirm the shish crystals formation mechanism’s modulation functionality, the similar bimodal PE samples with the HMW fraction possessing different ethyl branch contents (with different molecular weights from our previous studies) were employed. The shish-kebab formed at 129 °C with a lower shear rate of 1 s\textsuperscript{-1} was tracked by in situ SAXS and wide-angle X-ray diffraction (WAXD) techniques.

**EXPERIMENTAL**

**Materials and Preparation**

Three Ziegler-Natta-based polyethylene (PE) samples were prepared using a custom-built reactor, in which a two-step polymerization reaction was carried out to produce the bimodal-MW characteristics. The reaction conditions, such as temperature, pressure, and fed H\textsubscript{2} for the 1\textsuperscript{st} and 2\textsuperscript{nd} steps of polymerization, were carefully controlled in order to obtain a W\textsubscript{HMW-PE}/W\textsubscript{LMW-PE}=80:20 composition ratio, where W\textsubscript{LMW-PE} represents the low molecular weight fraction and W\textsubscript{HMW-PE} represents the high molecular weight fraction. The reaction conditions for the preparation of three samples were almost identical, except that a portion of 1-butene gas was added to the 2\textsuperscript{nd} step polymerization to produce ethyl branched (C2) sample (labeled as LMW-PE+HMW-PE-C2). The sample infor-
mation, such as molecular weight, polydispersity ($M_w/M_n$), branch content, melting temperature, and crystallization temperature, are illustrated in Table 1. Films of these three samples with a thickness of 0.7 mm were prepared by compression-molding at 180 °C. Disk-like specimens (diameter: 32 mm) were cut from the melt-compressed films for in situ shear X-ray measurements.

**Characterization**

*Gel permeation chromatography (GPC)*

The GPC profiles of the samples were evaluated by the 3D-GPC instrument (Polymer Char, Spain), equipped with an IRS-detector, an intrinsic viscometer and an eight-angle light-scattering (LS) detector (Wyatt Technology). Each sample was dissolved in 1,2,4-trichlorobenzene (TCB) at 160 °C before injected into the GPC column at a controlled temperature of 140 °C to minimize polymer degradation.

13C-nuclear magnetic resonance ($^{13}$C-NMR)

The comonomer content of the sample was measured by a 500 MHz ASCEND instrument (Bruker) equipped with a cryogenic 10 mm probe (see NMR spectra in Figs. S1, S2 and S3 in the electronic supplementary information, ESI), in which the gate 13C-NMR spectra were recorded at 120 °C, where the inverse gate 13C (zgig) of the pulse program with 90° of the pulse angle was used. The delay time (D1) was set to 10 s for quantitative analysis.

**Differential scanning calorimetry (DSC)**

DSC (Figs. S4, S5 and S6 in ESI) tests were performed using a Mettler Toledo DSC instrument under the protection of the nitrogen flow at a rate of 50 mL/min. Samples of about 7.0 mg were first heated to 180 °C for 3 min to eliminate the thermal history, then cooled to 20 °C at a rate of 10 °C/min, then heated to 180 °C at a rate of 10 °C/min.

**Melt viscosity**

The viscosity was measured with a rheometer DHR-3 (TA instrument) using the 25mm-parallel plate geometry under the N2 atmosphere. The time-dependent viscosity measurement was carried out based on the synchrotron experimental protocol in Fig. 1.

**RESULTS**

It is first necessary to briefly depict the three bimodal PE samples’ varied content of ethyl branch. The GPC curves of the three samples shown in Fig. 2 are similar, and they exhibit a bimodal molecular weight distribution clearly. The main difference between the two distributions lay on the HMW fraction, where the LMW-PE+HMW-PE contained no short chain branch, LMW-PE+HMW-PE-C2-0.11 and LMW-PE+HMW-PE-C2-0.30 samples contained 0.11% and 0.30% ethyl content, respectively. The ethyl incorporation retarded the crystallization chain. Once reaching 149 °C, the time-resolved SAXS and WAXD patterns were collected every 10 s. The melt was then cooled to the shear temperature of 129 °C at a rate of 30 °C/min. The chosen shear duration was sufficiently long to ensure steady-state behavior. After shear, the sample was subsequently cooled to 124 °C at a 30 °C/min rate, under which temperature the sample was held for complete crystallization in 30 min.

**Synchrotron X-ray experiments under shear**

A Linkam CSS-450 optical shear stage, modified for in situ X-ray studies, was used to shear the polymer melt according to the protocol described above. The sample was placed in the gap between two X-ray windows (i.e., a diamond window and a Kapton window) and wholly enclosed in the cavity of the shear cell. In situ SAXS and WAXD measurements were carried out at the DB5 beamline in Advanced Photon Source (APS) of Argonne National Laboratory. The chosen X-ray wavelength was 0.073 nm. Two-dimensional (2D) SAXS patterns and WAXD patterns were collected using a Rayonix X-ray detector (LX170HS) with a resolution of 2048 pixel × 2048 pixel (pixel size = 265.8 μm). The sample-to-detector distance for SAXS measurement was 8505 mm, calibrated with the Spin Si, and the minimum q detected by the SAXS was 0.025 nm$^{-1}$. For WAXD measurements, the sample-to-detector distance was 200 mm, calibrated by lanthanum hexaboride (LaB$_6$). All X-ray images were background scattering, air scattering, and beam fluctuations corrected.

**SAXS and WAXD data analysis**

The analyses of SAXD and WAXD data were carried out using the X-Polar software package. The average shish length, ($L_{shish}$), was determined by using the Ruland streak method to analyze the meridional streak feature in SAXS. The observed azimuthal width, Bob, can be related to the length of shish, ($L_{shish}$), and the azimuthal width, $B_{obs}$, due to misorientation of shish by the Eq. (1) if all azimuthal distributions can be modeled by Lorentz functions.

$$B_{obs} = \frac{1}{(L_{shish})^2} + B_o$$  \hspace{1cm} (1)

On the basis of Eq. (1), ($L_{shish}$) can be obtained from the slope, and thus the plot based on Eq. (1) was used to determine ($L_{shish}$). In WAXD analysis, the degree of crystal orientation was obtained using Herman’s method. In specific, the degree of orientation, $I_{100}$, was calculated from the azimuthal intensity distribution, I($\phi$) of the (110) crystal reflection. The degree of crystallinity was calculated according to the diffraction intensity of the crystalline phase and amorphous phase, and the diffraction intensity was obtained through the integration from the azimuthal angle between 0° and 180°.

![Fig. 1](https://doi.org/10.1007/s10118-021-2568-1)
of the HMW fraction, which led to slightly lower melting temperature ($T_m$) and crystallization temperature ($T_c$) with the increase of ethyl content (Table 1). The weight average molecular weight ($M_w$) of LMW-PE+HMW-PE was higher than that of PE with a 0.11% branch and much higher than that of PE with a 0.30% branch. The lower $M_w$ in PE with higher ethyl is due to the chain-transfer reaction of 1-butene and the propagating chains during the polymerization which is generally found in the fixed-condition polymerizations with the varying comonomer content.

Based on the synchrotron experimental protocol (Fig. 1), the viscosities of the three samples with different contents of ethyl branch in the HMW fraction at the shear temperature of 129 °C are illustrated in Fig. 3 (the shear rate $\gamma=1$ s$^{-1}$ and the shear duration $t_s=100$ s). Both samples with ethyl branch exhibited a distinct shear thinning behavior during shear, while LMW-PE+HMW-PE showed a high viscosity and shear thinning behavior in the first 20 s and shear thickening behavior after 20 s. That the viscosity of samples decreased with the increase of ethyl content is certainly consistent with the lower $M_w$ value. Typically, if we constrain the $M_w$ of the PE samples, the short chain branch always yields higher viscosity due to higher chain entanglement. However, in this case, $M_w$ and $M_w/M_n$ of the three samples are different due to 1-butene as mentioned. The shear thickening behavior for the sample without ethyl may be due to more entanglement because of high $M_w$ and high HMW fraction and more crystals obtained because of low shear temperature.

The information about the evolution of shish-kebab structure during shear and subsequent crystallization (cessation of shear) was extracted directly from the 2D SAXS patterns. Fig. 4 shows selected in situ SAXS patterns of bimodal PE having HMW fraction with different ethyl contents at a different time before shear, during shear with a low shear rate of 1 s$^{-1}$ at 129 °C and isothermal crystallization at 124 °C. It can be observed that there was no sign of crystallization before shear. This shear-induced crystallization behavior of the bimodal PE is quite different from those sheared at high temperatures of 139 °C.[43] During shear, a scattering streak nearly perpendicular to the shear direction, which emerged at the shear time of around 50 s for the LMW-PE+HMW-PE sample, indicates the existence of shish crystals. A closer examination indicated that a weak meridian streak could be seen in LMW-PE+HMW-PE-C2-0.11 at the shear time of 50 s, but it submerged into the signal of other crystals quickly. It should be noted that no signal of shish appeared during shear for LMW-PE+HMW-PE-C2-0.30. The above SAXS results of shear-induced crystallization behavior of the bimodal PE are different from those similar bimodal PE samples sheared at lower temperatures of 127 and 124 °C in the rate of 3 s$^{-1}$, where more shish-kebab crystals were obtained.[47] It was interesting to note that the orientation of the streak rotated slightly against the shear direction in the initial stage of shear, but it became utterly perpendicular to the shear direction at the initial stage of crystallization. The occurrence of the streak rotation was owing to the small perturbations in flow of small amount of crystals in melts with low viscosity, referred to as “log-rolling alignment”. As the sheared samples were cooled to 124 °C upon cessation of shear, the meridional scattering maxima (along the shear direction) for LMW-PE+HMW-PE appeared immediately, which increased with crystallization time. These scattering maxima were resulted from the growth of kebab crystals whose long period was calculated to be 77.5 nm. For LMW-PE+HMW-PE-C2-0.11 and LMW-PE+HMW-PE-C2-0.30, no shish-kebab crystal was formed during crystallization. It was interesting to see that the scattering streak for

![Fig. 2 GPC profiles of the three bimodal PE samples with different contents of C2.](image)

![Fig. 3 Schematic diagram of the shear experiment protocol with different samples; the shear rate $\gamma=1$ s$^{-1}$, shear duration $t_s=100$ s.](image)

![Table 1 Parameters of the bimodal PE samples.](table)

| Sample                  | Ratio | C2 a content b (mol) | $M_w$ (kg/mol) | $M_w/M_n$ | $T_m$ c (°C) | $T_c$ c (°C) | Degree of crystallization % |
|-------------------------|-------|----------------------|----------------|-----------|---------------|---------------|-----------------------------|
| LMW-PE+HMW-PE           | 80:20 | 0                    | 279            | 57        | 131.1         | 119.3         | 86.6                        |
| LMW-PE+HMW-PE-C2-0.11   | 80:20 | 0.11                 | 221            | 35        | 131.0         | 118.2         | 83.8                        |
| LMW-PE+HMW-PE-C2-0.30   | 80:20 | 0.30                 | 181            | 35        | 129.3         | 118.1         | 80.5                        |

a C2 is ethyl group; b With respect to the total PE; c The melting peak, crystallization peak and degree of crystallization were obtained from DSC at a heating and cooling rate of 10 °C/min.

[52,53]
LMW-PE+HMW-PE-C2-0.11 disappeared after shear, which is consistent with the result of Ma et al., that the shish crystals of polyethylene with broad molecular weight distribution were dissolved in the shear field.\(^4\) A scattering streak along the flow direction, which emerged at the crystallization time of around 20 s for LMW-PE+HMW-PE-C2-0.11 and LMW-PE+HMW-PE-C2-0.30, indicates the existence of oriented crystals with the different periods perpendicular to flow direction. It seemed that the intensity of the signal for LMW-PE+HMW-PE-C2-0.30 was worse than that for LMW-PE+HMW-PE-C2-0.11. The above SAXS results indicated that the PE with no branch formed shish-kebab crystal more easily than PE with branch at the shear temperature of 129 °C.

In Fig. 4, it was found that the orientation of the shish for LMW-PE+HMW-PE did not change during crystallization. The change of shish length can be estimated using Ruland’s method based on the SAXS results of Fig. 4.\(^46\)–\(^48\) The shish length during the crystallization stage is illustrated in Fig. 5. The shish length increased gradually from 940 nm to 1100 nm during the crystallization stage, which displayed a contrary tendency to that sheared at high temperatures.\(^49\) It is worth noting that the length of the signal during shear was much longer than that during crystallization, although the length of shish could not be calculated during shear, indicating the substantial increment of shish length during the whole shear and crystallization process. During crystallization at low temperature, the shish length finally increased to a value slightly longer than that at high temperature.\(^45\)

The in situ WAXS patterns of bimodal PE with different ethyl contents sheared at 129 °C and crystallized at 124 °C are shown in Fig. 6. It can be seen that only the amorphous signal existed before shear, indicating that the chosen melting temperature, 149 °C, was sufficiently high to remove the previous thermal history. During shear, the LMW-PE+HMW-PE sample indicated that the faint diffraction arcs from the center (110) and (200) emerged in the median direction at the shear time of 50 s, while LMW-PE+HMW-PE-C2-0.11 and LMW-PE+HMW-PE-C2-0.30 only showed an amorphous signal. The diffraction peaks (110) and (200) did not appear until 20 s during crystallization for LMW-PE+HMW-PE-C2-0.11 and LMW-PE+HMW-PE-C2-0.30. The intensity of diffraction peaks for LMW-PE+HMW-PE-C2-0.30 was much weaker than that for LMW-PE+HMW-PE-C2-0.11 during crystallization, and it was too weak to be observed at the crystallization time of 20 s. The intensity of both diffraction arcs increased with time. The (110) diffraction peak of LMW-PE+HMW-PE remains arc-like with high orientation in the meridian direction, whereas those peaks of LMW-PE+HMW-PE-C2 turned into the arc-like oriented with lower direction.

The degree of crystallinity and overall crystal orientation of the three samples were calculated based on the WAXD patterns in Fig. 6. The crystallinity is shown in Fig. 7. It was found that the degree of crystallization for all the samples increased fastly at the beginning, then slowly with the crystallization time. The degree of crystallization of LMW-PE+HMW-PE increased up to 7%, while those of LMW-PE+HMW-PE-C2-0.11 and LMW-PE+HMW-PE-C2-0.30 increased up to 23%. The LMW-PE+HMW-PE-C2-0.30 sample showed a slightly higher degree of crystallization than LMW-PE+HMW-PE-C2-0.11.

Fig. 8 illustrates the orientation factor estimated from the (110) diffraction peak for the three samples after shearing at isothermal crystallization. It can be observed that the orientation of the LMW-PE+HMW-PE sample remained at a high value (above 0.60) at the entire experimental process. The ori-

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**Fig. 4** In situ SAXS patterns of bimodal PE with different contents of C2 at different time before shear, during shear at 129 °C (shear rate \(γ=1\) s\(^{-1}\), shear duration \(t_s=100\) s) and after shear at 124 °C. (a, a’) C2=0, (b, b’) C2=0.11%, (c, c’) C2=0.30%. The cross indicated the center of SAXS pattern.

**Fig. 5** The shish length of bimodal PE with no branch at different time during shear and after shear at 124 °C (shear temperature \(T_s=129\) °C, shear duration \(t_s=100\) s).

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After shear (crystallization at 124 °C)

Before shear
Shear (129 °C)
Flow axis
30 s 50 s 100 s
0 s 10 s 20 s 30 s 100 s

Fig. 6 In situ WAXD patterns of bimodal PE with different content of C2 at different time before shear, during shear at 129 °C (shear rate \( \dot{\gamma} = 1 \) s\(^{-1}\), shear duration \( t_s = 100 \) s) and after shear at 124 °C: (a, a′) C2=0, (b, b′) C2=0.11%, (c, c′) C2=0.30%.

Fig. 7 The degree of crystallinity of bimodal PE with different contents of C2 at different time after shear at 124 °C (shear temperature \( T_s = 129 °C \), shear duration \( t_s = 100 \) s).

Fig. 8 The orientation of bimodal PE with different contents of C2 at different time after shear at 124 °C (shear temperature \( T_s = 129 °C \), shear duration \( t_s = 100 \) s).

DISCUSSION

It has been well documented that kebab crystals are nucleated from the shish crystal, forming the shish-kebab structure, but the shish formation mechanism is not precise. As described in the Introduction section, both the CST and stretched network models were proposed to account for the shish formation, while whether the long chains can be pulled out from the entanglement to disentanglement state under flow field is the crucial issue. It can be concluded from the results described above and our previous study,[45–47] different shear temperatures resulted in very different, even contrary results. When the shear temperature was as high as above the melting temperature, such as 139 and 136 °C, polymer chains were easy to be pulled out from entangled melt and underwent CST to form shish. When the shear temperature is as low as close to the melting point or even crystallization temperature in our experiments of this study and our previous work,[45] the entangled polymer network is hard to disentangle at a low shear rate due to the long relaxation time,[55,56] so the CST cannot occur. Considering that bimodal PE’s viscosity at 129, 127 and 124 °C was larger than that at 139 and 136 °C, more work was applied on the polymer chains at low shear temperatures (the work was in direct portion to the viscosity). Under this condition, the stretching of entangled chains can form a significant number of point nuclei and then align and aggregate along the flow direction with enough shear duration time, resulting in the formation of shish nuclei, just like the analysis in our previous work.[45] It is therefore reasonable that the stretched network should be responsible for the formation of shish-kebab crystals under the above shear condition.

It should be noted that point and shish nuclei may coexist in the flow at the low shear temperatures. At the shear temperatures of 127 and 124 °C close to crystallization temperature and the low shear rate of 3 s\(^{-1}\) in our previous work,[46] the nucleation barrier of lamellar crystals is relatively low, forming more nuclei of lamellar crystals. However, alignment and aggregation along the flow direction are challenging, so the process from point nuclei to shish nuclei is the critical pro-

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cess for forming shish crystals. Therefore, the sample of LMW-PE+HMW-PE-C2-0.30 formed more shish crystals than the two other samples because of low viscosity. In our experiment condition mentioned above, the shear temperature of 129 °C is closer to melting temperature, and the shear rate of 1 s⁻¹ is much lower, the nuclei of lamellar crystals are diffusely formed, and the alignment of point nuclei are relatively straightforward. Therefore, point nuclei formation is the critical process under such conditions for the formation of shish crystals. Considering that more work was applied on the polymer chains in LMW-PE+HMW-PE because of the higher viscosity compared with those of the other two samples, the formation of shish crystals probably took place more readily in LMW-PE+HMW-PE, which is likely to be the reason that only LMW-PE+HMW-PE formed shish crystals at the shear temperature of 129 °C.

It should be noted that the shish-kebab crystals caused by stretched entangled chains are different from those formed by CST. This kind of shish-kebab crystal is indeed macro shish-kebab crystal, just like Han’s results. It is widely accepted that the macro shish crystals grow continually during the development of the shish-kebab crystals, therefore, the result that the length of shish increased with the crystallization time is confirmed in Fig. 5 confirms that the formation mechanism of shish at the shear temperature of 129 °C is stretch of network. Recalling the results of the development of the length of shish at the high temperature of 139 °C in our previous study, the length of shish declined rapidly with the shear time, implying the chains with higher Mₜ formed shish earlier, and the average length dropped with the shish formation of a more relatively short chain in HMW fraction, which confirmed that the formation mechanism of shish at high temperature was CST. Therefore, the different manners of development of shish length strongly support the conclusion of the different formation mechanisms of shish at different shear temperatures.

According to the four-stage model of the formation of polymer shish crystals in the shear field proposed by Mykhaylyk et al. and the four-stage model in the stretch field produced by Li et al., the process from the nucleus of common crystals to the shish nucleus is a crucial process for the formation of shish crystals, which is confirmed by the results of bimodal PE sheared at the low temperature close to the crystallization temperature in our previous study. The results sheared under the temperature close to the melting point in this work reveal that enough point nuclei formation is also the critical process under the specific condition for shish crystals. Housmans et al. pointed out that spherulites were formed when the shear rate was low and shear time was short. Therefore, shish crystals cannot be formed when the shear flow is not enough to complete the process from the nucleus of common crystals to the shish nucleus.

According to the four-stage model mentioned above, the number of the general crystal nucleus is much more than that of the shish nucleus. Many nuclei remained after cooling for the sample with the branch since no shish-kebab crystals were formed, promoting the growth of lamellar crystal. When the shear work is sufficiently high to overcome the entangled chain’s energy barrier, the stretched chains can lead to the formation of shish crystals. When the shear work is not enough for the stretch of entangled chains to form shish crystals, the shear work can make more chains partly oriented, forming more crystal nuclei and subsequent more lamellar crystals. Therefore, the degree of crystallization for LMW-PE+HMW-PE-C2 was much higher than that for LMW-PE+HMW-PE (Fig. 7), and the degree of orientation for LMW-PE+HMW-PE-C2 was much lower than that for LMW-PE+HMW-PE (Fig. 8). The degree of crystallization of LMW-PE+HMW-PE increased with time due to the growth of shish-kebab crystals. Based on the above analysis, we can conclude that the formation mechanism of shish-kebab crystals at the low shear temperature of 129 °C, different from that at high shear temperature, belongs to the mechanism of the stretch of entangled chains, namely, the stretch of network.

CONCLUSIONS

The formation of shish-kebab crystals using bimodal polyethylene having high molecular weight (HMW) fraction with different short chain branch contents under shear at a low temperature of 129 °C, was investigated using in situ SAXS and WAXD techniques. Only bimodal PE with no branch formed shish-kebab crystals, while the bimodal PE with branch only formed partly oriented lamellar crystals. This study indicated that the highly stretched chains could lead to the formation of shish crystals when the shear work was sufficiently high to overcome the entangled chain’s energy barrier at the low temperature of 129 °C. Otherwise, the shear work could enable more chains partly oriented to form more partly oriented lamellar crystals. The shish length increased with the crystallization time confirmed that shish crystals’ formation was due to the stretch of entangled chains under shear at low temperature. The bimodal PE sheared at the low temperature close to the crystallization temperature illustrated that the process from the nucleus of common crystals to the shish nucleus was critical for the generation of shish crystals in our previous study. The results sheared at the temperature close to the melting point in this work reveal that the process of enough point nuclei formation is also the critical process for the generation of shish crystals. Summing all the results at the shear temperatures higher, closed to, and lower than the melting point, the modulation of shish crystals formation owing to different mechanisms of the CST and the stretched network was achieved by changing shear temperature in bimodal PE. We believe this research is essential to deepen our understanding of the shear-induced shish-kebab crystals and help us develop new methods for improving the mechanical properties of bimodal PE products.

Electronic Supplementary Information

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