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1 Flow-induced Crystallization of Long Chain 2 Aliphatic Polyamides under a Complex Flow 3 Field: Inverted Anisotropic Structure and 4 Formation Mechanism

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12 **Abstract**

13 The present work deals with the flow-induced multiple orientations and
14 crystallization structure of polymer melts under a complex flow field. This complex
15 flow field is characteristic of the consistent coupling of extensional “pulse” and
16 closely followed shear flow in a narrow channel. Utilizing an ingenious combination
17 of an advanced micro-injection device and long chain aliphatic polyamides (LCPA),
18 the flow-induced crystallization morphology was well preserved for ex-situ

synchrotron micro-focused wide angle X-ray scattering (μ WAXS) as well as small angle X-ray scattering (SAXS). An inverted anisotropic crystallization structure was observed in two directions: perpendicular and parallel to the flow direction (FD). The novel anisotropic morphology implies the occurrence of wall slip and “global” fountain flow under the complex flow field. The mechanism of structure formation is elucidated in detail. The experimental results clearly indicate that the effect of extensional pulse on the polymer melt is restrained and further diminished due to either the transverse tumble of fountain flow or the rapid retraction of stretched high molecular weight tails. However, the residual shish-kebab structures in the core layer of the far-end of channel suggest that the effect of extensional pulse should be considered in the small-scaled geometries or under the high strain rate condition.

1. Introduction

Flow-induced crystallization (FIC) of polymer melts is a fundamental issue of polymer physics. It is of clear theoretical significance, and very important in practical applications. Developing specific flow condition by using delicate flow geometries is an important method through which the cause-effect relationship among polymer-surface interactions, melt flow behavior and subsequent crystallization can be investigated. However, most studies of experimental protocols reported in these literatures involve only shear [1-8] or extensional flow [9-13], rather than complex flow field. The main reason might be perceived experimental difficulties and a lack of

39 correlation between molecular orientation and non-Newtonian flow behavior under
40 complex flow field. Although computer simulations provide many valuable
41 information of system on a macroscopic scale [14], i.e. flow pattern, viscosity, stress
42 profile, etc., there is still the need for probing the microscopic picture of flow
43 behavior under complex flow field as well as its effect on crystallization of polymers.

44 One of the most prominent industrial flow field is the consistent coupling of
45 extensional “pulse” and closely following shear flow. For example, in
46 injection-moulding processes, polymer melts usually experience short-term
47 extensional effect caused by converging flow at the sprue entrance, then flow rapidly
48 into the rather colder mould and solidify while subjected wall shear stress. Early
49 experiments suggested that the transient extensional effect is important during the
50 very early stage before the fully development of laminar shear flow [15]. Nevertheless,
51 most researchers tend to consider that the FIC in filling channel is dominated by shear
52 effect solely. While in some cases, the effect of so-called fountain flow, a two
53 dimensional flow restricted to a small region of the flow front, is also suggested
54 [16-18]. However, several phenomena in this widespread process have not been
55 sufficiently recognized. First, if one wants to reproduce the condition that polymer
56 experience during the industrial processes, how to deal with the non-isothermal nature
57 of those complex flow geometries, especially the temperature gradient between two
58 flow patterns, will become a very delicate task. Second, if converging flow is

generally referred to as a “strong” flow, which would generate considerable chain stretching conditions [19, 20], then why its contribution is not being valued. Indeed, the relaxation of oriented or stretched polymer chains might not allow the effect of extensional pulse to be observed in the final products. However, nowadays, the desire for high productivity in the industry makes the strain rate of processing grow by leaps and bounds. The effect of extensional pulse might not keep invisible anymore. Third, as the demand of micro or sub-micro components is rising rapidly, it is very necessary to consider the potential deviation of flow behavior from the typical shear field in those small-scaled geometries.

To explore the crystallization of polymer melt in the extensional-shear-coupled flow field, a simple case is studied in this work. Through a short entrance polymer melts are jetted into a thin and straight-walled channel, and subsequently crystallize under wall shear stress. An advanced micro-injection device was employed as a protocol to introduce this complex flow field. By applying the sprue-less design, the injection nozzle is in direct contact with a thin cavity. Flow visualization techniques showed that the transient extensional pulse occurs as the converging flow at the junction between the nozzle and the cavity, while the shear flow closely follows in the rest part of cavity [22]. As the cavity size decreases, several effects are promoted to help further understand FIC behavior under the complex flow field [21, 22]: (i) a considerably high strain rates can be imposed to secure the strong chain stretching

condition; (ii) the heat transfer becomes more efficient, thus an isothermal condition can be applied on the shear pureion; (iii) converging flow and shear flow are strongly coupled, since there is no room for radical free-surface flow (i.e. flow with zero lateral-stress).

Another question is the applicable polymer system. To deal with the non-isothermal condition, it is very important to use a polymer which can respond quickly to the processing history it experiences. To preserve the effect of flow condition, it should also have rather slow relaxation dynamics. In addition, the chain stretching condition of this polymer should be able to be quantitatively described. Based on those considerations, long chain aliphatic polyamides (LCPA) are introduced. By incorporating long alkane segments – typically more than ten methylene groups and hence diluting the amide linkages, LCPA serve as the example of a polymer possessing intrinsic flexibility and strong intermolecular interaction simultaneously [23]. Generally, at temperatures well above the melting point, the hydrogen bonds between the molecules of LCPA are weakened (both in terms of individual bond strength and total number), which leads to the exhibition of flexibility. Rheological models, such as the Doi-Edwards model, are applicable in this case. On the other side, when LCPA are cooled back towards the melting point, the strong chain interaction reconstructs again to affect the relaxation behavior and, most importantly, fasten crystallization dynamics [24]. The efficient heat transfer of experimental protocols

and special feature of LCPA could result in well-recorded crystallization morphology. Hence, it is possible and convenient to ex-situ probe the flow-induced hierarchical crystallization structure. In this work, synchrotron micro-focused wide angle X-ray scattering (μ WAXS) as well as small-angle X-ray scattering (SAXS) were used. The microscopic morphology can be spatially resolved directly using high-resolution scanning diffractometry of μ WAXS [25, 26]. Those methods require little sample preparation and thus diminish the risk of introducing artifacts [26, 27]. In combination with vastly exiting information, FIC behavior under complex flow field can be understand more thoroughly.

2. Experimental

2.1 Materials and sample preparation

The additive-free PA1012 was produced from bio-fermenting sources (Shandong Guangyin New Materials Co. Ltd, Zibo, China). The melting point was 189 °C determined by differential scanning calorimeter with heating rate of 10 °C/min. The melt flow index was 0.72 g/10min at 235 °C using 2.16 kg as loading. Since PA1012 has very similar molecular structure and physics properties to PA1212, the weight-average molecular weight ($\bar{M}_w$) of PA1012 was thus characterized by the empirical equation $[\eta] = 6.54 \times 10^{-2} \bar{M}_w^{0.70}$ for polyamide 1212 as reference. The molecular weight $\bar{M}_w$ of PA1012 was 265 kg/mol, where the intrinsic viscosity ($[\eta]$)

was 409.3 mL/g using m-cresol as the solvent. The molecular chain length of PA1012 with this $\bar{M}_w$ is long enough to form ordering structures.

Fig. 1 shows how temperature exercises influence upon the relaxation behavior of PA1012 melts. At short relaxation times, $G(t)$ changes little in a broad temperature range, which indicates the global configuration of the chain as well as stiffness of a single chain is less affected at temperature above the melting temperature, T_m . While at long times, $G(t)$ is explored into the terminal relaxation regime above 230 °C but into the plateau regime at 210 °C and 190 °C. The reconstruction and strength increase of hydrogen bonding at lower temperature give rise to a sudden leap of physical entanglement points leading to the slow relaxation dynamics of large motion units.

Fig. 1. Apparent stress relaxation modulus, $G(t) = \sigma(t)/\gamma$, plotted logarithmically against time for PA1012 at different temperature. The value of strain γ is 10% for all experiments.

The sprue-less micro-injection moulding device (Battenfeld Microsystem 50) was used to create the complex extensional-shear-coupled flow filed. The diameter of the nozzle was 5 mm. The dimension of followed straight-wall channel was 20.0×1.5×0.5

135 mm³ (length direction (LD) × width direction (WD) × thickness direction (TD)).

136 Converging flow occurred at the junction between nozzle and cavity. Fig. 2 shows the

137 sample for ex-situ investigation and the sites of the flow types adapted from

138 computational fluid dynamics simulation result [22]. The color of sample represents

139 the time scale of arrival flow front. The cavity temperature was set as 80 °C attaining

140 balance between processability and slow relaxation dynamics. The injection rate was

141 100 mm/s. The whole mould filling process would be finished within sub-0.1s. This

142 short processing time scale suggests the mould filling procedure is ahead of the

143 complete solidification of PA1012 at the moulding temperature. The material was

144 melted at 270 °C initially by a rotating screw positioned at a 45 °angle. It was pushed

145 by the screw in a very accurate metering chamber. Then, the injection piston jetted the

146 material through the barrel (270 °C) and the sprue-less nozzle (250 °C) into the cavity.

147 Highly repeatable process control and accurate material dosing were observed during

148 moulding by monitoring shot to shot variation of dosing performance and pressure

149 curves. PA1012 granules were kept in a vacuum oven at 80 °C for 24 h for drying

150 before preparation.

151 2.2 Micro-focus wide angle X-ray scattering scanning

Fig. 2. Sample for ex-situ probing and the supposed site of the flow types. The scheme of experimental geometry shows the procedure of μ WAXS scanning and resultant diffraction patterns (thumbnails). Insert: the actual plaque-shaped sample.

The X-ray source for diffractometry was BL15U, the hard X-ray micro-focused beamline at SSRF (Shanghai Synchrotron Radiation Facility). Using a Si/Rh coated K-B mirror-pair, the beam was focused on the sample with a $3 \times 3 \mu\text{m}^2$ beam size at focal position. The sample was mounted on a three-axis motorized translation stage. A standardized line scanning program with the X-ray beam perpendicular to the WD-LD plane was carried out at three different equidistant positions (Fig. 2) marked as ‘gate’, ‘center’ and ‘end’ to investigate the crystal structure and orientation changes both perpendicular and parallel to the flow direction (FD). The distance between the end position and the far-end of sample was 100 μm . The step size between each adjacent focus spot was 35 μm hence 43 individual diffraction patterns obtained at Gate, Center

and End positions separately. Data was collected using a MARCCD detector with an average pixel size of $79 \times 79 \mu\text{m}^2$. The photon energy was 18 KeV giving a wavelength of 0.688 Å with the sample-to-detector distance of 206.3 mm. The exposure time was 1 s. Each diffraction pattern frame was denominated using the initials of scan position plus the number of scan sequence at this position, i.e., frame 1 at gate position would be G1, frame 2 at center position C2, frame 3 at end position E3, etc. Background reduction and automated batch-operation of μWAXS patterns were conducted using the Fit2D software package. Self-designed Matlab programs were used to give pattern visualization and plotting.

The phase content for internal comparison within the batches is presented as crystallinity index (χ_c):

$$\chi_c = \frac{A_c}{\sum A_c + A_A} \quad (1)$$

where A_c is the integrated area of crystalline peaks belonging to a specific crystal phase and A_A is the integrated area of amorphous halo.

The peak deconvolution was performed with the constraint conditions (see **Supporting Information**) and these constraint conditions were necessary to determine the center of amorphous halo and each reflection separately because the amorphous halo and multiple phase signals were combined together in the origin testing data. To fulfill the description of the whole orientation state, the approach

derived from Wu and Schultz's [28] was adopted to quantify the mesophase contents.

The percentage of the mesophase (P_{meso}) can be calculated as:

$$P_{\text{meso}} = POP - \sum \chi_c \quad (2)$$

$$POP = \frac{\int_0^{2\pi} [\int_S I(s, \phi) ds - I_b(\phi)] d\phi}{\int_0^{2\pi} \int_S I(s, \phi) ds d\phi} \quad (3)$$

where POP is the percentage of oriented phases; s is the scattering vector; ϕ is the azimuthal angle; $I(s, \phi)$ is the background-corrected intensity from the diffraction pattern; $I_b(\phi)$ is the baseline of the azimuthal intensity profile resulted solely from the integral over a domain S of $I(s, \phi)$, herein S is as the same scattering angular range as the one used in calculating χ_c .

To manifestly demonstrate the crystallization structure, as shown in Fig. 3, the xy-coordinate pattern is transformed to polar coordinates with the scattering angle ranging from 8.0 °to 11.4 °and the azimuthal angle from 0 to 360 °.

Fig. 3. Demonstration of the regions used for generating the polar coordinate pattern from the xy-coordinate pattern. E and M represent the equatorial and meridian direction, respectively. The definition of azimuthal angle are also shown.

2.3 Small angle X-ray scattering

SAXS data at gate, center and end position were collected on the BL16B beamline of SSRF. To mitigate against a resolution problem from simultaneous scattering from two different highly oriented layers, the skin layer was blocked (sides) or cut away (top/bottom) deliberately in the SAXS experiments. The focus spot size was $0.3 \times 0.2 \text{ mm}^2$. A radiation wavelength of $1.24 \text{ \AA}$ was applied with the data collected using the same type of MARCCD detector as used for the BL15U experiment. Two different sample-to-detector distances, 2074.7 mm and 5088.6 mm, were employed to explore lamellae reflection and central diffuse scattering signal, respectively. The exposure time was 60s and 20s, respectively. According to the reciprocal relationship in scattering, the central diffuse scattering signal from fibrils or shishes would be much larger and more intense in the case of long s-d distance. Thus, to avoid overexposure, shorter exposure time was used for longer s-d distance. In addition, the high vacuum optical path in BL16B ensures that the atmospheric scattering in both cases is greatly eliminated. All SAXS patterns were corrected for background and X-ray fluctuation. To obtain the 1D scattering profile, $q=4\pi(\sin \theta)/\lambda$ was used, where q is the module of scattering vector; θ is one half the scattering angle; λ is the X-ray wavelength.

3. Results and Discussion

3.1 Determining flow regime of extensional pulse.

220 The dimensionless group Weissenberg number (Wi) is used to rheology characterize
 221 the strength of extensional pulse due to converging flow. In the case of extensional
 222 flow at channel entry, two Wi related to two different time scale can be expressed as
 223 [19, 29]:

$$224 \quad Wi_{rep} = \tau_{rep} \ln \left[\left(\frac{R_o}{R_c} \right)^2 \right] \left(\frac{4Q}{\pi R_c^3} \right) \quad (4)$$

$$225 \quad Wi_s = \tau_s \ln \left[\left(\frac{R_o}{R_c} \right)^2 \right] \left(\frac{4Q}{\pi R_c^3} \right) \quad (5)$$

226 where τ_{rep} is the reptation time; τ_s is the time scale for faster chain retraction (Rouse
 227 relaxation time); R_o is the radius of nozzle; R_c is the equivalent radius of cavity and
 228 the R_c of cavity is 0.455 mm calculated from Huebscher equation.; Q is the
 229 volumetric flow rate. The largest reptation time for high molecular weight (HMW)
 230 tails, τ_{rep}^{HMW} , is the proper choice for τ_{rep} due to the crucial role of them in forming
 231 oriented structure [9, 19, 30] and is estimated as 6s at 250 °C from the relaxation time
 232 spectrum (see **Supporting Information**). According to Doi–Edwards theory [31], the
 233 relation between above two relaxation time is $\tau_s = \tau_{rep}^{HMW} / 3Z$, where Z is the average
 234 number of entanglements and $Z = M_w / M_e$. The molecular mass between
 235 entanglements M_e , calculated from $M_e = \rho RT / G_N^0$, is 21.7 kg/mol for PA1012 at 250
 236 °C, resulting in a Z value of 12. For the rheological description, τ_{rep} and τ_s are regarded
 237 as orientation relaxation time and stretch relaxation time, respectively. In the flow
 238 regime Wi_{rep} , $Wi_s > 1$, a strain rate greater than $1/\tau_{rep}$ and $1/\tau_s$ indicates the fast flow

condition. As a result, chain sections are strongly oriented and the chain conformation becomes similar to that of the crystalline state. The calculated magnitude of Wi_{rep} is about 5.43×10^5 . Such a large magnitude of Wi_{rep} guarantees the strong oriented counter path of polymer chains. Moreover, the magnitude of Wi_s following from τ_s is considerably larger than 1 (1.51×10^4), suggesting the polymer chain of HMW is strongly stretched. Hence, the strong extensional flow at nozzle entrance and relative low entanglement density ensure the sufficient stretch of the polymer chains or chain sections to fulfil the formation of oriented nuclei. It is also noticed that the calculated Z value is comparable to the simulation result $Z \leq 10$ for which the $G(t)$ shows no sign of plateau regime [32]. This is reconciled with the rheology data at 250 °C and thus confirms the reliability of calculation of Wi_s .

3.2 Analysis of crystallization structure

Fig. 4a shows the first frame collected at the gate position (G1). This diffraction pattern is similar to that found in highly oriented polyamide samples [33]. The major difference between this pattern and the one of common highly oriented polyamide is the distinguishable coexistence of α -phase and β -phase crystals in the present case. Two signals superposed at the inner layer ($2\theta = 9.11^\circ$) are contributed from the diffraction of both $\alpha 100$ and $\beta 100$ planes. Another two signals emerging at outer layers ($2\theta = 9.95^\circ$ and 10.43° , respectively) can be indexed to $\alpha 010/110$ and $\beta 020/120$ planes, respectively. Since the diffraction arcs are not fully separated, the β -phase is

inferred from the relatively greater outer arcing due to the presence of β 020/120 diffraction signals [35]. In addition, it can be observed that the reflection maximum shifts about 7 degree from the equatorial.

Fig. 4. The wide angle X-ray reflection signals at (a) G1; (b) G2; (c) G3 and (d) G10 in polar coordinates. The graphics to the right represent the corresponding azimuthal intensity profiles. The colored arrows indicate the specific reflection. The β 020/120 profiles marked * inevitably overlap with α 010/110 profiles. Oriented β -phase can be observed from the peak around 180 °

Next to the G1, G2 (Fig. 4b) shows that the α 010/110 planes superposed in G1 have separated into four off-equatorial and intensity-unequal arcs. This pattern formation

nevertheless results from, statistically, precessional rotation of uniaxial oriented crystals. The peak position of $\alpha 010$ is split by $\pm 30^\circ$ and the $\alpha 110$ by $\pm 18^\circ$ about the equator. Using the unit cell for α -phase of PA1012 reported by Jones *et al.* [36] ($a=0.459$ nm, $b=0.530$ nm, $c=2.98$ nm, $\alpha=50^\circ$, $\beta=77^\circ$, $\gamma=64^\circ$), the ideal reciprocal space angles in the X-ray diffraction patterns from lamellar-crystal mats (taken with X-ray beam parallel to the lamellae surface) can be concluded as follows: the 100 should be split by $\pm 5^\circ$, the 010 by $\pm 38^\circ$ and the 110 by $\pm 33^\circ$ about the either side of equator. The implication of this difference, according to Dreyfuss and Keller's observation in polyamide 66, 610 and 612, accounts for the partial randomization around the a-axis [37]. Because the a-axis is the direction of hydrogen bond progression corresponding with the fastest crystal growth, this pattern is favorably consistent with the structure of α -phase crystals as the incomplete twisting chain-fold lamellae [1, 38]. The separation of $\alpha 010/110$ reflections also makes the shadowed $\beta 020/120$ signals more apparent in G2. Although the α -phase crystals lose orientation uniformity in at least in one direction, it seems that the orientation state of β -phase remains unchanged.

G3 (Fig. 4c) shows very different formations. Two strong peaks at the equatorial are characteristic of β -phases present in both G1 and G2. However, in G3, sharp peaks cannot be found either from the inner layer or from the outer layers, which indicates that there is no β -phase present at this location. Moreover, the disorientation of the

290 α -phase can be observed from the relative larger spreads, particularly along the $\alpha 100$
 291 arcs. Comparing to X-ray diffraction patterns from lamellar-crystal mats, the intensity
 292 differences of α -phase signals (unequal arcs) also indicate the incomplete twisting of
 293 lamellae.

294 **Fig. 5.** The wide angle X-ray reflection signals at (a) C22; (b) E22 and their intensity
 295 profiles. Colored arrows indicate the specific reflection. The $\beta 020/120$ profiles
 296 marked * have the same meaning with those in Fig. 4.

298 The β -phase crystals can be seen again at G8 located at about 245 μm from the edge
 299 of the sample and is present up to G38, which is located at almost the same distance
 300 from the opposite edge. Between those two frames, the diffraction patterns clearly

present a superposition of arcs from the α -phase and sharp equatorial reflections from the β -phase, as presented in Fig. 4d, and indicates that while both α -phase and β -phase crystals are uniaxial oriented the β -phase exhibits a more highly oriented state.

Crystallization structure changes within the WD at the center and end positions follow similar rules to those seen at the gate position. However, the strong meridian signals found in around the centerline of above two positions, such as C22 and E22 (Fig. 5), are clear enough to indicate the evolution tendency of the flow field along the FD. Since the azimuthal intensity distributions of the α 100 reflections and the β 100 reflections in samples C22 and E22 remain comparatively unchanged compared to G8, the appearance of the meridian signals cannot be simply interpreted as the ensemble rotation of crystals, but should be still considered as a consequence from a random orientation about the a-axis [1]. If the X-ray is vertical to the fiber axis, a uniformly twisting lamellae, which is equivalent to a completely random state around the a-axis, would generate a pattern with α 010 reflections center on the meridian with spreads decreasing towards the equatorial and the α 110 has the maxima between the meridian and equatorial with decreasing intensity to each direction [37]. Nevertheless the α 100 reflection should be less affected by this twisting structure. Similar oriented and twisting texture for α -phase crystals of polyamides can be found in some spherulites [34] and the transcrystallites growing epitaxially on fibers [39]. In addition, given that

β -phase crystals are highly oriented in both cases, the most possible morphology represented by C22 and E22 is that α -phase crystals, in a complete twisting mode, epitaxially grew on the long-range ordered β -phase crystals.

3.3 Analysis of anisotropic structure

The so-called skin-core morphology, an anisotropy perpendicular to the FD, is a typical inhomogeneous structure resulted by different regimes of shear flow [19, 40].

Fig. 5 shows the normalized azimuthal intensity scans of different reflections at three positions. The profile data are plotted to a color scale image with full azimuthal angle as the x-axis and real-space scan position as the y-axis. On this basis, three distinct structural layers are identified.

Fig. 6. Normalized azimuthal intensity scans of different reflections (rows) at each position (columns). The rows from the top to the bottom represent the overlapped

334 α 100/ β 100 reflections (a, d, g), the α 010/110 reflections (b, e, h) and the β 020/120
335 reflections at gate position (c, f, i), respectively. The columns from the left to the right
336 represent the reflections at gate (a, b, c), center (d, e, f) and end position (g, h, i),
337 respectively. Note the unequal arcs (UA) and meridian signal (MS) emerging in the
338 α 010/110 reflections at different positions. The reduction of color contrast along the
339 FD represents the decreasing of overall orientation.

340 The skin layer is the strongest oriented layer containing both α -phase and β -phase
341 crystals. The skin layer was only found in the first and last one or two frames. As can
342 be inferred from the reflection maximum off-equatorial shifting, the crystals in this
343 layer show a rotational tilting inward toward the cavity center. The next layer, termed
344 “shell layer”, features larger spreads in α 100 reflection (Fig. 6a-6c) and arcs with
345 different splitting distance in α 010/110 reflections (Fig. 6d-6f). This interesting texture
346 can be attributed to the disorientation and, more prominently, twisting lamellae of the
347 α -phase as mentioned above. Moreover, the most significant characterization of the
348 shell layer can be made by considering the deficiency of β 020/120 signals (Fig. 6g-6i).
349 The thickening of the shell layer along the FD can be thus noticed. The core layer,
350 differing markedly from the conventional parts originated from pure shear flow, is
351 uniformly dominated by a highly oriented structure instead of the widely reported
352 large or deformed spherulites.

Another important but often neglected inhomogeneous structure is the structural distribution along the FD. In our case, while the thickness of skin layers remain the same, the reflection signals with both α -phase and β -phase exhibit maxima on about $\pm 7^\circ$, $\pm 6^\circ$ and $\pm 5^\circ$ to equatorial for the gate, center and end position, respectively. This suggests a non-parallel and varying orientation direction with respect to the FD as mentioned before. The shell layers increase in depth along the LD while core layer narrows down. For those two inner layers, an expected reduction of overall degree of orientation at increasing distance from gate can be observed. However, as can be seen from the shift of reflection maxima (highlighted by white dash dot lines in Fig. 6d-6e and 6g-6h), the crystals of the two inner layers (especially for the shell layer), split by the centerline, tend to tilt outward toward the wall. Notably, this bending direction is totally different from that of skin layer. The maximum tilt degree increases with distance from gate to end but decreases with the distance away from the component surface.

Fig. 7. The crystallinity index as a function of scanning sequence at (a) gate, (b) center, and (c) end. The crystallinity is identified as total ($\alpha+\beta$) CI.

The change of phase contents (Fig. 7) again suggests above two anisotropies. The maximum crystallinity is always observed in the skin layer at each position but its magnitude is less obvious at the gate position. The changes of α -phase CI (χ_α) are complicated. For the gate and the center position, the χ_α in the skin layer is lower than that in the shell and core layers, but for the end position the results show the contrary is true. The β -phase CI (χ_β) shows similar distribution through the WD at each position but dramatically decreases with distance from the gate towards the end. The change of mesophase basically follows the trend of the β -phase, which indicates that the β -phase were formed by crystallization of oriented melts and that relaxation of orientation certainly occurs in the shell layer or in the location away from the nozzle entrance. The sharp boundaries between skin-shell-core layers are contrasted by the abrupt changes of χ_β and the percentage of mesophase.

Fig. 8. (a) The SAXS pattern collected at the center position. The spread lamellae reflection was highlighted by the blue dash dot lines. (b) 1D scattering profile of lamellae reflection with integration sector demonstrated by dark dot lines. To exclude

equatorial streak, regions were integrated from -65 °to -180 °. The cartoon portrays the origin of lamellae reflection in SAXS patterns.

3.4 Molecular origins of anisotropic structure

The SAXS pattern collected at the center position (Fig. 8a) shows an azimuthally narrow equatorial streak and meridian blob-like lamellae reflection. This pattern generally indicates that the presence of oriented shish-kebab structure [27, 41, 42]. Except for those two parts, a rather spread and weak lamellae reflection occurred at larger q can be observed. Figure 8b shows the corresponding lamellae reflection profiles were best fitted by two overlapping peaks. The sharp peak at smaller q is from the lamellar stacks of kebabs [38, 42]. The weak peak belonging to the spread lamellae reflection might be assigned to the “row structure”-those lamellae stacks with smaller long periods and broader orientation distributions [1, 41].

Fig. 9. (a) From left to right, the SAXS patterns at gate, center and end, respectively.

(b) The average length of shish-kebabs (L) and integration breadth defining the disorientation degree (B_{eq}) is calculated using $q^2 B_{\pi/2}^2(q) = 1/L^2 + q^2 B_{eq}^2$, where $B_{\pi/2}(q)$ the integration breadth along azimuthal scan at specific is scattering angle.

Since the beam size used in SAXS experiments is much larger than that in μ WAXS, the SAXS patterns should contain aggregated information from different layers. The crystallization morphology in the core layer is represented by shish-kebab structure. This suggestion is based on two above observations: first, the β -phase crystals in the core layer are oriented steadily parallel to the FD and form nuclei from strained melts, which, in smaller structural levels, accords with the fibrous morphology of shish; second, the kebabs themselves could be straight or twisted [38, 43] and possess some degree of freedom to orient with the FD [5], which is only observed in α -phase. It is most possible that the shish backbone consists of β -phase, while continued growth of α -phase forms kebab structures. Mechanically, this conclusion is reconciled when consider the β -phase crystals adopt a less organized alternative sheet stacking arrangement and thus kinetically promote the formation of shish nuclei from oriented melt, while the α -phase crystallize in all sheet stacking progressively, which thermodynamically favors folded-chain lamellae. On the other side, for the shell layer, it is prudent to relate the period system formed by incomplete twisting α -phase crystals to the so-called row structure. Considering the chains and lamellae normals of α -phase crystals are non-parallel, the formation of row structure would be more readily [1].

Since an unexpected core layer structure was observed, it's necessary to quantitatively demonstrate changes of shish-kebab structure in the core layer along

the FD. A larger sample-to-detector distance was used to investigate such behavior.

Fig. 9a shows the SAXS patterns collected at gate, center and end. The length scale dimension and orientation state of the shish-kebabs are calculated by Ruland's streak fitting method [43-45]. The results in Fig. 9b show that the average length of the shish-kebabs (L) at the gate is around 250 nm but drastically decreases to only 26 nm at the end position. The disorientation degree, represented by values of B_{eq} , gradually increases along the FD. This observation suggests that the shish-kebabs are thin and long-range ordered at the gate while discrete and less oriented one at the end. The average length of shish-kebabs at the end is surprisingly small. However, it might make sense in the case of polyamides. Due to the large decrease in free energy on crystallization as a result of the hydrogen bonding, the long period and lamellae thickness for polyamides is only about 6 ~ 10 nm and 4 nm, respectively. The value of long period is significantly lower than that for polyethylene or polypropylene, which is in the range 18 to 30 nm depending on crystallization condition. The apparent long period at end position is about 10 nm. Morphologically, the scaffold feature of shish-kebab can be satisfied. In fact, the value of 26 nm is very close to the recent result in which the microshish in the initial stage of scaffold-network nuclei was about 30 nm [42]. Considering the shish-kebab structures in end position formed under the extensive relaxation condition, the length value of shish would be reasonable.

In addition, two apparent phenomena should also be stressed. One is that the equatorial scattering intensity of center streaks drops faster with distance away from the nozzle entrance, which may be attributed to an increase in interference between the weakly correlated discrete shishes arising from imperfect orientation as well as limited length [46]. The other is that even though the long period of lamellae reflection wouldn't change much, their scattering intensity decreases from gate to end. These two phenomena together indicate that the density of shish-kebabs in the core layer decreases along the FD, which can be confirmed by the WAXS data. Although the WAXS deconvolution results cannot fully represent the structural fraction of larger structures, the relative variations indeed reflect the relaxation of long-range order and loss in average orientation along the FD.

Fig. 10. Schematic illustrations of the crystallization morphology of the skin-shell-core layer structure at different positions within the component. Blue and green stacks represent α -phase crystals and β -phase crystals, respectively. The sheets in β -phase stacks are parallel to lamellae normal while those in straight α -phase stacks are not. The number inside indicate the position of layer border. The scale of lamellae between each layer is not exactly the same.

These analyses declare the observation of novel anisotropic structures of PA1012 under the extensional-shear-coupled flow field Fig. 10 shows the schematic illustration demonstrating the molecular origins of this skin-shell-core layer structure and its evolution along the FD. Nearing the cavity wall, the crystals in the skin layer show a fibrillar texture. The overall ($\alpha+\beta$) crystallinity index remains constant along FD. High proportions of mesophase observed in this layer indicate a broad range of high orientation states. Typically, the molecular chain or lamellae normal lie parallel with the surface of the component in the skin layer and that skin layer will narrow down from the gate to end [47]. However, the preferred oriented axis in this case may bend inward to the inner parts at the gate position and become increasingly parallel to cavity surface away from gate position. Moreover, the obvious thinning of the skin layer in common components originated from pure shear geometry cannot be observed, instead, the orientation regularity of lamellae would further increase at the far-end.

Finding no trace of β -phase, the next layer, the shell layer, can thus be recognized. The α -phase crystals in the shell layer exhibit the so-called row structure. This texture can be represented by the relative larger spreads of α -phase reflections and the specific splitting angle of the overlapped $\alpha 010/110$ [39, 41]. Given the contrasts of azimuthal intensity in this layer are still recognizable even at the end position, the existence of isotropic spherulites is denied. The lowest mesophase contents are observed in the shell layer, which means a large number of stretched chains relaxed here. Another notable aspect is that it is observed at the center and end of the component, and that the preferred axis of row structures tends to tilt outward toward the wall (in contrast to the case in the skin layer).

As discussed above, the core layer is characterized by the observation of shish-kebab morphology. The shish is composed of β -phase crystals and, necessarily, of mesophase [44, 48], while the α -phase crystals fall into kebab structures and change from untwisting to complete twisting. The μ WAXS and SAXS data together suggest the shish-kebab entities in the core layer shorten in length scale and increase in distribution of orientation along the FD. The evolution of shish-kebabs from gate to end is consistent with the previous investigation [49]: the lower flow rate generates a lower shish density and would enhance the twisting growth of kebabs thereafter.

3.5 Analysis of crystallization dynamics under the complex flow field

Although the reduction of overall orientation along the FD is expected, it is still interesting to recognize two inverted anisotropic features compared to components originated from pure shear flow geometry. (i) For the skin layer, thinning or loss of orientation cannot be detected. The bending fibrils structure at the gate position gradually becomes parallel to the cavity wall along the FD. Moreover, the orientation regularity increases further at the far-end of the cavity. (ii) The intermediate layer (identified as “shell layer” in this case) is most often characterized by the fine-grained morphology or the shish-kebabs corresponding to different flow or pulse rate rates. While the core layer is isotropic or, at best, deformed spherulites either for macro or micro components [19, 27, 47, 50, 51]. Some special technologies, such as oscillation shear injection molding [50] and gas-assisted injection molding [52] may generate thicker oriented layers, but the regularity that orientation degree consecutively reduces from skin to core remains unchanged. However, a completely opposite is observed in this case: the core layer is dominated by high level of orientation structure whereas the shell layer is not.

Fig. 11. Schematic illustration of flow condition and its effect on polymer chain sections. (a) Extensional pulse resulting in stretched of HMW tails. (b) Solidified skin

is dragged to deform before any debonding occurs. At the end position, strong wall slip results in huge increases in wall shear stress while at the gate position, weak slip only brings about affine deformation. (c) The instantaneous flow geometry of fountain flow in cavity and shear gradient based on previous studies [16-18, 53]. The active area of transverse flow locates near the slip wall where the shear flow emerges. The flow field is separated into two distinguished regions by the red dash lines: the transverse tumble dominant region and retraction dominant region.

The unusual anisotropic crystallization morphology of PA1012 cannot be simply interpreted as the consequence of shear-induced crystallization in different flow regime. Due to the strong coupling between extensional flow and shear flow, the flow patterns deviated from pure shear flow. Most importantly, this deviation was recorded owing to the special combination of material and experimental protocol.

As discussed before, HMW tails of PA1012 were strongly stretched due to the severe extension effect at the nozzle entrance (Fig. 11a). Once the melt entered into the cavity, considering the mould temperature, 80 °C, which is close to the glass transition temperature of PA1012, fast solidification (Fig. 11b) would occur at the location near to the cavity wall [54]. However, crystallization was enhanced by the strong stretched polymer chains and, as such, a highly oriented fibrils structure was observed in the skin layer. In addition, because of the high adhesive energy provided by polar amide group, polymer chain of PA1012 would stick to the cavity wall, which

will result in wall slip behavior [55, 56]. The unusual variation trend of the skin layer can be attributed to a “strong-to-weak” wall slip effect [55]. Due to the wall slip effect, the thin skin, with one side being adsorbed to the wall, was dragged by the high-velocity flow elements in the center space of cavity. This effect resulted in bending fibrils structure at the gate, which is much like the affine deformation of a rubber network under an external shear field. A similar texture was observed in a study on gas-assisted injection moulding processing in which the central fluid was high pressure gas [52]. As for the end position, since the fluid elements at this position entered the cavity earlier, a larger magnitude of flow velocity would generate a more strong slip in consequence of debonding of polymer-wall interfacial region [55]. Therefore, more regular and less rotationally tilted fibril crystals were observed.

Since the external characteristic lengths of geometries reduce enormously compared to the ideal condition, laminar flow would not fully develop after the rapidly extensional pulse. The implication is that the flow behavior would be more close to a “global” fountain flow. The fountain effect for polymer generates a localized hydrodynamic phenomenon demonstrated by the complex two-dimensional flow (axial and transverse) [16, 57, 58]. Question on whether fountain flow influences the molecular orientation still remains nowadays [59, 60]. Fig. 11c shows the instantaneous flow profile of the fountain flow at the end and gate positions in which fluid elements between the centerline and slip interface would decelerate in the

direction of flow and would acquire a transverse velocity spilling outward toward the wall [16, 53, 57]. According to the chain behavior proposed by Chu et al [38, 61, 62], this transverse velocity perpendicular to the flow could bring about hydrodynamic drag forces and tumble effect to coil the stretched chains at an intermediate region near to the wall, for which relaxation might be accelerated. It is most possible that the fast relaxation caused by tumble effect lead to the formation of twisting row structure in the shell layer, since this kind of period structure is favored under intermediate strain condition [1]. Referring to the thickness of shell layer, the transvers tumble dominant regions are identified. As highlighted by the red dotted line, the maximum transverse velocity located on the side nearing to slip wall and its active area would be largest at flow front [16, 57]. Considering that, it is convenient to understand the sharp shell-core layer border. The higher and wider-area transverse flow at the flow front results in the thicker and less oriented shell layer at end position, and notably, the larger tilt of crystals in the shell layer as well as part of the core layer at the far end will be observed.

Although the magnitude of the transverse velocity is much smaller around the centerline, the stretch chains in this region would get through continuous retraction. However, in our case, reconstruction of hydrogen bonding between polymer chains slowed the retraction process of stretched HMW tails, which was enough for the development of shish nuclei in core layer. On the other side, the morphological

differences of kebab in core layer could clearly distinguish the different relaxation degree along the FD [38, 49]. One should notice that, even though extensional pulse was sufficiently strong and PA 1012 solidified rapidly, a dramatic decrease of density and length of shish at the center and end position could be observed. This suggests, for most cases, the effect of extensional pulse on the polymer melt would be restrained and further diminished along the FD. Hence, it is also very important to know that no observable trend of deformation and orientation phase in core layer means zero-stress boundary in the centerline of cavity but does not necessarily mean nothing happens there.

4. Conclusions

A special combination of experimental protocols and polymer system was presented for investigating the flow-induced crystallization of polymer melts under the complex flow field. The line-scan collections of synchrotron μ WAXS at three different positions of final component provide a clue to comprehensively assess the crystallization textures and flow behavior of polymer melts. The crystallization structure, multiple orientation and phase contents together indicate a novel inverted anisotropic structure: along the FD, a skin layer showing more regular and less rotational tilted orientation at the far-end of the cavity; perpendicular to the flow, the shell layer showing less oriented twisting row structures consisted of α -phase crystals only, while the core layer showing shish-kebabs for which the complete twisting

α -phase lamellae epitaxially growing on the β -phase shish. These textures were confirmed by small-angle X-ray scattering. The inverted layer structure implies the wall slip and a global fountain flow happened under the complex flow field. Certain question was stressed on whether the fountain flow influences the molecular orientation. The answer seems to be that the fountain flow itself would not enhance the molecular orientation. On the contrary, if polymer chains are sufficiently extended, the transverse tumble of fountain flow would speed up the retraction of oriented chains in intermediate region between skin and core. The quantitative analysis on the shish-kebabs in the core layer suggests the effect of extensional pulse should be valued in the small-scaled geometries or under the high strain rate condition.

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References

- [1] Keller A, Machin MJ. J Macromol Sci Part B Phys 1967;1(1):41-91.
- [2] Kumaraswamy G, Issaian AM, Kornfield JA. Macromolecules 1999;32(22):7537-47.
- [3] Somani RH, Hsiao BS, Nogales A, Srinivas S, Tsou AH, Sics I, Balta-Calleja FJ, Ezquerro TA. Macromolecules 2000;33(25):9385-94.

- 613 [4] Somani RH, Hsiao BS, Nogales A, Fruitwala H, Srinivas S, Tsou AH.
614 *Macromolecules* 2001;34(17):5902-09.
- 615 [5] Li L, de Jeu W. Flow-induced mesophases in crystallizable polymers. *Interphases and*
616 *Mesophases in Polymer Crystallization II*, vol. 181: Springer Berlin Heidelberg, 2005.
617 pp. 75-120.
- 618 [6] Liedauer S, Eder G, Janeschitz-Kriegl H, Jerschow P, Geymayer W, Ingolic E. *Int*
619 *Polym Proc* 1993;8(3):236-44.
- 620 [7] Ratajski E, Janeschitz-Kriegl H. *Polym Bull* 2012;68(6):1723-30.
- 621 [8] Duplay C, Monasse B, Haudin JM, Costa JL. *J Mater Sci* 2000;35(24):6093-103.
- 622 [9] Cui K, Meng L, Ji Y, Li J, Zhu S, Li X, Tian N, Liu D, Li L. *Macromolecules*
623 2014;47(2):677-86.
- 624 [10] Cogswell FN. *J Rheol* 1972;16(3):383-403.
- 625 [11] Bischoff White E, Henning Winter H, Rothstein J. *Rheol Acta* 2012;51(4):303-14.
- 626 [12] Bushman AC, McHugh AJ. *J Appl Polym Sci* 1997;64(11):2165-76.
- 627 [13] Stadlbauer M, Janeschitz-Kriegl H, Eder G, Ratajski E. *J Rheol* 2004;48(3):631-39.
- 628 [14] Graham RS. *Chem Commun* 2014;50(27):3531-45.
- 629 [15] Gogos CG, Huang C-F, Schmidt LR. *Polym Eng Sci* 1986;26(20):1457-66.
- 630 [16] Mavridis H, Hrymak AN, Vlachopoulos J. *J Rheol* 1988;32(6):639-63.
- 631 [17] Bensaad S, Jasse B, Noel C. *Polymer* 1999;40(26):7295-301.
- 632 [18] Patham B, Papworth P, Jayaraman K, Shu C, Wolkowicz MD. *J Appl Polym Sci*
633 2005;96(2):423-34.
- 634 [19] van Meerveld J, Peters GM, Hütter M. *Rheol Acta* 2004;44(2):119-34.
- 635 [20] Jeong J-H, Leonov AI. *Polym Eng Sci* 2008;48(12):2340-53.
- 636 [21] Whiteside BR, Martyn MT, Coates PD, Greenway G, Allen P, Hornsby P. *Plast*
637 *Rubber Compos* 2004;33(1):11-17.
- 638 [22] Whiteside BR, Spares R, Brown EC, Norris K, Coates PD, Kobayashi M, Jen CK,
639 Cheng CC. *Plast Rubber Compos* 2008;37(2-4):57-66.
- 640 [23] Boussia AC, Vouyiouka SN, Porfiris AD, Papaspyrides CD. *Macromol Mater Eng*
641 2010;295(9):812-21.
- 642 [24] Seguela R. *J Macromol Sc. Part C Poly R* 2005;45(3):263-87.
- 643 [25] Zafeiropoulos NE, Davies RJ, Roth SV, Burghammer M, Schneider K, Riekel C,
644 Stamm M. *Macromol Rapid Commun* 2005;26(19):1547-51.
- 645 [26] Davies RJ, Burghammer M, Riekel C. *Macromolecules* 2007;40(14):5038-46.
- 646 [27] Schrauwen BAG, Breemen LCAv, Spoelstra AB, Govaert LE, Peters GWM, Meijer
647 HEH. *Macromolecules* 2004;37(23):8618-33.
- 648 [28] Wu J, Schultz JM. *Polymer* 2002;43(25):6695-700.
- 649 [29] Dealy JM. *Rheol Bull* 2010;79(2):14-18.
- 650 [30] Zhong Y, Fang H, Zhang Y, Wang Z, Yang J, Wang Z. *ACS Sust Chem Eng*
651 2013;1(6):663-72.
- 652 [31] Doi M, Edwards SF. *The Theory of Polymer Dynamics*: Clarendon Press: Oxford,
653 1986.

- 654 [32] Hou J-X, Svaneborg C, Everaers R, Grest GS. *Phys Rev Lett* 2010;105(6):068301.
- 655 [33] Hsiao BS, Kennedy AD, Leach RA, Chu B, Harney P. *J Appl Crystallogr*
- 656 1997;30(6):1084-95.
- 657 [34] Lotz, B, Cheng, SZD *Polymer* 2005; 46(3): 577-610.
- 658 [35] Jones Na, Atkins EDT, Hill MJ, Cooper SJ, Franco L. *Polymer* 1997;38(11):2689-99.
- 659 [36] Jones NA, Atkins EDT, Hill MJ, Cooper SJ, Franco L. *Macromolecules*
- 660 1997;30(12):3569-78.
- 661 [37] Dreyfuss P, Keller A. *J Macromol Sci Part B* 1970;4(4):811-35.
- 662 [38] Somani RH, Yang L, Zhu L, Hsiao BS. *Polymer* 2005;46(20):8587-623.
- 663 [39] Feldman AY, Fernanda Gonzalez M, Wachtel E, Moret MP, Marom G. *Polymer*
- 664 2004;45(21):7239-45.
- 665 [40] Jerschow P, Janeschitz-Kriegl H. *Rheol Acta* 1996;35(2):127-33.
- 666 [41] Wu J, Schultz JM, Yeh F, Hsiao BS, Chu B. *Macromolecules* 2000;33(5):1765-77.
- 667 [42] Liu D, Tian N, Cui K, Zhou W, Li X, Li L. *Macromolecules* 2013;46(9):3435-43.
- 668 [43] Yang L, Somani RH, Sics I, Hsiao BS, Kolb R, Fruitwala H, Ong C. *Macromolecules*
- 669 2004;37(13):4845-59.
- 670 [44] Hsiao BS, Yang L, Somani RH, Avila-Orta CA, Zhu L. *Phys Rev Lett*
- 671 2005;94(11):117802.
- 672 [45] Thünemann AF, Ruland W. *Macromolecules* 2000;33(5):1848-52.
- 673 [46] Murthy NS, Bednarczyk C, Moore RAF, Grubb DT. *J Polym Sci Poly Phys*
- 674 1996;34(5):821-34.
- 675 [47] Katti SS, Schultz M. *Polym Eng Sci* 1982;22(16):1001-17.
- 676 [48] Kimata S, Sakurai T, Nozue Y, Kasahara T, Yamaguchi N, Karino T, Shibayama M,
- 677 Kornfield JA. *Science* 2007;316(5827):1014-17.
- 678 [49] Keum JK, Burger C, Zuo F, Hsiao BS. *Polymer* 2007;48(15):4511-19.
- 679 [50] Yang H-R, Lei J, Li L, Fu Q, Li Z-M. *Macromolecules* 2012;45(16):6600-10.
- 680 [51] Lin X, Caton-Rose F, Ren D, Wang K, Coates P. *J Polym Res* 2013;20(4):1-12.
- 681 [52] Wang L, Wang JH, Yang B, Wang Y, Zhang QP, Yang MB, Feng JM. *Colloid Polym*
- 682 *Sci* 2013;291(6):1503-11.
- 683 [53] Lee H-S. *Polym Eng Sci* 1997;37(3):559-67.
- 684 [54] Fitchmun DR, Mencik Z. *J Polym Sci Poly Phys* 1973;11(5):951-71.
- 685 [55] Joshi YM, Lele AK, Mashelkar RA. *J Non-Newtonian Fluid Mech* 2000;94(2-
- 686 3):135-49.
- 687 [56] Boukany PE, Wang S-Q. *Macromolecules* 2009;42(6):2222-28.
- 688 [57] Coyle DJ, Blake JW, Macosko CW. *AIChE J* 1987;33(7):1168-77.
- 689 [58] Hsiung CM, Cakmak M, Ulcer Y. *Polymer* 1996;37(20):4555-71.
- 690 [59] Nguyen-Chung T, Mennig G. *Plast Rubber Compos* 2006;35(10):418-24.
- 691 [60] Kobayashi Y, Otsuki Y, Kanai T. *Polym Eng Sci* 2010;50(11):2182-89.
- 692 [61] Somani RH, Yang L, Hsiao BS, Sun T, Pogodina NV, Lustiger A. *Macromolecules*
- 693 2005;38(4):1244-55.
- 694 [62] Smith DE, Babcock HP, Chu S. *Science* 1999;283(5408):1724-27