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Better Choice: Linear Long Chains Rather than Branched Ones to Improve Mechanical Performance of Polyethylene through Generating Shish-Kebabs

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Electronic Supplementary Information

Abstract We utilized two structurally different long chains (linear and branched ultra-high molecular weight polyethylene) to reveal the dependence of flow-induced crystallization on long chain architecture, and prepared two bi-disperse systems of 98 wt% short chain and 2 wt% long chain. A flow field was applied to the bi-disperse polyethylene melt by a modified injection-molding machine, known as oscillation shear injection molding (OSIM). For the first time, the structural influence of long chains on flow-induced shish-kebab formation was systematically investigated. For the intermediate layer of OSIM samples, the branched long chains were better than the linear long chains at inducing shish-kebab formation, agreeing with the reported literatures, because the branches can maintain their oriented conformations longer. But unexpectedly, the reverse is the case for the core layer of OSIM samples, where the shear flow was much weaker than the intermediate layer. To understand the unexpected phenomenon, the lifetime of shishes induced by different long chains was compared. Result demonstrated that the linear-induced shishes possessed higher thermal stability than the branched-induced ones so that the linear-induced shishes could survive in the core layer of OSIM samples. Additionally, unlike other methods for flow-induced crystallization, OSIM could create samples for measuring mechanical properties, and thus offer the chance to reveal the relationship between structure and performance. The mechanical results demonstrated that both long chains remarkably enhanced the mechanical properties because of the significant promoting effect of long chains and intense flow fields on shish-kebab formation. However, the linear long chains induced more stable and flawless shishes with higher tensile strength and modulus (80.4 and 1613.5 MPa, respectively) than the branched ones (74.4 and 1489.3 MPa). Our research not only helps elucidate the mechanism of shish-kebab formation but also provides a better choice to reinforce polymers by adding long chains with suitable structure.

Keywords Polyethylene; Crystallization; Shear-induced; Long chain; Short chain

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INTRODUCTION

Since the first discovery of the shish-kebab structure by Pennings *et al.* in 1965, many studies have explored the shish-kebab formation mechanism because it is of interest scientifically and is also an important industrial issue.^[1–6] A landmark discovery determined that long chain molecules could promote shish-kebab formation under flow fields more effectively than short ones because the long relaxation time of long chains can maintain their flow-induced oriented structure longer to more easily form shishes.^[7–10] Therefore, the positive effect of long chains on promoting shish-kebab formation provides a signifi-

cant method for adjusting the mechanical, optical, and physical properties in manufacturing processes.^[11–13] Additionally, from an industrial perspective, it is feasible to add a small quantity of long chains into the matrix of common commercial products to balance mechanical performance and processability. For instance, improved mechanical properties and puncture resistance can be achieved by adding a small quantity of long chains in biaxially oriented polypropylene processing.

However, most studies in this field to date have only cared about the effect of the fraction and molecular weight of the long chain component on shish-kebab formation under flow fields.^[14–18] Little research has paid attention to the role of the molecular architecture of long chains in shish-kebab formation. Since the long relaxation time of long chains is the major mechanism facilitating shish formation, their molecular structure should be a crucial factor in generating flow-induced shish-kebabs because molecular relaxation behaviors

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depend strongly on molecular structure.^[19–21] The structures of molecular chains include branching and cross-linking as well as linear backbone structure, as illustrated in Fig. 1. According to the tube theory, the simplest linear molecules (Fig. 1a) lose their oriented configuration by reptation, in which they diffuse curvilinearly along their confining tubes.^[22–24] Cross-linking (Fig. 1c) is an excellent way to suppress relaxation.^[25,26] Our previous results also show that a small amount of lightly cross-linked polyethylene (LCPE) could significantly promote shish-kebab formation, but redundant LCPE would lead to deficient shish structure.^[27,28] Another way to postpone relaxation is branching (Fig. 1b), because the branched molecule cannot reptate owing to the branch points. Instead, they renew their configurations by contour length fluctuations of the branched arms.^[29–32] Thus, chain branching can certainly influence flow-induced crystallization. Hsiao *et al.* observed that long chain branched (LCB) polypropylene could accelerate the crystallization kinetics during shish-kebab formation under shear by more than an order of magnitude compared to linear polypropylene.^[33] Wang *et al.* also demonstrated that LCB polylactide (PLA) can induce shish-kebab formation, but the linear PLA molecules cannot be stretched to generate shish-kebabs under a low shear rate of 1 s^{-1} .^[34] Moreover, Wang *et al.* ascribed the enhancement of nucleation ability and morphological evolution from spherulites to shish-kebabs under flow to the broadened and complex relaxation behaviors of the LCB structure. Here, we must emphasize that their experiments were performed in uniform polymer systems (*i.e.*, without any short chain matrix) and differed from most flow-induced crystallization experiments, where long chains are only a small quantity in a short chain matrix. Naturally, we are curious if long chains with different architectures can lead to different flow induced crystallization behaviors and properties when small quantities of them are added into a matrix of short chains. This is an interesting and meaningful question, which can provide deeper understanding of the effect of long chains on shish-kebab formation and also provide a reference to selecting different long chains in industry.

Therefore, we recently investigated the influences of linear and branched long chains on the formation of shish-kebab under the combination of pressure and flow by utilizing the custom-designed pressuring and shearing device and using ultra-high molecular weight polyethylene (UHMWPE) as a model polymer. Industrialized ultra-high molecular weight polyethylene is generally branched due to the use of a multi-active-site catalyst. In addition to the branched long chain

polyethylene (bcPE), linear long chain polyethylene (lcPE) was utilized in the work, which is a new species of UHMWPE and was synthesized by a heterogeneous single-active-site Ziegler-Natta catalyst at low temperatures. A synergistic effect between linear long chains and pressure on flow-induced shish-kebab was revealed.^[35] Nevertheless, the applied shear was weak and the mechanical properties of the prepared sample could not be measured owing to the limit of the device. Therefore, this work was carried out using a modified injection molding technique, known as oscillation shear injection molding (OSIM, see the electronic supplementary information, ESI).^[36,37] Unlike other devices for flow-induced crystallization investigation, OSIM technology can process samples for mechanical performance measurement, and thus offer the chance to reveal the relationship between structure and performance. A small amount (2 wt%) of branched and linear long chain polyethylene was added into short chain polyethylene (scPE) to obtain two bi-disperse systems for comparison. We explored the crystal morphology and structure, mechanical properties, and the shish-kebab formation mechanism upon application of a shear flow field afforded by OSIM. We observed novel and meaningful results: (i) linear long chains were better at inducing shish-kebab formation in the core layer of OSIM samples than the branched ones, and conversely, the branched long chains more easily retained their oriented configurations than the linear ones in the intermediate layer of OSIM samples, so shish-kebabs formed more easily; (ii) in the shish stability experiment, the shishes that contained branched long chains disintegrated more quickly than those containing linear ones, *i.e.*, the linear long chains could create shishes with higher stability than the branched ones; and (iii) higher tensile strength and modulus were obtained using linear long chains. These results not only give us a new viewpoint into the shish-kebab formation mechanism but also provide a better choice to reinforce polymeric products.

EXPERIMENTAL

Materials

scPE (trade marked as 2911) was purchased from Fushun Petroleum Chemical Co., Fushun, Liaoning Province, China. It is a short chain polyethylene with a melt flow rate (MFR) of 20 g/10min (190 °C, 2.16 kg), $M_w = 6 \times 10^4$ g/mol, and $M_w/M_n = 3.3$, where M_w and M_n are the weight-average and the number-average molecular weight, respectively. bcPE is branched UHMWPE ($M_w = 5.5 \times 10^6$ g/mol to 6.0×10^6 g/mol), which was synthesized by multi-site Ziegler-Natta catalysts coupled with

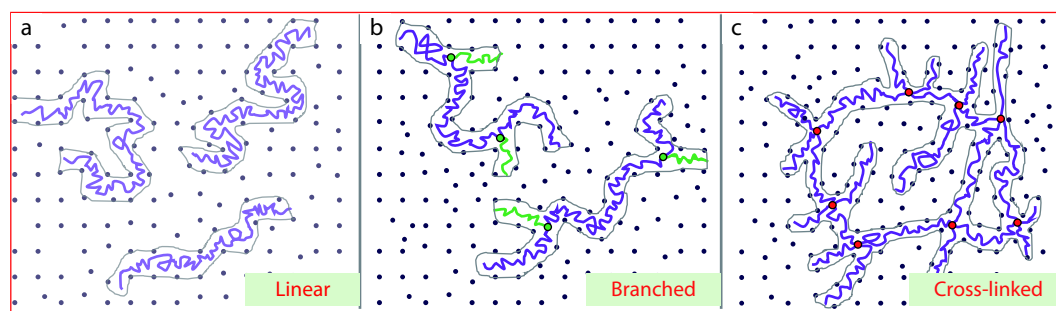


Fig. 1 Three types of molecules with different structures: (a) linear, (b) branched, and (c) cross-linked molecules.

the high polymerization temperatures (60–100 °C). This technique produces more chances for chain transfer between neighbouring and inner chains, which results in large amounts of branched chains and a hyperbranched UHMWPE structure. It was provided by Second Auxiliary Factory, Beijing, China. *lc*PE is linear UHMWPE ($M_w = 3.0 \times 10^6$ g/mol), which is a new species and kindly provided by the Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, China. The melting temperatures of *sc*PE, *bc*PE, and *lc*PE raw materials are 132.5, 141.1, and 141.4 °C, respectively (Fig. S1 in ESI). One prominent feature of *lc*PE is that its molecules are in a state of disentanglement, so it can flow above its melting point even with its M_w surpassing 3.0×10^6 g/mol and can also be processed with common methods such as injection molding. The molecular structure of the two UHMWPEs was characterized by melt-state ^{13}C -NMR and rheological tests. The results are in ESI. Additionally, to quantitatively discuss the effect of flow fields on molecular stretch, we list detailed molecular weight information and relaxation times of the three types of polyethylene in ESI.

Sample Preparation

20 wt% UHMWPE was mixed with *sc*PE by a solution blending procedure to ensure that the two species were well mixed at the molecular level. First, UHMWPE and *sc*PE were dissolved in xylene at 140 °C by continuous stirring in an oil bath to obtain uniform dispersion. Then, the solution was extracted by adding alcohol. After that, the extracted solid mixture was filtered and dried in a vacuum oven at 60 °C. The above dried *sc*PE/UHMWPE blend was used as a master batch to fabricate the system containing 2 wt% UHMWPE for injection molding by melt mixing in a twin-screw extruder. The concentration of 2 wt% UHMWPE is higher than the overlap concentration (c^*) of UHMWPE ($c^* = 0.23$ wt% and 0.18 wt% for linear and branched UHMWPE according to the equation $c^* = 3\overline{M}_w / \left(4\pi \left[\langle R_g^2 \rangle^{1/2} \right]^3 N_A \right)$, where $\langle R_g^2 \rangle^{1/2} / \overline{M}_w^{1/2}$ was approximately 0.46^[10,38]). The temperature of the extruder was maintained at 120, 180, 200, 200, 200, and 165 °C from hopper to die, and the screw speed was approximately 120 r/m. Finally, the dumbbell samples were molded by the OSIM technique as described in ESI and the temperature profile from hopper to nozzle was maintained at 120, 200, 200, 200, and 160 °C. For comparison, the samples were also prepared by conventional injection molding (CIM) under the same processing conditions but without oscillation shear flow. The CIM samples of *sc*PE blends with 2 wt% linear and branched UHMWPEs are coded as C-*sc*PE, C-*lc*PE, and C-*bc*PE, respectively, and the corresponding OSIM samples are denoted as O-*sc*PE, O-*lc*PE, and O-*bc*PE, respectively.

Two-dimensional WAXD Measurement

Two-dimensional (2D) wide-angle X-ray diffraction (WAXD) was conducted at the Advanced Polymers Beamline (X27C, $\lambda = 1.371$ Å) with a Mar CCD (with a resolution of 512×512 pixels and pixel size = 158 μm) as a detector in the National Synchrotron Light Source, Brookhaven National Laboratory. The sample-to-detector distance was 152 mm. Air and other background scatterings were subtracted from the experimental data in all data analyses. Seven positions (0, 500 (skin layer),

1000, 1500, 2000 (intermediate layer), 2500, and 3000 μm (core layer)) down from surface to interior were scanned. For evaluation of molecular orientation, the orientation parameter was calculated mathematically using Hermans' orientation function from the (110) reflection of WAXD for PE.^[39]

$$f_H = \frac{3 \langle \cos^2 \varphi \rangle - 1}{2}$$

where φ is the angle between the crystal plane normal and the reference direction (flow direction). $\langle \cos^2 \varphi \rangle$ is defined as follow,

$$\langle \cos^2 \varphi \rangle = \frac{\int_0^{\pi/2} I(\varphi) \cos^2 \varphi \sin \varphi d\varphi}{\int_0^{\pi/2} I(\varphi) \sin \varphi d\varphi}$$

where $I(\varphi)$ is the integrated intensity along with the azimuthal angle after background subtraction. The value of $f_H = 1$ indicates that the crystal planes are perfectly aligned perpendicular to the flow direction, and $f_H = 0$ means no preferred orientation.

Scanning Electron Microscopy (SEM)

For morphological observation of the crystalline phase, the samples were first cryogenically fractured in liquid nitrogen and then etched by a 1% solution of potassium permanganate in a blend of sulfuric acid and nitric acid. After that, the etched samples were coated with gold for better electrical conductivity. Observation was performed via a field emission SEM (Inspect-F, Fei, Finland), operating at 20 kV.

Differential Scanning Calorimetry (DSC)

DSC was performed using a TA-DSC Q2000 system with a constant heating rate of 10 °C/min under a nitrogen atmosphere. The data were collected from 60 °C to 160 °C and the sample weight was approximately 4–7 mg. To obtain more information about the variance in oriented structure induced by different long chains, thermal treatment experiments of OSIM samples to above the equilibrium melting point and recrystallization at 128 °C were performed. The experimental procedures for the annealing and recrystallization are described as follows. First, a specimen (4–7 mg) from the intermediate layer of the OSIM sample was heated to the thermal treatment temperature at 50 °C/min and held for 10 min to destroy the oriented structure. Subsequently, the specimen was cooled at 20 °C/min to the recrystallization temperature of 128 °C and held for 1 h.

Mechanical Properties Test

Tensile properties of all samples were studied at 23 °C using an Instron Instrument Model 5576 according to ASTM D-638 at a cross-head speed of 50 mm/min.

RESULTS

Hierarchic Crystalline Structure and Orientation

During conventional injection molding, the melt experiences a strong shear in the filling process, while OSIM allows the melt to undergo consistent shear until the sprue freezing that generally happens during the time when the melt in the intermediate layer is solidified. In other words, the melts of CIM and OSIM samples experience different shears, especially in different layers. Therefore, considering the possible relation between crystalline structure and the location in the injection-molded

sample, we characterized the crystal structure of CIM and OSIM samples at different locations *via* WAXD. The results can aid in understanding the influence of long chain architectures on flow field-induced crystalline structure.

Fig. 2 shows the 2D WAXD patterns, all of which exhibit two diffraction reflections indexed as (110) and (200) from inner to outer for PE, respectively. Because flow usually induces oriented crystals, the (110) intensity distribution along the azimuthal angle between 0° and 360° was integrated to reveal the crystal orientation, as shown in Fig. 3. Furthermore, the orientation parameters for OSIM samples were also estimated from the azimuthal distributions of (110) reflection (Table 1). For C-scPE, we can see isotropic diffraction circles (Fig. 2) without variation in azimuthal intensity (Fig. 3a) from the skin to the core layer, which suggests that there is no appreciable oriented structure. Generally, it is common for CIM samples to contain some oriented structure in the skin layer because of rapid crystallization and freezing during filling. However, oriented crystals do not appear in C-scPE. This confirms the fast molecular relaxation of the short chains of the PE matrix caused by the high mold temperature (60°C). For C-bcPE and C-lcPE, slightly discrete (110) reflections can be seen, indicating a weak molecular orientation. The corresponding wide azimuthal integration of both C-bcPE and C-lcPE also provides evidence to confirm the weak molecular orientation. Thus, we can reliably conclude that both linear and branched long chains are helpful for oriented structure

formation. This phenomenon may be attributed to the stronger ability of long chain components to remain in oriented conformations that were generated during mold filling.

Unlike CIM samples, OSIM samples show distinct arc-like diffractions that represent crystals oriented because of the application of the strong flow field. For the O-scPE sample, the arc-like diffractions of the (110) plane are clearly seen at the 500 and 1000 μm positions in the patterns. This outer region oriented structure can also be confirmed by the narrow peak in Fig. 3(a1) and the high orientation parameter (0.64) at 1000 μm (Table 1). Comparing the WAXD data of O-scPE with those of C-scPE, the oriented crystals in O-scPE should undoubtedly be ascribed to the intense shear provided by OSIM. In the inner regions (distance surpassing 1000 μm), the diffractions become isotropic and the azimuthal width is also broader than that of the skin layers ($< 1000 \mu\text{m}$). The weak orientation of the inner regions stemmed from significant relaxation of flow-induced oriented molecules due to slow solidification and cessation of shear after the mold gates froze. This result demonstrates that it is hard to generate large oriented crystals in samples for PE matrices of only short chains, especially in the inner regions, even when using the OSIM technique. For O-bcPE, a high orientation signal appears in the larger regions from 500 μm to 2000 μm (Fig. 2) and the degree of orientation reaches 0.88. Formation of many oriented crystals in O-bcPE implies that bcPE is more beneficial in promoting oriented structure formation, which is due to

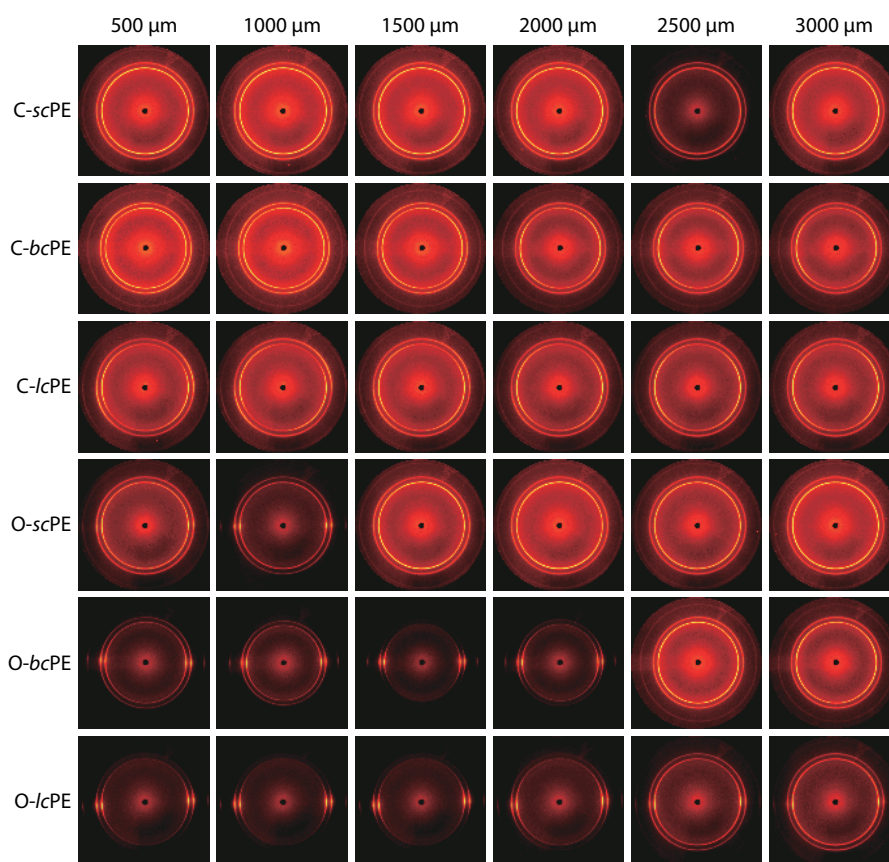


Fig. 2 2D-WAXD patterns. The numbers at top of the patterns indicate the positions away from the surface of specimens, where X-rays irradiate. The flow is in vertical direction, and the flow condition is released in ESI.

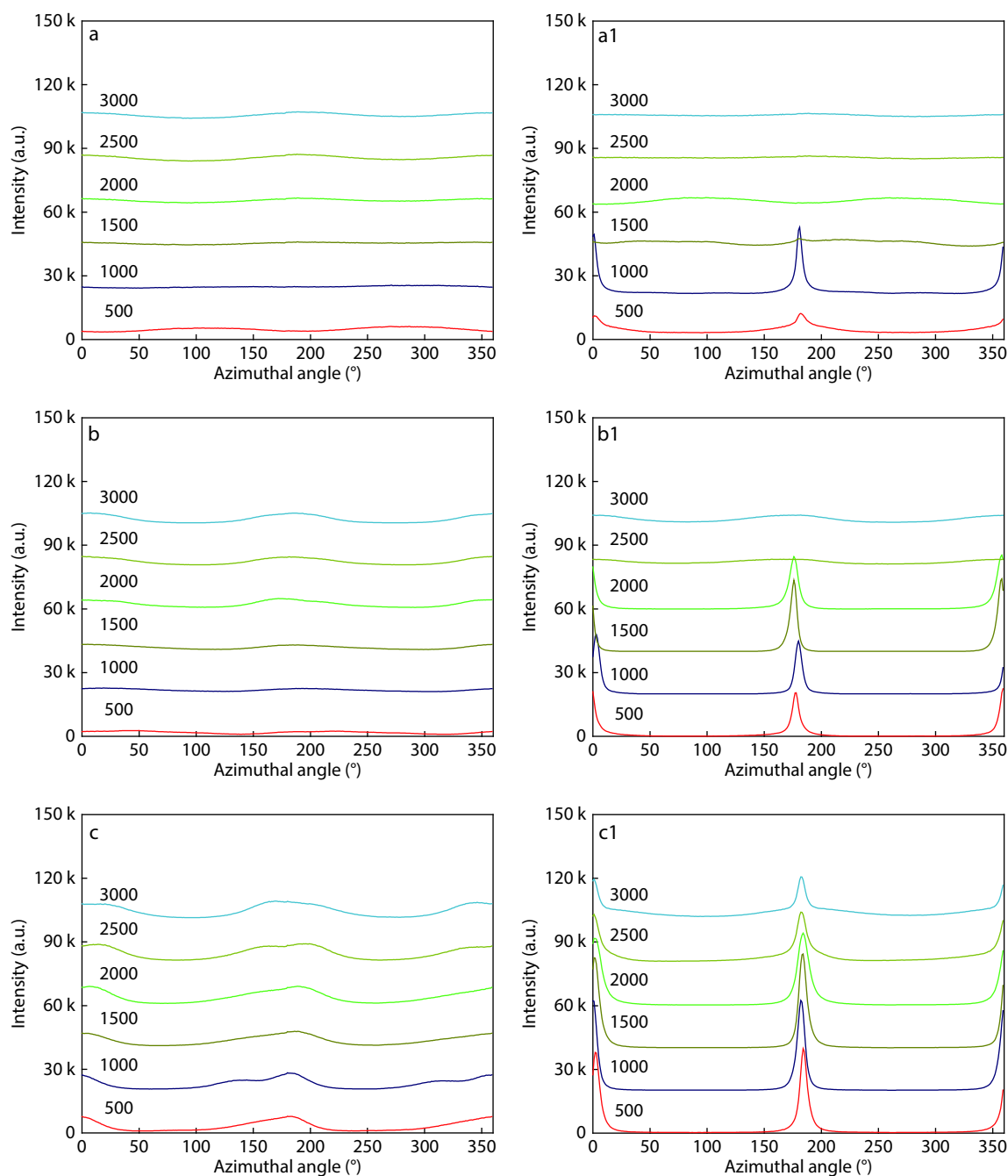


Fig. 3 Intensity distribution of crystal planes along the azimuthal angle from 0° to 360°: (a) C-scPE, (b) C-bcPE, (c) C-lcPE, and (a1–c1) the corresponding OSIM samples. The numbers above curves represent the positions sampled.

Table 1 Orientation parameter of OSIM samples calculated from the azimuth diffraction curves of the (110) plane.

	Position (distance away from surface, μm)					
	500	1000	1500	2000	2500	3000
O-scPE	0.43	0.64	0.03	0.07	0.03	0.03
O-bcPE	0.68	0.83	0.88	0.60	0.13	0.24
O-lcPE	0.81	0.80	0.81	0.77	0.74	0.47

the longer relaxation time of UHMWPE components compared to scPE. Additionally, isotropic diffractions appear in the regions from 2500 μm to 3000 μm (*i.e.*, the core layers), as

shown in Fig. 2. Finally, the azimuthal width of the core layers is broader than that of the outer layers (Fig. 3b1) and the orientation parameters decrease to ~ 0.24 (Table 1). We believe the low orientation in the core layer of O-bcPE originates from the branched arms that increase the difficulty for the long chains to be oriented under weak shear. To our surprise, unlike O-bcPE, after the linear long chains were incorporated (sample O-lcPE), the diffraction reflections of the (110) plane are highly anisotropic in all the regions from 500 μm to 3000 μm away from the surface, as depicted in Fig. 2. One can also see that the azimuthal width of each layer is sharp and

narrow (Fig. 3c1) and that all the orientation parameters reach 0.80 or above (Table 1). These results indicate the highly oriented nature of crystals throughout the whole O-*lc*PE sample and are unexpected from the common point of view. Generally, it is believed that branched molecules effectively suppress their relaxation when oriented under flow due to their broadened and complex relaxation behavior.^[40,41] Thus, one may suppose that it is easier for branched molecules under flow to retain oriented conformations and form oriented crystals than linear ones.^[33,34] However, we obtained different results from this traditional view. These intriguing results give us a chance to deeply understand the mechanism of shish-kebab formation and let us query if the conventional conclusion can be applied to our systems because the linear and branched long chains are surrounded by significantly shorter chains rather than other linear and branched long ones (*i.e.*, a melt that contains only long chains). We speculate that this abnormal phenomenon has two causes. First, oriented structures containing branched long chains relax more easily compared to those containing linear ones. Second, branched chains are more difficult to orient under a weak shear than the linear ones due to the hindrance of the branched arms of the branched long chains.

In addition to the crystalline structure, the crystallinity of OSIM samples may be related to the long chain architecture. To examine the dependence of crystallinity on the long chain structure, we circularly integrated intensities of 2D-WAXD patterns to gain 1D-WAXD profiles. Three Gaussian functions were used to fit the crystalline peaks (110 and 200) and the amorphous peak according to the deconvolution-peak technique.^[15,42] The peak parameters, *i.e.*, height, width, and area of each crystal reflection, were obtained after the iterative peak-fitting procedure. The overall crystallinity (X_c) was calculated using the following equation:^[15,36]

$$X_c = \frac{\sum A_{\text{cryst}}}{\sum A_{\text{cryst}} + \sum A_{\text{amorp}}} \quad (1)$$

where A_{cryst} and A_{amorp} are the fitted areas of the crystalline and amorphous phases, respectively. The estimated crystallinity at different positions of the OSIM samples is depicted in Fig. 4. One can see that the crystallinity of O-*sc*PE is the highest (79%) at a position 1000 μm away from the surface, where there is a strong shear field. At the same location, the highest orientation parameter is observed (Table 1). We believe this is a direct correlation between crystallinity and flow field, not coincidental. When polymer chains are oriented and stretched, the entropy and energy barrier to form crystals are notably reduced and the related crystalline kinetics are accelerated.^[43–46] In the meantime, ordered chains can enter the lattice more easily than random ones. Hence, the crystallinity can be enhanced by shear. For positions where the orientation degree is low, the crystallinity is low as well. This can be ascribed to the relaxation of oriented molecular chains. In other words, high orientation will lead to high crystallinity for our systems. When inspecting the inner regions, the crystallinity rises from 55% at 2000 μm to 62% at 3000 μm . The discrepancy of crystallinity among regions across the section of sample can be explained from the perspective of the crystallization process and conditions. Crystallinity depends on multiple factors, such as nucleation and growth rates of crystals and crystallization time, which all vary at

different sample positions. The total crystallinity at a given position in OSIM specimens is a comprehensive result. The high crystallinity at 1000 μm simply demonstrates that the shear flow overwhelmingly dominated the crystallization. Conversely, in the core layer, the crystallization time was long due to the slow solidification and hence led to a relatively high crystallinity despite the weakest shear flow compared with that at 2000 μm . When the long chain PE component was added, one can see that the crystallinity at all positions for both O-*lc*PE and O-*bc*PE samples is higher than that of O-*sc*PE. This suggests that long chains are favorable not only to facilitate oriented crystals formation but also to enhance crystallinity. Comparing O-*bc*PE with O-*lc*PE, the crystallinity of O-*bc*PE is higher than that of O-*lc*PE in the outer regions (below 2000 μm). The higher crystallinity of O-*bc*PE can be ascribed to the higher nucleation density and longer relaxation time for branched structures^[34] at the same position. In the inner regions (≥ 2500 μm), the crystallinity of O-*bc*PE decreases quickly to approximately 70%, less than the 77% of O-*lc*PE. These results indicate an interesting conclusion that linear long chains can more notably promote crystallization under a weak flow field than branched ones. Meanwhile, branched long chains are more dependent on the flow field to enhance crystallinity than linear chains. In other words, it is more difficult to orient branched long chains under weak shear (in the core regions, here) than linear ones. Therefore, the O-*bc*PE sample possesses low crystallinity because of the low degree of orientation. In contrast with the outer regions of O-*lc*PE, the crystallinity in the inner regions of O-*lc*PE decreases only slightly, showing a trend of change similar to the orientation parameters. This long chain structural dependence of crystalline structure and crystallinity is intriguing and is seen for the first time for flow-induced crystallization.

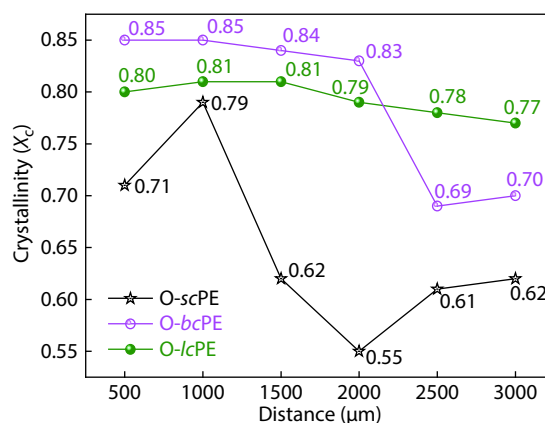


Fig. 4 Evolution of the total crystallinity (X_c) of OSIM samples obtained by deconvolution the peaks of 1D-WAXD profiles as a function of distance.

Crystalline Morphology

To obtain a clear understanding of the crystalline morphology of CIM and OSIM samples, direct observation was performed with a high resolution SEM, as shown in Figs. 5 and 6, respectively. We only picked up images at 1500 μm away from the surface because the shear contrast between CIM and OSIM samples is the strongest there and more information on the influence of shear on crystalline morphology can be gained.

Fig. 5 shows the crystalline morphology 1500 μm away from the surface of CIM samples. It is seen that random lamellae exist in C-scPE without any trace of preferential orientation (Fig. 5a). The absence of oriented structure is due to the weak shear, short molecular chains, relatively high mold temperature, and slow solidification leaving sufficient relaxation time for the oriented molecules formed during mold filling. Some slightly oriented lamellae also appear in both C-bcPE and C-lcPE (Figs. 5b and 5c). This difference still demonstrates that long chains are helpful for oriented crystal formation even when the shear flow is weak or lasts a short time. At the same position, for OSIM samples (Fig. 6a1), no clear oriented lamellae are observed in O-scPE, while an amazingly large number of oriented crystals in typical shish-kebab superstructures (Figs. 6b1 and 6c1) appear in both O-lcPE and O-bcPE. The marked crystalline morphology disparities between OSIM samples indicate that both the branched and linear long chains could facilitate shish-kebab formation. Fig. 6(a2) shows the crystalline morphology 1000 μm away from the surface of O-scPE. One can see clear shish-kebabs, in good agreement with the WAXD result. Since the two regions (1000 and 1500

μm) have strong flow and the sole difference between them is the cooling time, we can ascribe the absence of shish-kebabs at 1500 μm to the notable relaxation of oriented molecular conformations caused by slow solidification. Thus, to form shish-kebabs, a sufficient flow field and suitable cooling rate are necessary. Comparing the SEM images of the core layer of O-lcPE and O-bcPE samples (i.e., Figs. 6b2 and 6c2), we find that shish-kebabs were detected only in O-lcPE, also in line with the WAXD results. This phenomenon can be explained by orientation and relaxation. The branched long chain is more difficult to orient under a weak shear field. Meanwhile, the oriented structure relaxation of the branched long chains is faster than the linear ones, and there are therefore no shish-kebabs in the core layer of O-bcPE.

Thermal Behavior (DSC)

To further examine the discrepancy of shish-kebabs formed by different long chains, the thermal behaviors of OSIM samples (1500 μm away from the surface) were investigated by DSC (Fig. 7). One can see two melting peaks in the O-lcPE and O-bcPE samples, while there is only one for O-scPE. The low

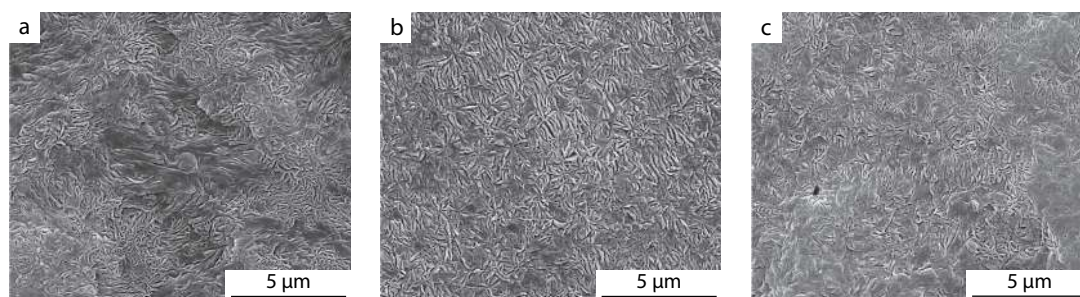


Fig. 5 SEM micrographs at the position of 1500 μm away from the surfaces of CIM samples after etched: (a) C-scPE, (b) C-lcPE, and (c) C-bcPE.

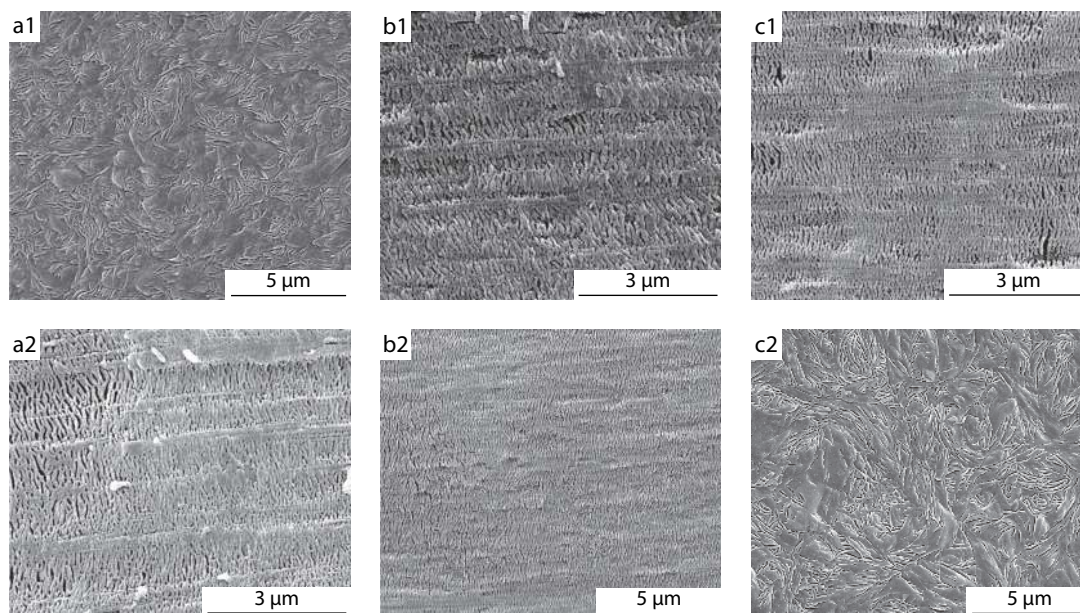


Fig. 6 SEM micrographs of different positions of OSIM samples after etched: (a1) O-scPE, (b1) O-lcPE, and (c1) O-bcPE at the position of 1500 μm away from the surfaces; (b2) O-lcPE and (c2) O-bcPE at the position of 3000 μm away from the surface; (a2) the crystalline morphology at the position of 1000 μm away from the surface of O-scPE. The flow direction is horizontal.

temperature melting peak of O-*lc*PE and O-*bc*PE and the sole melting peak of O-*sc*PE are almost the same, at approximately 132.4 °C, while the high melting peaks of O-*lc*PE and O-*bc*PE are 136.6 and 136.0 °C, approximately 3.6 and 4.2 °C higher than the low melting temperature, respectively. Considering the crystalline structures observed in the SEM images, *i.e.*, the abundant shish-kebabs in the intermediate layers of O-*bc*PE and O-*lc*PE, we conjecture that the low and high melting peaks must be from the melting of kebabs (lamellae) and shishes, respectively.^[27,47] O-*sc*PE has only one melting peak, but it does not mean the absence of shishes. As observed from the SEM images (Fig. 6a2), the shish-kebabs exist, but their content is very possibly too low to be detected by DSC. The same lamellar melting temperature for O-*sc*PE, O-*bc*PE, and O-*lc*PE implies that *sc*PE and the long chain-based systems formed lamellae with a nearly identical thickness distribution. It is conceivable because the growth of kebab is associated with the diffusion of coiled segments onto the shish^[48,49] and the formation of kebabs during cooling depends on the crystallizability (chain mobility) of individual chains as the shishes have already formed.^[50] As to the higher shish melting point (*i.e.*, high temperature peak) of O-*lc*PE than O-*bc*PE, we speculate it resulted from the higher integrity of the shish structure in O-*lc*PE. There are two possible factors leading to incomplete shish formation for branched long chains. First, it is more difficult for the branched chains to disentangle or to adjust their configurations in the melt relative to the linear ones because the branched points cannot disentangle (and can even block the whole molecule slipping), but the physically entangled points in linear chain can. Therefore, the regular arrangement of long chains in shishes was impeded for O-*bc*PE. Second, branched chains could lead to incompact stacking when incorporated in crystals.^[51]

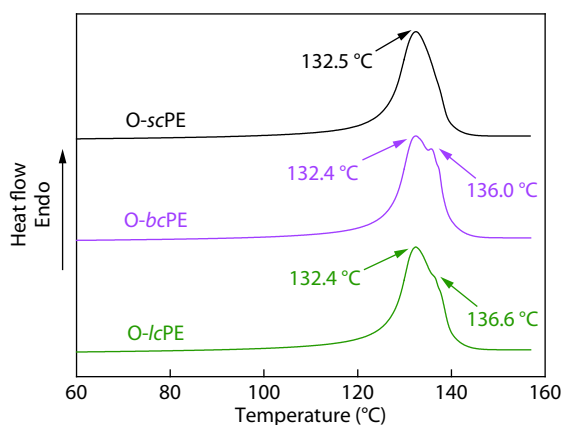


Fig. 7 DSC melting curves of O-*sc*PE, O-*lc*PE, and O-*bc*PE samples at 1500 μm away from the surface nearby.

According to the above results, we find there are three types of shishes generated in our OSIM samples: shishes existing only in O-*sc*PE, which were created by only *sc*PE, shishes from both *lc*PE and *sc*PE molecules in O-*lc*PE, and shishes from both *bc*PE and *sc*PE molecules in O-*bc*PE. For simplicity, we name the two types of shishes that contain branched and linear long chains B-shish and L-shish, respectively. To further explore the structural differences between the L- and B-

shishes, we designed a melting recrystallization experiment to estimate their lifetimes. This test could be performed because shishes are more stable than kebabs or common lamellae,^[52,53] as shown in Fig. 8. Therefore, it is reasonable to expect a portion of highly oriented shishes to remain, but the kebabs are completely melted during thermal treatment (the temperature is just above the equilibrium melting point of polyethylene, $T_m^0 \sim 145.5$ °C^[12]). The oriented structures remaining after heat treatment can serve as nuclei for recrystallization; thus, a high crystallization rate means more stable shishes (longer lifetimes). In this case, the half-time crystallization ($t_{1/2}$, which is defined as the time taken from the onset of crystallization until 50% completion of the crystallization process^[54]) was used to evaluate the shish lifetime. The half-time crystallization ($t_{1/2}$) versus annealing temperature (T_a) is shown in Fig. 8(b). O-*sc*PE was specifically excluded because we focused on the shishes induced by the long chains, and the shish content is low for O-*sc*PE. Fig. 8(b) shows that both O-*lc*PE and O-*bc*PE have a short $t_{1/2}$ when the annealing temperatures were above 180 °C, and the difference between their $t_{1/2}$ values is small. However, once the heat treatment temperature was increased to 220 °C, $t_{1/2}$ of O-*bc*PE promptly increased from 6.84 min (180 °C) to 13.13 min, while that of O-*lc*PE gradually rose from 6.62 min (180 °C) to 8.99 min, suggesting a faster crystallization rate of O-*lc*PE. These results in-

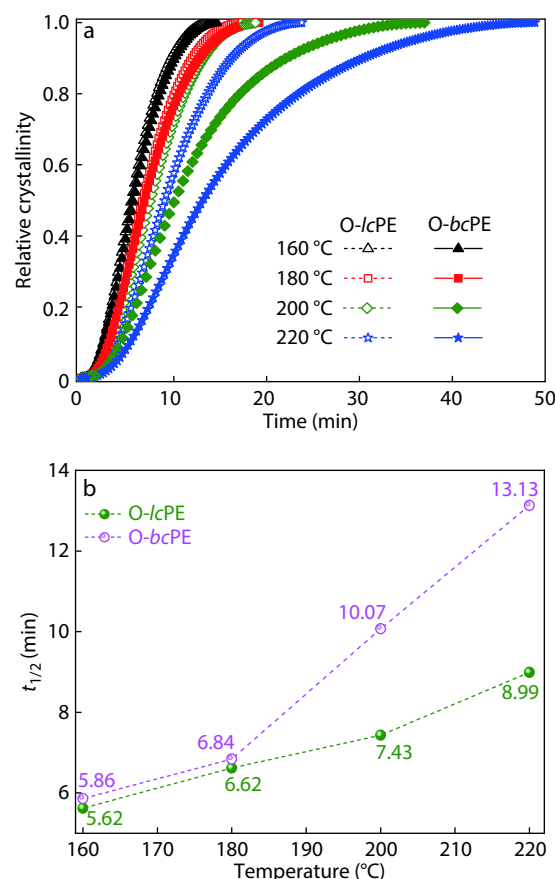


Fig. 8 DSC results: (a) relative crystallinity $X(t)$ versus different crystallization times t in the process of isothermal crystallization at 128 °C for OSIM samples; (b) half-time crystallization ($t_{1/2}$) against annealing temperature (T_a) for O-*lc*PE and O-*bc*PE samples.

dicating that the L-shishes are more stable than the B-shishes. In other words, the shishes containing *bc*PE quickly collapsed during annealing at a higher temperature ($> 180\text{ }^{\circ}\text{C}$), whereas gradual melting occurred for the shishes with linear chains. We ascribe this phenomenon to the more compact structure of L-shishes compared to B-shishes because the linear chains are favorable for entering lattice and compact arrangements. Conversely, the branched chains of *bc*PE are a hindrance to regular crystal packing of its main chains, resulting in loose and imperfect shishes. Besides, the branched arms with strong movement ability can facilitate the dissolution of shishes. The quiescent experiment results (*i.e.*, the *bc*PE has a faster crystallization rate under quiescent conditions than the *lc*PE because the branch points can serve as nucleation points^[34]) further testify that the accelerated crystallization of O-*lc*PE during the heat treatment experiment likely arose from the residual oriented nuclei of more stable shishes.

Mechanical Properties

Studies on flow-induced polymer crystallization have been broadly performed, but the relationship between mechanical properties and flow-induced structure receives limited attention because of the lack of research equipment that can process samples for mechanical measurement. A prominent advantage of our OSIM technology based on traditional injection molding is its capability of allowing simultaneous study on crystal structure and mechanical performance. Fig. 9(a) illustrates the stress-strain curves of CIM and OSIM samples. The CIM samples present normal stress-strain curves with ductile failure, and the elongations at break are 570%, 148%, and 140% for C-*sc*PE, C-*bc*PE, and C-*lc*PE, respectively. Undoubtedly, the addition of long chains caused the drop in elongation at break because the long chains promoted oriented crystal formation and enhanced entanglement of molecules, thereby preventing molecular chain slippage under stress. For all OSIM samples, the elongation at break further dramatically decreased to approximately 25%. First, this drop mainly stemmed from the flow-induced anisotropic structure (shish-kebab) because two neighboring shish-kebabs can mesh with each other, *i.e.*, a lamella in a shish-kebab may grow into the space between two lamellae of an adjoining shish-kebab. Samples with this intermeshing structure certainly can bear larger stress under load and prevent necking, exhibiting a brittle behavior dependent on the quantity and distribution of shish-kebabs. Second, according to our calculation, the values of crystallinity for C-*sc*PE, C-*lc*PE, and C-*bc*PE are 0.59, 0.66, and 0.68, respectively, much lower than those of the corresponding OSIM samples (0.65, 0.79, and 0.79, respectively). The increased crystallinity in OSIM samples indicates that more rigid components exist in the system. Furthermore, the enhancement of crystallinity means that more entanglements were excluded to the amorphous regions. The enhanced entanglements in amorphous regions further intensify the connection between different crystals and impede molecular slippage, leading to a lower elongation at break.^[55,56] Fig. 9(b) presents the tensile strength and modulus of as-prepared samples. For CIM samples, one can see that addition of 2 wt% branched and linear long chains brought about an increase of 5.5 and 9.4 MPa, respectively, for tensile strength compared to *sc*PE. This result indicates that a very small number of long chains can also show a reinforcing effect under the CIM

condition. Presuming that oriented crystallites can strengthen mechanical properties, the reinforcement should be linked to a great number of oriented crystals generated in the specimens as per our previous research results.^[28,57] Additionally, the WAXD results show there are indeed oriented structures in C-*bc*PE and C-*lc*PE, although the orientation degree is low. As for the modulus of CIM samples, one can see a slight decrease caused by the addition of long chain components. This is likely because some long chains were excluded to the amorphous regions in C-*bc*PE and C-*lc*PE and even influenced the matrix crystallization.

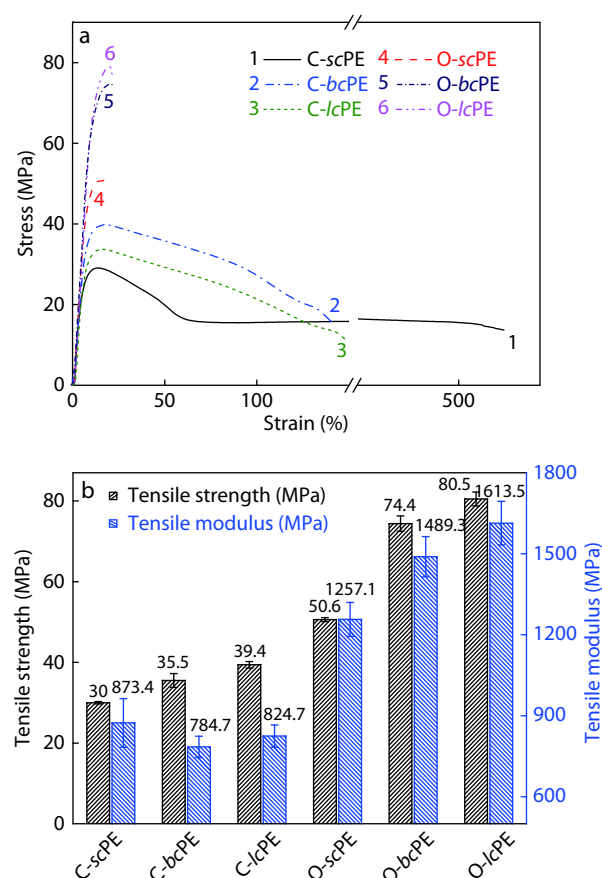


Fig. 9 Tensile properties of injection molding samples: (a) stress-strain curves; (b) tensile strength and modulus.

When the OSIM technique was employed, the tensile strength and modulus of samples markedly increased. As seen from Fig. 9(b), the tensile strength of O-*sc*PE increased notably from 30.0 MPa of C-*sc*PE to 50.6 MPa, while the Young's modulus was enhanced from 873.4 MPa to 1257.1 MPa. The considerable mechanical property changes should be associated with the flow-induced structural transition from isotropic spherulites to highly oriented shish-kebabs and the increased crystallinity and entanglements in the amorphous region. The most attractive result is the remarkable reinforcement of OSIM samples with long chains. The tensile strengths of O-*bc*PE and O-*lc*PE reach 74.4 and 80.5 MPa, respectively, which are 44.4 and 50.5 MPa above that of C-*sc*PE. The tensile moduli of O-*bc*PE and O-*lc*PE reach 1489.3 and 1613.5 MPa,

respectively, 232.1 and 356.4 MPa higher than that of C-scPE. The further reinforcement must be due to structural changes in O-lcPE and O-bcPE samples from long chains, that is, a large number of oriented lamellae were created as evidenced by SEM and WAXD data. The discrepancy between O-lcPE and O-bcPE in mechanical properties should come from the different distribution of shish-kebab across the sample section, *i.e.*, the core layer of the O-lcPE sample contains shish-kebabs while there are only spherulites and some lightly oriented lamellae in the core layer of the O-bcPE sample, as suggested by WAXD and SEM results.

DISCUSSION

The above experimental results demonstrate that both branched and linear long chains are beneficial to the formation of shish-kebab under a flow field and hence lead to a dramatic increase in mechanical performance—tensile strength increased from 30.0 MPa to 74.4 MPa for the branched and to 80.5 MPa for the linear. Even more attractively, an unusual molecular architecture dependence of shish-kebab formation was observed for the first time. B-shishes did not appear in the core layer of OSIM sample, while L-shishes did. Beyond that, the B-shishes showed a shorter lifetime than the L-shishes, especially at the high heat treatment temperature. This study is of importance not only for guiding practical processes to reinforce polymer products through promoting shish-kebab formation but also for allowing us to rethink the mechanism of shish-kebab formation under flow. Further discussion is needed to better understand the influence of long chain architecture on shish-kebab formation under flow fields.

Structure and Constituent of Shishes

For systems containing long chains, the constituents of flow-induced shishes have been disputed. Kanaya *et al.* disclosed the hierarchic structure of long object (or row structure) that was caused by deformed networks of high molecular weight components.^[58] They verified that oriented chain segments would recruit short chains adjacent to them to form shishes.^[59] Furthermore, Hsiao *et al.* found that the solvent-extracted UHMWPE residues of shear-induced shishes revealed the existence of multiple shishes, instead of a single shish, in the shish-kebab structure.^[49] The above results clearly indicate that shishes are composed of both deformed molecular networks and the chains of the matrix. If these are true, as shear flow is applied on melt in our present study, the networks which are formed by long chains would be oriented and stretched. The deformed networks are aligned along the flow field and can recruit neighboring chains (usually short chains of the matrix) to join them to form shishes. Thus, shishes contain short chains as well as long chains. Moreover, L-shishes are compact due to the relatively easy slippage or disentanglement among linear long chains, while for the branched chains, slippage between chains is difficult because of the branched arms. Hence, partial branched chains are certainly included in the deformed networks to generate shishes, leading to a loose stack and more crystal defects. The difference in shish structure between O-bcPE and O-lcPE can be demonstrated by the fact that the B-shishes show a lower melting point than L-shishes.

Furthermore, the different shish lifetimes give us a hint about their structures and constituents. Under the heat treatment temperatures, the oriented lamellae (*i.e.*, kebabs) melt completely. Hence, the promotion effect on recrystallization mainly comes from the more stable oriented crystals (*i.e.*, shishes). The discrepancy of the sample half-time crystallizations can certainly reflect the difference in the shishes they contain. To reveal shish structure, we have to analyze the shish melting process, *i.e.*, a relaxation process from orientation to disorder. To achieve re-equilibration during melting, each chain in shishes needs to disengage from all clusters in which it is involved. Alfonso *et al.*^[53,60] found that the lifetime of shish is much longer than the longest chain's rheological relaxation time. The relaxation time of shishes commonly decreases when increasing the annealing temperature, with an Arrhenius dependence. From the Arrhenius plots, Janeschitz-Kriegl *et al.*^[61,62] computed the apparent activation energy of the relaxation process of flow-induced oriented nucleus to be much greater than that of viscous flow. These facts indicate that the relaxation of shish is not the simple recovery of unperturbed molecular conformation but is rather related to detachment of chain segments from the lateral surfaces of oriented structures. In general, the dissolution of shish depends on its size, constitution, degree of order, population, and so on.^[63,64] For example, according to the classic nucleation, only when the size of a nucleus surpasses the critical value can it stably exist to induce further crystal growth, and others will be dissolved. Balzano *et al.*^[48] studied the dissolution of shear-induced shish in polyethylene and found that the initial part of dissolution evolution can be described well by the modified Doi-Edwards memory function and the dimensions determine the subsequent evolution of crystallization or relaxation. Fu *et al.*^[65] also disclosed that the larger shishes produced at a higher shear rate have a longer lifetime. The ordered aggregates (ordered packing) restrict the chain movement and lead to a prolonged relaxation process. Cui *et al.*^[66] suggested that the shish with the highest order has the highest stability. Except for the shortest shish, the long shish will also relax and consequently break back into relatively short ones because of the defective sections. Li *et al.*^[67] claimed that interactions between flow induced helices of *i*PP dominate the dissolution rates and the helices with interactions relax more slowly than those without interactions. Obviously, internal restrictions in shish can retard relaxation. As the same way, external constraints can also lead to the delayed relaxation. Patil *et al.*^[68] proved that the presence of SWCNTs promotes precursor formation due to increase in the chain relaxation time favoring the stability of oriented metastable structure. Strong fixing effects that have retarded the relaxation of polymer chains can preserve the original orientation of the polymer stems even at a high temperature. However, only considering constraints from external particles is pitifully inadequate. Phillips *et al.*^[69] found that the existing particles can induce lower molecular weight chains to participate in shish formation. The lower molecular weight chains in shish can accelerate the shish dissolution process. In line with the same mechanism, by using a broadly distributed molecular weight polyethylene, Ma *et al.*^[70] found that increased strain rates can cause more low molecular weight molecules

to participate in shish formation, leading to an accelerated dissolution process. On the contrary, deferred reptation for the molecules in shishes may decrease the relaxation rate.^[28] These experimental facts prove that shish relaxation depends on its constituents and that the long relaxation time of basic units in shishes can effectively postpone the shish relaxation. Therefore, as Balzano *et al.*^[48] reported, shish dissolution is controlled by the relaxation of the longest chain. In light of these results, shishes composed of *bcPE* can remain longer in the heat treatment process because *bcPE* has a longer relaxation time. However, our results show that the shishes that contain *bcPE* disappear faster than the shishes composed of *lcPE*, indicating that the simple detachment model for shishes needs to be modified and that shish relaxation is also affected by the defects it contains and the branched arms with strong movement ability. According to above discussion, we think that the relaxation of shishes includes two stages as Hsiao *et al.* suggested,^[14] *i.e.*, the decrease of packing density and topological relaxation of stretched UHMWPE chains (shish backbones). First, when the temperature is below 180 °C, short matrix chains detach consecutively from the outer surface of the shishes followed by their diffusion into the melt,^[48,60] while the oriented networks of long linear and branched chains are confined in the shish microstructures. At this time, there is no obvious distinction between the abilities of chains or segments to detach from the surface of the two types of shishes because these chains or segments mainly come from the short chain matrix. Correspondingly, a short half-crystallization time was observed because many oriented crystals (long chain backbones) still exist. Second, once the temperature surpasses 180 °C, topological relaxation of stretched long chain networks occurs, restoring the random melt entanglement states. The relaxation of long chain backbones differs because two types of UHMWPEs with different molecular architectures form them. Actually, a much quicker increase in half-time crystallization with temperature was observed for *O-bcPE*. This increasing tendency is faster than stage one. As we have discussed before, the accelerated dissolution can be ascribed to the defects and the small units with strong movement ability (*e.g.* branched arms) in shishes. Therefore, we think the recrystallization results are not only powerful evidence that the shish backbones are formed by long chain components but also an important clue that shish relaxation is affected by both the relaxation of its longest chain and the shish structure. For example, some defects, short chains, or branched chains can all dramatically change the shish relaxation behavior.

Influence of Long Chain Architecture on Shish Formation

In order to evaluate the effect of long chains on the shish-kebab formation, we need to understand the flow field condition in the OSIM samples. We figured out the shear rate distribution in the OSIM sample during injection (Fig. S6 in ESI), while it should be noted that the different crystallization behaviors between *lcPE* and *bcPE* were not considered when estimating the shear rate distribution. The effects of flow on the polymer chains include orientating the contour path and even stretching of the segments. For a specific flow condition, we can utilize two Weissenberg numbers, $W_{i(\text{orientation})} = \tau_D \cdot \dot{\gamma}$ and $W_{i(\text{stretch})} =$

$\tau_R \cdot \dot{\gamma}$ to quantitatively assess the molecular deformation.^[48,70] In principle, polymer chains will be oriented when $W_{i(\text{stretch})} > 1$ and be stretched when $W_{i(\text{orientation})} > 1$. According to the tube model, the reptation time (τ_R) and the rouse time (τ_D) can be obtained by the following equations:

$$\tau_R = \tau_e \cdot Z^2 \quad \text{and} \quad \tau_D = 3\tau_e \cdot Z^3 \left(1 - \frac{1.51}{\sqrt{Z}}\right)^2$$

where τ_e and Z are the entanglement equilibration time and the average number of entanglements per chain, respectively. These corresponding parameters can be seen in Table S1 (in ESI). Since the shear rate at 500 μm is 962 s^{-1} , for *scPE*, the estimated $W_{i(\text{orientation})}$ and $W_{i(\text{stretch})}$ are 8.37 and 0.066, respectively. It seems that *scPE* cannot be stretched by the flow (962 s^{-1}). However, the SEM result shows that shishes exist in *O-scPE*, which indicates the occurrence of molecular stretch. One possible explanation is that *scPE* has molecular weight diversity and contains high molecular weight component that can be stretched at a relatively low shear. $W_{i(\text{stretch})}$ is larger than 1 for the molecules whose molecular weight is 230 k when the shear rate ($\dot{\gamma}$) is 962 s^{-1} . According to the GPC data, there are 5 wt% molecules whose molecular weight surpasses 230 k in *scPE*. For this molecular weight (230 k), the overlapping concentration is only 0.85 wt%, which indicates that those long chains in *scPE* can form entangled networks and the chain segments between two neighbouring entanglement points in the same chain can be stretched under the shear field in our experiment. Thus, the strong flow field afforded by OSIM can stretch *scPE* to induce shish-kebabs. Undoubtedly, *lcPE* and *bcPE* can also be stretched to induce shish-kebab formation.

With different architectures, the linear and branched long chains have different relaxation behaviors, which will strongly influence the flow-induced crystallization process. The linear molecules relax *via* a reptation mode, while the branched ones cannot relax by reptation. Instead, a branched polymer relaxes its configuration through arm retraction, that is, the tip of a branched arm occasionally retracts diffusively along its tube, all the way to the branch point.^[32,71,72] According to prior work, it is easier to form shish-kebabs from branched molecules than with linear ones under the same flow conditions because of the broadened and complex relaxation behaviors of the branched molecules.^[33,73] Our work shows similar results when the shear flow is intense enough, *e.g.*, in the intermediate regions (500–2000 μm from the surface) of OSIM samples. However, the opposite phenomenon appears in the weak shear regions (core regions). In other words, *bcPE* could not induce the shish-kebab formation in the core layer of the OSIM sample but *lcPE* could.

Commonly, the differences of the two long chains in promoting shish-kebab formation are also understood from the viewpoint of dimensionless Weissenberg number and flow work. To form shish nuclei, the chains must be oriented at the monomer bond level and this level of orientation can only be produced by chain stretching. We can also borrow the dimensionless Weissenberg number to evaluate the degree of stretching.^[48,70] The branched chains have a larger τ_R (branched structure and high molecular weight) and this can lead to larger stretching than the linear ones at the same shear. Furthermore, according to Janeschitz-Kriegl's hypothesis,^[74] the resulting morphology is controlled by work

done on a sheared polymer melt, and this work relies deeply on the matrix viscosity. Because the viscosity of branched molecules is higher than that of linear ones,^[33,34,73] it is reasonable to obtain the results in our work, *i.e.*, both the branched and linear long chains can orient themselves strongly enough to induce shish-kebabs as long as the flow is sufficiently strong, while the branched ones cannot be oriented (the linear ones can) under a weak shear field due to the hindrance of the branched arms and the accelerated effect on shish dissolution.

To describe the processes of flow-induced crystallization for binary systems containing long chains with different architectures more vividly, Fig. 10 displays it in cartoon format. For both systems, the long chains are uniformly located within the short chain matrix because of the homogeneous chemical composition. Under a strong flow, entangled chains (networks) are distorted from their equilibrium coiled states to oriented conformations, namely, molecular networks are aligned along the flow direction. Thus, both the entropic and kinetic barriers to nucleation are decreased. In the meantime, nuclei are generated mainly at certain spots of deformed networks because of high stability (long relaxation time). Those nuclei that are located in the same deformed network develop and finally connect with each other to form shish backbones, which are primarily composed of entangled molecular networks. The backbones can absorb short matrix chains to increase their diameter, turning into the resultant shishes. Then, short chains use the surfaces of shishes as anchor points to develop kebabs. After the cessation of flow and pri-

or to the structure being fixed by crystallization, the oriented networks have chances to relax and return to coil states, depending on the factors such as time interval, cooling rate, orientation degree, the molecular structure, *etc.* Eventually, it is possible only for the networks whose oriented conformations remain to form shishes. Under an intense shear flow, long chains (either linear or branched) are beneficial to shish formation because of the large possibility of being oriented and their long relaxation time. However, the branched chains have longer relaxation time than the linear ones and the branched points can facilitate nucleation, resulting in higher crystallization rates.^[34] Thus, the *bcPE* networks can more easily be induced to form shishes. Furthermore, the stable networks (*bcPE*) can even make many oriented short chains remain longer after shear cessation, resulting in a condition helpful to promoting the crystallization process of short chains. Therefore, the system containing *bcPE*s has a higher crystallinity than the linear ones. In comparison with the shish backbones that are generated by *lcPE*s, the backbones with the branched chains are looser and contain more defects because of the branched arms and hence collapse more easily during heat treatment, leading to a longer half-time crystallization during high temperature heat treatment for the OSIM sample regions having a strong shear flow. Furthermore, in the long annealing process, the branched arms with a high movement ability can adjust their configurations by retraction and expanding along different tubes and eventually lead to accelerated collapse of shishes. Because the shish outer layer is mainly composed of short matrix chains, the struc-

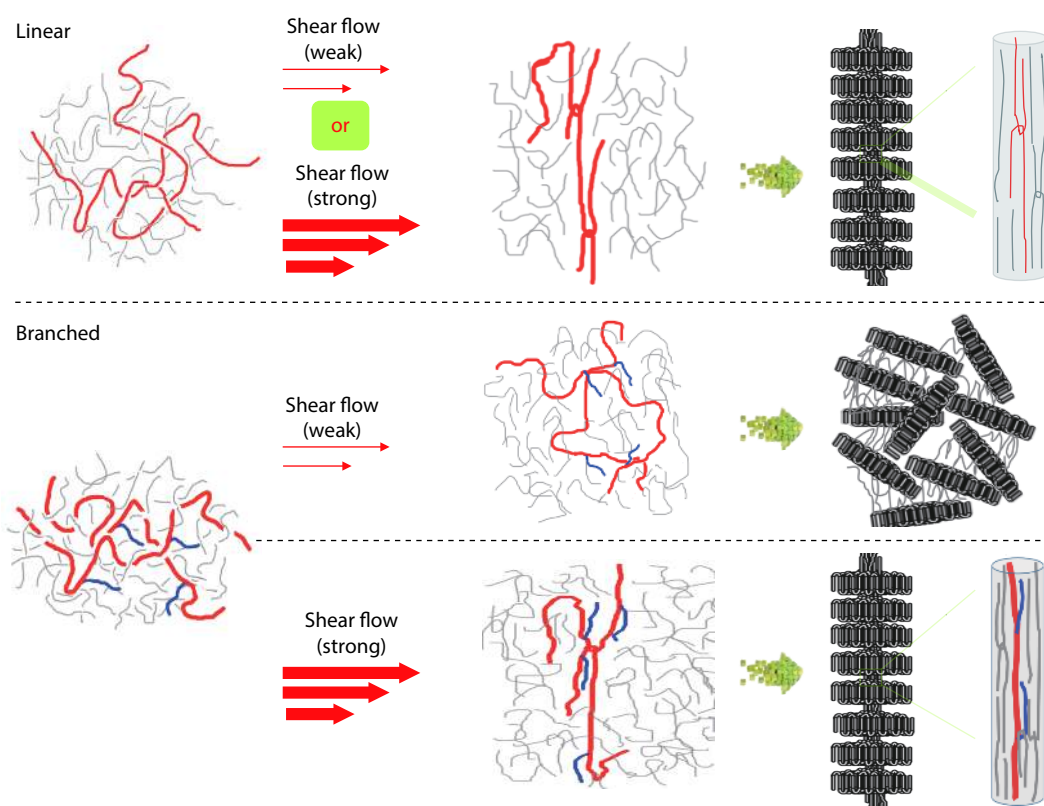


Fig. 10 Schematic of shish formation processes for the binary systems with linear and branched long chains.

tures generated by the two long chains should have a similar structure, which is why their half-time crystallization during temperature heat treatment is almost the same.

However, shish-kebab formation is different under a weak flow field, *i.e.*, in the core regions of the OSIM sample. In our work, the low shear rate and long solidification time in the core layer can still orient the networks of linear long chains to induce shish-kebabs, while it is relatively difficult for the branched ones because of the hindrance of branched arms and the fast collapse of oriented structure with defects. Hence, the system with *lc*PE possesses shish-kebabs in the core sample layer, but the system with the branched ones does not.

CONCLUSIONS

In summary, mechanical properties were significantly enhanced without any heterogeneous filler through adding long chain components into a short chain matrix and using the OSIM technique. These results can afford significant guidance in real polymer processing to enhance the properties of polymeric products *via* adding a small number of long chain molecules into a short chain matrix. Moreover, the linear long chains more strongly promoted shish-kebab formation under a weak shear flow (core regions of OSIM sample) than branched ones, while the reverse is the case under an intense shear. The discrepancy resulted from the difference between their architectures, that is, the branched arms hindered entangled networks from orienting along the flow direction. However, a strong shear could weaken the difference between architectures, so there is no notable discrepancy in shish-kebabs in the intermediate regions (shear layers of the OSIM sample) except the crystallinity. The recrystallization results demonstrated that shishes are composed of both long chain components and short matrix chains. In detail, the shish backbones are generated mainly by deformed long chain networks, while the shish outer layers comprise mainly short matrix chains. Our results display a promising application of selecting long chains with different structures to strengthen the mechanical properties of plastic products in actual processing. For instance, it is difficult for polyethylene to create biaxially oriented films. Incorporating a small amount of long chains (generally with branched chains) can partially help but not be overly effective. Our results suggest a better solution—adding linear long chain molecules rather than branched ones.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <https://doi.org/10.1007/s10118-020-2397-7>.

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REFERENCES

- 1 Pennings, A. J.; Kiel, A. M. Fractionation of polymers by crystallization from solution. III. On the morphology of fibrillar polyethylene crystals grown in solution. *Colloid Polym. Sci.* **1965**, *205*, 160–162.
- 2 Keller, A. Polymer crystals. *Rep. Prog. Phys.* **1968**, *31*, 623–704.
- 3 Zwijnenburg, A.; Pennings, A. J. Longitudinal growth of polymer crystals from flowing solutions. III. Polyethylene crystals in Couette flow. *Colloid Polym. Sci.* **1976**, *254*, 868–881.
- 4 Somani, R. H.; Yang, L.; Hsiao, B. S.; Agarwal, P. K.; Fruitwala, H. A.; Tsou, A. H. Shear-induced precursor structures in isotactic polypropylene melt by *in-situ* rheo-SAXS and rheo-WAXD studies. *Macromolecules* **2002**, *35*, 9096–9104.
- 5 Seki, M.; Thurman, D. W.; Oberhauser, J. P.; Kornfield, J. A. Shear-mediated crystallization of isotactic polypropylene: the role of long chain-long chain overlap. *Macromolecules* **2002**, *35*, 2583–2594.
- 6 Matsuura, T.; Murakami, M.; Inoue, R.; Nishida, K.; Ogawa, H.; Ohta, N.; Kanaya, T. Microbeam wide-angle X-ray scattering study on precursor of shish kebab. Effects of shear rate and annealing on inner structure. *Macromolecules* **2015**, *48*, 3337–3343.
- 7 Mackley, M. R.; Keller, A. Flow induced crystallization of polyethylene melts. *Polymer* **1973**, *14*, 16–20.
- 8 Keller, A.; Kolnaar, J. W. H. Chain extension and orientation: fundamentals and relevance to processing and products orientational phenomena in polymers. *Steinkopff* **1993**, 81–102.
- 9 Jerschow, P.; Janeschitz-Kriegl, H. The role of long molecules and nucleating agents in shear induced crystallization of isotactic polypropylenes. *Int. Polym. Proc.* **1997**, *12*, 72–77.
- 10 Nogales, A.; Hsiao, B. S.; Somani, R. H. Shear-induced crystallization of isotactic polypropylene with different molecular weight distributions: *in situ* small-and wide-angle X-ray scattering studies. *Polymer* **2001**, *42*, 5247–5256.
- 11 Zhao, Z. H.; Wang, F. H.; Zhou, M.; Shen, K. Z.; Zhang, J. Altering the hierarchical morphology distribution of injection molded polyethylene by the introduction of crosslink network and periodical shear. *Chinese J. Polym. Sci.* **2016**, *34*, 1479–1489.
- 12 Xu, Z. B.; Su, L. Y.; Wang, P. F.; Peng, M. Effect of oscillatory shear on the mechanical properties and crystalline morphology of linear low density polyethylene. *Chinese J. Polym. Sci.* **2015**, *33*, 1114–1124.
- 13 Jiang, K.; Yu, F. L.; Su, R.; Yang, J. H.; Zhou, T. N.; Gao, J.; Deng, H.; Wang, K.; Zhang, Q.; Chen, F.; Fu, Q. High speed injection molding of high density polyethylene-effects of injection speed on structure and properties. *Chinese J. Polym. Sci.* **2011**, *29*, 456–464.
- 14 Keum, J. K.; Zuo, F.; Hsiao, B. S. Formation and stability of shear-induced shish-kebab structure in highly entangled melts of UHMWPE/HDPE blends. *Macromolecules* **2008**, *41*, 4766–4776.
- 15 Yang, L.; Somani, R. H.; Sics, I.; Hsiao, B. S.; Kolb, R.; Fruitwala, H.; Ong, C. Shear-induced crystallization precursor studies in model polyethylene blends by *in-situ* rheo-SAXS and rheo-WAXD. *Macromolecules* **2004**, *37*, 4845–4859.
- 16 Bashir, Z.; Odell, J. A.; Keller, A. Stiff and strong polyethylene with shish kebab morphology by continuous melt extrusion. *J. Mater. Sci.* **1986**, *21*, 3993–4002.
- 17 Matsuba, G.; Sakamoto, S.; Ogino, Y.; Nishida, K.; Kanaya, T. Crystallization of polyethylene blends under shear flow. Effects of crystallization temperature and ultrahigh molecular weight component. *Macromolecules* **2007**, *40*, 7270–7275.
- 18 Ogino, Y.; Fukushima, H.; Matsuba, G.; Takahashi, N.; Nishida, K.; Kanaya, T. Effects of high molecular weight component on crystallization of polyethylene under shear flow. *Polymer* **2006**, *47*, 5669–5677.

- 19 Gabriel, C.; Kaschta, J.; Munstedt, H. Influence of molecular structure on rheological properties of polyethylenes. *Rheol. Acta*. **1998**, 37, 7–20.
- 20 Kessner, U.; Kaschta, J.; Stadler, F. J.; Duff, C. S. L.; Drooghaag, X.; Munstedt, H. Thermorheological behavior of various short-and long-chain branched polyethylenes and their correlations with the molecular structure. *Macromolecules* **2010**, 43, 7341–7350.
- 21 Ning, W.; Zhu, W. X.; Zhang, B. Q.; Li, C. C.; Liu, C. Y.; Wang, D. J. Effect of chemical structure of polycarbonates on entanglement spacing. *Chinese J. Polym. Sci.* **2012**, 30, 343–349.
- 22 Milner, S. T.; McLeish, T. C. B. Reptation and contour-length fluctuations in melts of linear polymers. *Phys. Rev. Lett.* **1998**, 81, 725–728.
- 23 de Gennes, P. G. Coil-stretch transition of dilute flexible polymers under ultrahigh velocity gradients. *J. Chem. Phys.* **1974**, 60, 5030–5042.
- 24 Edwards, S. F. The statistical mechanics of polymerized material. *Proc. Phys. Soc.* **1967**, 92, 9–16.
- 25 Zhao, B. J.; Li, X. Y.; Huang, Y. J.; Cong, Y. H.; Ma, Z.; Shao, C. G.; An, H. N.; Yan, T. Z.; Li, L. B. Inducing crystallization of polymer through stretched network. *Macromolecules* **2009**, 42, 1428–1432.
- 26 Brown, E.; Willms, R.; Rae, P.; Cady, C.; Vecchio, K.; Flowers, J.; Martinez, M. Influence of molecular conformation on the constitutive response of polyethylene: a comparison of HDPE, UHMWPE, and PEX. *Exp. Mech.* **2007**, 47, 381–393.
- 27 Yang, H. R.; Lei, J.; Li, L. B.; Fu, Q.; Li, Z. M. Formation of interlinked shish-kebabs in injection-molded polyethylene under the coexistence of lightly cross-linked chain network and oscillation shear flow. *Macromolecules* **2012**, 45, 6600–6610.
- 28 Zhou, D.; Yang, S. G.; Lei, J.; Hsiao, B. S.; Li, Z. M. Role of stably entangled chain network density in shish-kebab formation in polyethylene under an intense flow field. *Macromolecules* **2015**, 48, 6652–6661.
- 29 Carella, J. M.; Gotro, J. T.; Graessley, W. W. Thermorheological effects of long-chain branching in entangled polymer melts. *Macromolecules* **1986**, 19, 659–667.
- 30 Stadler, F. J.; Kaschta, J.; Munstedt, H. Thermorheological behavior of various long-chain branched polyethylenes. *Macromolecules* **2008**, 41, 1328–1333.
- 31 Frischknecht, A. L.; Milner, S. T.; Pryke, A.; Young, R. N.; Hawkins, R.; McLeish, T. C. B. Rheology of three-arm asymmetric star polymer melts. *Macromolecules* **2002**, 35, 4801–4820.
- 32 Zamponi, M.; Pyckhout-Hintzen, W.; Wischnewski, A.; Monkenbusch, M.; Willner, L.; Kali, G.; Richter, D. Molecular observation of branch point motion in star polymer melts. *Macromolecules* **2010**, 43, 518–524.
- 33 Agarwal, P. K.; Somani, R. H.; Weng, W. Q.; Mehta, A.; Yang, L.; Ran, S. F.; Liu, L. Z.; Hsiao, B. S. Shear-induced crystallization in novel long chain branched polypropylenes by *in situ* rheo-SAXS and WAXD. *Macromolecules* **2003**, 36, 5226–5235.
- 34 Fang, H. G.; Zhang, Y. Q.; Bai, J.; Wang, Z. G. Shear-induced nucleation and morphological evolution for bimodal long chain branched polylactide. *Macromolecules* **2013**, 46, 6555–6565.
- 35 Zhang, X. X.; Yang, S. G.; Hua, W. Q.; Lin, J. M.; Lei, J.; Bian, F. G.; Xu, L.; Li, Z. M. Role of pressure in flow-induced shish-kebab in binary blend of long- and short-chain polyethylenes. *Polym. Cryst.* **2019**, 2, e10059.
- 36 Zhang, Z. C.; Zhang, R.; Huang, Y. F.; Lei, J.; Chen, Y. H.; Tang, J. H.; Li, Z. M. Efficient utilization of atactic polypropylene in its isotactic polypropylene blends via “structuring” processing. *Ind. Eng. Chem. Res.* **2014**, 53, 10144–10154.
- 37 Chen, Y. H.; Zhong, G. J.; Wang, Y.; Li, Z. M.; Li, L. B. Unusual tuning of mechanical properties of isotactic polypropylene using counteraction of shear flow and β -nucleating agent on β -form nucleation. *Macromolecules* **2009**, 42, 4343–4348.
- 38 Ballard, D. G. H.; Cheshier, P.; Longman, G. W.; Schelten, J. Small-angle neutron scattering studies of isotropic polypropylene. *Polymer* **1978**, 19, 379–385.
- 39 Picken, S. J.; Aerts, J.; Visser, R.; Northolt, M. G. Structure and rheology of aramid solutions: X-ray scattering measurements. *Macromolecules* **1990**, 23, 3849–3854.
- 40 Kitade, S.; Asuka, K.; Akiba, I.; Sanada, Y.; Sakurai, K.; Masunaga, H. Shear-induced pre-crystallization structures of long chain branched polypropylene under steady shear flow near the melting temperature. *Polymer* **2013**, 54, 246–257.
- 41 Bustos, F.; Cassagnau, P.; Fulchiron, R. Effect of molecular architecture on quiescent and shear-induced crystallization of polyethylene. *J. Polym. Sci., Part B: Polym. Phys.* **2006**, 44, 1597–1607.
- 42 Somani, R. H.; Hsiao, B. S.; Nogales, A.; Fruitwala, H.; Srinivas, S.; Tsou, A. H. Structure development during shear flow induced crystallization of *i*-PP: *in situ* wide-angle X-ray diffraction study. *Macromolecules* **2001**, 34, 5902–5909.
- 43 Somani, R. H.; Yang, L.; Hsiao, B. S.; Sun, T.; Pogodina, N. V.; Lustiger, A. Shear-induced molecular orientation and crystallization in isotactic polypropylene: effects of the deformation rate and strain. *Macromolecules* **2005**, 38, 1244–1255.
- 44 Cai, J. L.; Hsiao, B. S.; Gross, R. A. Real-time structure changes during uniaxial stretching of poly(ω -pentadecalactone) by *in situ* synchrotron WAXD/SAXS techniques. *Macromolecules* **2011**, 44, 3874–3883.
- 45 Wang, Z. P.; Huang, Y. F.; Xu, J. Z.; Niu, B.; Zhang, X. L.; Zhong, G. J.; Xu, L.; Li, Z. M. Injection-molded hydroxyapatite/polyethylene bone-analogue biocomposites via structure manipulation. *J. Mater. Chem. B*. **2015**, 3, 7585–7593.
- 46 Ye, L.; Li, H.; Qiu, Z.; Yan, S. The melt-recrystallization behavior of highly oriented α -iPP fibers embedded in a HIPS matrix. *Phys. Chem. Chem. Phys.* **2015**, 17, 7576–7580.
- 47 Kalay, G.; Kalay, C. *In-situ* microfibrillation of polystyrene (PS)/polybutene-1(PB-1) composites prepared via melt drawing: morphological evolution and properties. *J. Polym. Sci., Part B: Polym. Phys.* **2002**, 40, 1828–1834.
- 48 Balzano, L.; Kukalyekar, N.; Rastogi, S.; Peters, G. W. M.; Chadwick, J. C. Crystallization and dissolution of flow-induced precursors. *Phys. Rev. Lett.* **2008**, 100, 048302.
- 49 Hsiao, B. S.; Yang, L.; Somani, R. H.; Avila-Orta, C. A.; Zhu, L. Unexpected shish-kebab structure in a sheared polyethylene melt. *Phys. Rev. Lett.* **2005**, 94, 117802.
- 50 Liang, S.; Wang, K.; Tang, C. Y.; Zhang, Q.; Du, R. N.; Fu, Q. Unexpected molecular weight dependence of shish-kebab structure in the oriented linear low density polyethylene/high density polyethylene blends. *J. Chem. Phys.* **2008**, 128, 174902.
- 51 Baker, A. M. E.; Windle, A. H. The effects of branching and fibre drawing on the crystal structure of polyethylene. *Polymer* **2001**, 42, 651–665.
- 52 Hill, M. J.; Barham, P. J.; Keller, A. On the hairdressing of shish-kebabs. *Colloid Polym. Sci.* **1980**, 258, 1023–1037.
- 53 Cavallo, D.; Azzurri, F.; Balzano, L.; Funari, S. S.; Alfonso, G. C. Flow memory and stability of shear-induced nucleation precursors in isotactic polypropylene. *Macromolecules* **2010**, 43, 9394–9400.
- 54 Li, L. Y.; Li, C. Y.; Ni, C. Y.; Rong, L. X.; Hsiao, B. Structure and crystallization behavior of Nylon 66/multi-walled carbon nanotube nanocomposites at low carbon nanotube contents. *Polymer* **2007**, 48, 3452–3460.
- 55 Men, Y. F.; Strobl, G. Critical strains determining the yield behavior of s-PP*. *J. Macromol. Sci., Part B: Phys.* **2001**, 40, 775–796.
- 56 Men, Y. F.; Rieger, J.; Strobl, G. Role of the entangled amorphous network in tensile deformation of semicrystalline polymers. *Phys.*

- Rev. Lett.* **2003**, *91*, 095502.
- 57 Xu, L.; Chen, C.; Zhong, G. J.; Lei, J.; Xu, J. Z.; Hsiao, B. S.; Li, Z. M. Tuning the superstructure of ultrahigh-molecular-weight polyethylene/low-molecular-weight polyethylene blend for artificial joint application. *ACS Appl. Mater. Interfaces* **2012**, *4*, 1521–1529.
 - 58 Kanaya, T.; Matsuba, G.; Ogino, Y.; Nishida, K.; Shimizu, H. M.; Shinohara, T.; Oku, T.; Suzuki, J.; Otomo, T. Hierarchic structure of shish-kebab by neutron scattering in a wide Q range. *Macromolecules* **2007**, *40*, 3650–3654.
 - 59 Kimata, S.; Sakurai, T.; Nozue, Y.; Kasahara, T.; Yamaguchi, N.; Karino, T.; Shibayama, M.; Kornfield, J. A. Molecular basis of the shish-kebab morphology in polymer crystallization. *Science* **2007**, *316*, 1014–1017.
 - 60 Azzurri, F.; Alfonso, G. C. Insights into formation and relaxation of shear-induced nucleation precursors in isotactic polystyrene. *Macromolecules* **2008**, *41*, 1377–1383.
 - 61 Janeschitz-Kriegl, H.; Eder, G. Shear induced crystallization, a relaxation phenomenon in polymer melts: a recollection. *J. Macromol. Sci., Part B: Phys.* **2007**, *46*, 591–601.
 - 62 Hamad, F. G.; Colby, R. H.; Milner, S. T. Lifetime of flow-induced precursors in isotactic polypropylene. *Macromolecules* **2015**, *48*, 7286–7299.
 - 63 Shen, B.; Liang, Y.; Kornfield, J. A.; Han, C. C. Mechanism for shish formation under shear flow: an interpretation from an *in situ* morphological study. *Macromolecules* **2013**, *46*, 1528–1542.
 - 64 Zhao, Y.; Hayasaka, K.; Matsuba, G.; Ito, H. *In situ* observations of flow-induced precursors during shear flow. *Macromolecules* **2012**, *46*, 172–178.
 - 65 Na, B.; Wang, Y.; Zhang, Q.; Fu, Q. Shish and its relaxation dependence of re-crystallization of isotactic polypropylene from an oriented melt in the blends with high-density polyethylene. *Polymer* **2004**, *45*, 6245–6260.
 - 66 Cui, K.; Ma, Z.; Wang, Z.; Ji, Y.; Liu, D.; Huang, N.; Chen, L.; Zhang, W.; Li, L. Kinetic process of shish formation: from stretched network to stabilized nuclei. *Macromolecules* **2015**, *48*, 5276–5285.
 - 67 An, H.; Li, X.; Geng, Y. Shear-induced conformational ordering, relaxation, and crystallization of isotactic polypropylene. *J. Phys. Chem. B* **2008**, *112*, 12256–12262.
 - 68 Patil, N.; Balzano, L.; Portale, G.; Rastogi, S. A study on the chain-particle interaction and aspect ratio of nanoparticles on structure development of a linear polymer. *Macromolecules* **2010**, *43*, 6749–6759.
 - 69 Phillips, A. W.; Bhatia, A.; Zhu, P. Shish formation and relaxation in sheared isotactic polypropylene containing nucleating particles. *Macromolecules* **2011**, *44*, 3517–3528.
 - 70 Ma, Z.; Balzano, L.; Peters, G. W. M. Dissolution and re-emergence of flow-induced shish in polyethylene with a broad molecular weight distribution. *Macromolecules* **2016**, *49*, 2724–2730.
 - 71 Das, C.; Inkson, N. J.; Read, D. J.; Kelmanson, M. A.; McLeish, T. C. Computational linear rheology of general branch-on-branch polymers. *J. Rheol.* **2006**, *50*, 207–234.
 - 72 Bero, C.; Roland, C. Terminal relaxations in linear and three-arm star polyisoprenes. *Macromolecules* **1996**, *29*, 1562–1568.
 - 73 Heeley, E. L.; Fernyhough, C. M.; Graham, R. S.; Olmsted, P. D.; Inkson, N. J.; Embery, J.; Groves, D. J.; McLeish, T. C.; Morgovan, A. C.; Meneau, F. Shear-induced crystallization in blends of model linear and long-chain branched hydrogenated polybutadienes. *Macromolecules* **2006**, *39*, 5058–5071.
 - 74 Janeschitz-Kriegl, H.; Ratajski, E.; Stadlbauer, M. Flow as an effective promotor of nucleation in polymer melts: a quantitative evaluation. *Rheol. Acta* **2003**, *42*, 355–364.