Structural Evolution of LLDPE-LMW/HMW Blend during Uniaxial Deformation as Revealed by In Situ Synchrotron Radiation X-ray Scattering

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Abstract The structural evolutions of LLDPE-LMW/HMW blend during uniaxial deformation at temperatures of 80 and 120 °C were investigated by the in situ synchrotron radiation small- and wide-angle X-ray scattering (SR-SAXS/WAXS). The magic sandwich echo (MSE) sequence was used to detect a virtually dead-time-free induction decay (FID) for solid-state NMR analysis. The thermal property of the blend was first checked by DSC, and the temperature dependence of the overall crystallinity was obtained by MSE-FID. The onset melting temperature is determined to be 116 °C (DSC), and the enhanced n-flip motions in the crystalline domains are clearly observed at T>60 °C by MSE-FID. For deformation at 80 °C, the lamellae become staggered in the strain-softening region as shown by the four-point SAXS pattern, whereas further deformation leads to the melting-recrystallization in the strain-hardening region. For deformation at 120 °C, the six-point SR-SAXS signal appears just after the four-point SR-SAXS signal, which indicates the formation of new lamellae along deformation direction. In addition, no phase transition occurs in the whole deformation process at both temperatures. Current work shows the detailed temperature dependence microstructural evolution of LLDPE-LMW/HMW blend. This is expected to provide more structural information for correlating microscopic structure with macroscopic mechanical performance.

Keywords Polyethylene; In situ SAXS/WAXS; NMR; Microstructural evolution

INTRODUCTION

Polyethylene (PE) is the simplest linear polymer without any side group but the most productive polymeric materials.\(^1\)\(^\text{-}\)\(^3\) With the addition of different commoners and changing synthesis method, various kinds of PE are commercially available.\(^4\)\(^\text{-}\)\(^6\) i.e. high-density polyethylene (HDPE, branching unit <10/1000),\(^7\)\(^\text{-}\)\(^9\) low-density polyethylene (LDPE, branching unit 20–40/1000),\(^10\)\(^\text{-}\)\(^12\) linear low-density polyethylene (LLDPE, ethylene/α-olefin copolymer),\(^9\)\(^\text{-}\)\(^11\) and ultra-high molecular weight polyethylene (UHMWPE, \(M_w>1.5\times10^6 \text{ g/mol}\)).\(^12\) Linear low molecular weight polyethylene (LLDPE-LMW) is one type of LLDPE and owns low mechanical performance. The main usages for LLDPE-LMW are pigment dispersant, anticrosive coating, ink abrasives, and industrial lubricant (i.e. poly(vinyl chloride) and vulcanized rubber). After laboratory preparation, some researchers found that under appropriate crystallization conditions it is possible to form crystallites whose thicknesses are comparable to the extended-chain length of the molecule. It is also possible to develop much smaller sizes in the same sample.\(^13\) But with respect to its structural evolution mechanism, few literature could be found because of its low processability. The mechanical performance is highly related to crystallinity and chain orientation. However, the crystallinity of LLDPE-LMW is quite higher (over 80% at room temperature) than other types of PE.\(^4\)\(^\text{-}\)\(^6\) Thus, the structural evolution of LLDPE-LMW is crucial for us to understand the origin of mechanical properties.

The crystal structure plays an important role in determining the macroscopic performance of polymer products.\(^15\) There exist three crystalline phases, namely, orthorhombic,\(^16\)\(^\text{-}\)\(^17\) monoclinic,\(^18\)\(^\text{-}\)\(^19\) and hexagonal\(^20\) phase for PE. The orthorhombic phase is the most thermally stable phase, whereas the monoclinic and hexagonal phases appear under special conditions. For the monoclinic phase, Butler and Donald\(^21\) confirmed two main factors influencing the formation of the monoclinic phase under deformation. First, the monoclinic phase is formed more readily at lower temperatures (usually lower than 70 °C), and second, it is formed more readily in more crystalline polyethylenes (depending on the
PE’s type). Yamamoto et al.\textsuperscript{[20]} observed the hexagonal phase of oriented polyethylene under the high-temperature and high-pressure conditions. Tashiri\textsuperscript{[24]} then confirmed the existence of the conformationally disordered chains in the hexagonal phase under the same condition. In all the cases, both intrinsic molecular characteristics (branching content) and external parameters (i.e., temperature, pressure, and deformation) together determine the crystalline phase of PE. Despite different phases, the molecular conformation remains zig-zag.

Due to the extreme macroscopic performances, i.e., ultra-drawability, and low price, PE is widely blended with other materials, i.e., polyolefin, polyester, and rubber.\textsuperscript{[23–29]} Meanwhile, different kinds of PE are always blended to balance their different performances. Take the blend of HDPE and LDPE as a typical example. Despite molecular weight and polydispersity differences, the major molecular characteristics difference is the branching content and comonomer type as mentioned above. When the blends are crystallized, the relatively linear chains of HDPE permit the formation of spherulites. In contrast, branches of LDPE are excluded in the interlamellar phase.\textsuperscript{[30]} The branches increase the strain on the crystal, decreasing the thickness and lowering the melting temperature. It is assumed that these branches also act as barriers to chains of HDPE and subsequent co-crystallization.\textsuperscript{[30]} Fu et al.\textsuperscript{[31]} controls the relative content of HDPE and LDPE in amorphous and crystalline domains by selecting the temperature as the melting temperature of LDPE is much lower than that of HDPE. Since the experimental temperature stays between the melting temperatures of LDPE and HDPE, LDPE all stays in the amorphous phase, while the crystalline domain consists of HDPE. They confirmed the existence of a homogeneous strain distribution in the semi-crystalline polymers by the tensile deformation in HDPE/LDPE blends, which shows two-step processes, with two kinds of PE crystals being broken down at different strains (HDPE broke first). It inferred that in order to improve the product or processing performance, these two types of PE in the blends need to own vastly different characteristics. In addition to the control of branching degree, molecular weight control is also used in PE blends.\textsuperscript{[32,33]} The melting temperature and the width of the melting peak of PE samples are often affected by molecular weight and molecular weight distribution. However, quite few studies related to the molecular weight lower than 6k ($M_m$ g/mol) of LLDPE have been reported.

The non-linear stress-strain curve of PE is highly related to the hierarchical structure evolution during deformation. As a result, it is crucial to obtain the detailed structure evolution information. The combination of wide-/small-angle X-ray scattering is able to characterize the hierarchical structure of PE system ranging from sub-nm to several ten nm.\textsuperscript{[34,35]} With the discovery and application of synchrotron radiation X-rays, time resolution has been increased from hours to milliseconds. Polyethylene is also one of the earliest polymers to carry out in situ extension researching using synchrotron radiation wide-/small-angle X-ray scattering (SR-SAXS/WAXS).\textsuperscript{[36–41]} Jiang et al.\textsuperscript{[35]} studied the structural evolution of tensile-deformed HDPE at the lamellae level and found that different degrees of deformation correspond to different micro-mechanisms. Interlamellar crystalline block slips were activated at small deformations, whereas stress-induced fragmentation and recrystallization process proceeded at a larger strain. Also, the mobility in the crystalline lamellae and amorphous phase of PE was characterized by low-field NMR.\textsuperscript{[42]} Li et al.\textsuperscript{[12,43]} focused on both the flow-induced crystallization and the deformation mechanism of PE and revealed that the deformation behaviors of polymer crystals are determined by the interplay between intrinsic structural dynamic or chains mobility and external stress field.

In this work, the structural evolutions of LLDPE-LMW/HHW blend during stretching at 80 and 120 °C were investigated by the time-resolved in situ SR-SAXS and SR-WAXS methods. The transient structure information, i.e., long period at different directions, crystallinity, and the lateral crystallite size evolution, is obtained at different strains and temperatures, which provides basic structural information to understand the melt-recrystallization for PE processing.

**EXPERIMENTAL**

**Materials**

The PE samples used in this study were supplied by SIAM CEMENT GROUP (SCG), Thailand, which were prepared in lab-scale with the variation of comonomer contents in high molecular weight tail (LMW:HMW=80:20, W:W). The samples have the number-average molecular weight ($M_n$) of 6 kg/mol, and the mass-average molecular weight ($M_M$) of 220 kg/mol. The gel permeation chromatography (GPC) data is shown in the electronic supplementary information (ESI). The thermal properties of samples were characterized by differential scanning calorimetry. The melting temperature ($T_m$) and the crystallization temperature ($T_c$) of samples were measured to be 130.9 and 118.2 °C, respectively. The size of each strip-like specimen was 50 mm × 12 mm × 0.5 mm.

**Tensile Test**

A specially designed uniaxial tensile machine was used to conduct the drawing test. Stretch was carried out through two motor-driven clamps in the machine direction. The force information in the film stretching process was recorded by a tension sensor, and combined with the high time resolution of synchrotron radiation X-ray scattering techniques.\textsuperscript{[44]} During stretching, the tensile speed was set as 0.1 mm/s. Stretching began when the temperature reached the set point (80 and 120 °C in this study). Note: the maximal measuring strain of this extensile machine is 10.

**In Situ SR-SAXS and SR-WAXS Measurements**

The structures of PE films were characterized by in situ SR-SAXS and SR-WAXS measurement simultaneously at beamline BL16B, Shanghai Synchrotron Radiation Facility (SSRF). The wavelength of the X-ray was 0.124 nm and a Mar165 CCD detector was employed to collect the SR-SAXS patterns. The distance between sample and Mar165 CCD was 2020 mm. Meanwhile, a Pilatus 200K detector was put just below the uniaxial tensile machine to acquire the SR-WAXS patterns with the distance of 197.4 mm from sample to Pilatus 200K. The SR-WAXS/WAXS patterns were collected simultaneously during stretching with a time resolution of 20 s. Due to the lack of the amorphous signal near the small q value in 2D SR-WAXS pattern, the crystallinity would be smaller than the calculation results.
Differential Scanning Calorimetry (DSC)
DSC measurement was performed with an apparatus (DSC Q2000, TA Instruments) calibrated for temperature and melting enthalpy by using high-purity indium. The heating rate was 1 °C/min.

Solid-state Nuclear Magnetic Resonance
The time-domain (TD) NMR was performed with a Bruker minispec mq20 1H- low-field spectrometer, operating at 19.95 MHz for proton. The spectrometer features a 90° pulse length of 2.69 μs and the receiver dead time of 8.64 μs. The recycle delay (RD) time was set as 2 s, and the number of scans was set as 32 to ensure sufficiently high signal-to-noise ratio. The sample temperature range was set as 40−160 °C, and equilibrated for 20 min before any measurements. The temperature was regulated by a BVT3000 heater and the accuracy was controlled as ±0.5 °C by using nitrogen as the heat-transfer medium. The magic sandwich echo (MSE) sequence was used to detect a virtually dead-time-free induction decay (FID) which infers to the chain dynamics of PE. The Hahn echo sequence is combined in the MSE sequence, which refocuses losses due to the inhomogeneities of the magnetic field. Due to molecular mobility differences, three characteristic components (amorphous, interphase, and crystalline) in polyethylene can be well resolved in 1H-FID spectrum. And the weight ratio of each component could be determined by nonlinear fitting of the curve using Eq. (1).

\[ I_{\text{norm}}(t) = f_e e^{-0.5\sigma^2\sin bt} + (1 - f_e - f_a) e^{-\frac{t}{\tau_s}} + f_a e^{-\frac{t}{\tau_a}} \]  

where \( \tau_s \) is an apparent spin-spin relaxation time, which mainly contains information about dynamics and is also affected by strong static dipolar interactions, uniformity of magnetic field, and additional refocusing problems caused by the device. The exponent \( n \) can vary between 1 and the rigid-solid Gaussian limit value of 2. The prefactors \( f_e \) and \( f_a \) are related to the weight ratio of crystalline and amorphous components. The MSE-FID signal of PE is related to the flip motion of PE in the crystalline domain. Therefore, the apparent crystallinity obtained by MSE-FID may differ from that obtained by other techniques, but the general tendency holds.

DATA ANALYSIS

Lateral Crystallite Size
To evaluate the variations of lateral crystallite size, the full widths at half maximum (FWHM, \( \beta \)) of the (110) and (200) planes were estimated. The intensity distribution on the equator was extracted from the original SR-WAXS pattern and each peak was fitted with Gaussian function as shown in Fig. 1(a). After gathering each lattice plane’s peak position (2θ) and \( \beta \), the lateral crystallite size was estimated by using the Scherrer equation as follows:[49]

\[ L_{HKL} = \frac{K\lambda}{\beta_0 \cos \theta} \]  

Long Period
2D SR-SAXS patterns were integrated to obtain the 1D intensity distribution as a function of the module of scattering vector \( q \). To obtain the long period of lamellae along the meridional direction (\( L_{\|} \)) and equatorial direction (\( L_{\perp} \)) respectively, the integration regions only cover a certain azimuthal angle range in the meridian and equator. Through 1D integrated curves, the peak position \( q_{\text{max}} \) can be obtained, and the long period of lamellae \( L_{HKL} \) was calculated according to Bragg’s law:

\[ L_{HKL} = \frac{2\pi}{q_{\text{max}}} \]  

RESULTS

Temperature Dependence of the Crystallinity
The thermal property of the polymer blend was first checked by DSC as shown in Fig. 2(a). During the first heating, a wide melting peak appears. The onset of melting temperature is \( T_{\text{onset}}=116 \) °C, and \( T_{\text{onset}}=130 \) °C. The wide melting range is common in polymer blends, which suggests structural heterogeneity of the initial sample. The temperature-dependent structural evolution was further investigated by MSE-FID as shown in Fig. 2(b). The apparent crystallinity obtained by Eq. (1) as a function of temperature is shown in Fig. 2(c). A significant drop of the apparent crystallinity is observed within 60−100 °C. But compared with the DSC curve with the same heating rate where the onset of melting is determined to be 116 °C, such...
significant decrement of the apparent crystallinity may not be related to the destruction of the crystalline component. The recovery efficiency of MSE fails when the segmental dynamics is close to the time scale of the MSE pulse length. PE is a typical α, mobile semi-crystalline polymer, where there exists the chain dynamics, or more specifically n-flip motion in the crystalline domains. Therefore, once the thermally activated n-flip motion reaches the time scale of MSE pulse length, a significant decrement of the initial FID amplitude would be observed. In other words, the relaxation time of the n-flip motion in the PE crystalline domains reaches ~10 kHz within 60–100 °C in the current study. This could significantly underestimate the crystallinity, as the T2 value of the crystalline domain is much smaller than that of the amorphous part. Based on this dynamics information, the following microstructure evolution investigation would be conducted at 80 and 120 °C.

**Mechanical Properties of PE Film at Various Temperatures**

The stress-strain curves of PE film stretched at 80 and 120 °C are shown in Fig. 3(a) together with the CCD images of the tensile PE specimen at different strains (80 °C) as shown in Fig. 3(b). The true stress-true strain curve and the Haward-Thackray model at 80 and 120 °C are shown in Fig. S2 (in ESI). At the very beginning of the stress-strain curve at 80 °C, the stress σ grows rapidly with the increment of the strain ε before the yield point (ε_yield=ca. 0.33). The value of the stress at the yield point is σ_yield=ca. 7.4 MPa, and a slight shrink is found on the side of the PE specimen at the yield point. Keeping stretching would lead to a decrement of the stress till ε=ca. 1.45 with the obvious double V-shaped shrinks at the center of the specimen (forming the necking). σ slowly drops to ca. 4.6 MPa at that time. In the rest of the curve, σ remains a constant (ca. 4.6 MPa) with the expansion of the necking according to the macroscopic morphology of the specimen. The mechanical results at 120 °C have the similar yield strain to that at 80 °C (ε_yield=ca. 0.36), while σ_yield of ca. 2.6 MPa is much lower than that at 80 °C. Such softening should be attributed to faster chain dynamics and lower crystallinity. The offset strain of the strain-softening or the onset strain of the necking ie=ca. 1.25 and stress is kept at the stress value of ca. 1.9 MPa before fracture.

**Uniaxial Stretching of PE Film as In Situ Tracked by SR-SAXS/WAXS**

The stress-strain curves together with the selected 2D SR-SAXS/WAXS patterns at 80 and 120 °C are depicted in Figs. 4(a) and 4(b), respectively. (Note: meridian is defined as the stretching direction while equator aligns the vertical direction.) Before stretching, a round ring that represents the isotropic crystal compound could be found on the SR-SAXS pattern at 80 °C. The round ring gradually becomes ellipse under the initial load before the yield point. At ε=0.39, near the yield point (ε_yield=ca. 0.33), the ellipse starts to split into two arcs in the equatorial direction. At the strain-softening part (ε=0.66), the two arcs gradually shrink towards each center (V-shape signal) and form the four-point signal (ε=0.92). Further stretching leads to the appearance of a semi-circle signal in the meridian direction where the four-spot pattern disappears. At the onset strain of the necking (ε=0.92), the original two arcs (become two tips at larger q range) in the equatorial direction vanish completely. And for the corresponding SR-WAXS patterns, two arcs which are assigned to (110) and (200) planes converge towards the equator gradually. Less obvious splitting of the (110) plane could be found at ε=0.92 and the results of the azimuthal integration of the (110) plane would be shown later.

For stretching at 120 °C, there also exists a ring on SR-SAXS pattern before tensile, while it is not as clear as that at 80 °C. Within ε<ε_yield, the evolution of the SR-SAXS patterns is similar to that at 80 °C where two arcs are also separate from the ellipse. However, there still remains some ordinal compound near the beamstop. The well-resolved four-point pattern is
Fig. 3  (a) Stress-strain curves of PE film at various temperatures (Note: the dotted line represents the expansion of the necking.). (b) CCD images of the tensile PE specimen at different strains when stretching at 80 °C.

Fig. 4  The stress-strain curve and selected 2D SR-SAXS/WAXS patterns acquired during uniaxial tensile deformation at (a) 80 °C and (b) 120 °C together with corresponding strain. The stretching direction (SD) is shown by the red double-headed arrow. The azimuthal integration curves at different strains with an interval of ε=0.13 at 120 °C are shown in Fig. S3 (in ESI).
also formed in the strain-softening part (0.36<\varepsilon<1.25). Compared to that at 80 °C, the new six-point pattern appears at \varepsilon=1.13 indicating a new ordinal structure formed along the tensile direction. Besides, the two tips (larger q range) do not occur in the equatorial direction like that at 80 °C. The evolution of the SR-WAXS patterns looks similar to that at 80 °C without quantitative analysis.

Periodicity Information of the PE Lamellae during Deformation

In order to obtain the lamellar thickness of the PE lamellae in the meridional and equatorial directions, the 1D integrated SAXS intensity curves are shown in Fig. 5, where the shift of the peak position is highlighted with a red arrow. The mask protocol of the 2D SR-SAXS patterns used for integration is shown in the inset. The evolution trend of \( q_{\text{max}} \) is similar at these two temperatures. In the meridian direction, for stretching at 80 °C, \( q_{\text{max}} \) decreases first (ca. 0.21 nm\(^{-1}\) to ca. 0.18 nm\(^{-1}\)) with the increment of the strain. After a short range of strain, where the peaks of the I-q curves are not clear (crystalline melting), \( q_{\text{max}} \) increases (ca. 0.24 nm\(^{-1}\) to ca. 0.29 nm\(^{-1}\)) with increasing strain. In the equatorial direction, \( q_{\text{max}} \) increases (ca. 0.21 nm\(^{-1}\) to ca. 0.34 nm\(^{-1}\)) with the increment of the strain. The evolution trend of the results at 120 °C is similar to that at 80 °C, though the turning points are different. The value of the long period of the lamellae is calculated using Eq. (3) and the result is shown below in Fig. 6. The decreasing trend of long period value in the equatorial direction at large strain indicates the fibrillar transition process, which is consistent with the previous studies.\(^{[21,53]}\)

Structure Evolution of PE Film under Uniaxial Extension at Different Temperatures

1D integrated SR-WAXS intensity profiles at different strains are shown in Figs. 6(a) (80 °C) and 6(c) (120 °C). Only (110) and (200) planes are found in the 1D integrated SR-WAXS intensity curves, which means no phase transition occurs at both two temperatures (only the orthorhombic phase exists). There is nothing unexpected in our finding because the monoclinic phase was not formed at higher temperatures.\(^{[21,52]}\) Thus, this result would simplify the quantitative analysis.

The detailed structural evolutions of PE film, i.e. long periods of lamellae (\( L_{m,e} \)), crystallinity (\( \chi_c \)), and stress-strain curve, at different temperatures during uniaxial extension are summarized in Figs. 6(b) and 6(d). For 80 °C, as shown in Fig. 6(b), the structural evolution process can be generally divided into three regions according to the stress-strain curve and the \( \chi_c \) curve. Before stretching, \( \chi_c =ca. 39.4\% \) (the apparent crystallinity. Note: if there is no special mark, it is the result measured by SR-WAXS) which is much higher than that in HDPE\(^{[53]}\) and LLDPE.\(^{[54]}\) \( L_m \) and \( L_e \) share the same value of ca. 25.6 nm according to the round ring in the initial 2D SR-SAXS pattern. In region I, before the yield point (\( \varepsilon<0.33 \)), \( \sigma \) would reach the

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**Fig. 5** The strain dependence of the 1D integrated SAXS scattering intensity of PE film during uniaxial extension along the meridional direction (a, 80 °C; c, 120 °C) and the equatorial direction (b, 80 °C; d, 120 °C). The insets show the masked region for integration.
maximum (ca. 7.4 MPa) and \( \chi_c \) reduces slightly with the strain (\( \rightarrow \) ca. 68.9%). \( L_m \) increases with the increment of strain and reaches the maximum value of ca. 28.1 nm, while \( L_e \) decreases with the increment of strain with \( L_e=ca. \) 22.7 nm at the yield point. In region II, \( \sigma \) drops to ca. 4.6 MPa in this strain-softening part. After analyzing the detailed microscopic structural information, two parts could be further divided into this region. In the former part of region II (0.33<\( \varepsilon <0.92 \)), \( L_e \) keeps decreasing to ca. 15.1 nm, while \( L_m \) cannot be obtained for which the period structure disappeared along the meridian direction on the SR-SAXS pattern as shown in Fig. 4(a). The decreasing slope of \( \chi_c \) is much sharper than that in region I and \( \chi_c \) drops to ca. 60.8% at \( \varepsilon =9.92 \). However, in the latter part of this region (0.92<\( \varepsilon <1.45 \)), \( L_m \) reappears from ca. 22.4 nm with \( L_e \) missing its value. \( L_m \) decreases to ca. 18.9 nm with the increment of strain. Although \( \chi_c \) keeps reducing, the decreasing rate of \( \chi_c \) slows down obviously and \( \chi_c \) reaches a minimum value of ca. 55.6% at \( \varepsilon =1.45 \), the boundary of region II/III. In region III (\( \varepsilon >1.45 \)), the necking part, owing to the locking of the beam location, the microscopic structural information would not change.

Further increasing temperature to 120 °C leads to the appearance of the six-point signal on SR-SAXS pattern as shown in Fig. 4(b). The structural evolution process can be also generally divided into three regions according to a similar method at 80 °C. The approximate value of the initial \( L_m \) (ca. 30.1 nm) was cited in Fig. 6(d) in that it is hard to fit \( q_{\text{max}} \) on the SR-SAXS pattern before deformation. \( L_m \) increases with the increment of the temperature; however, the initial \( \chi_c=ca. \) 53.6% is much lower than that at 80 °C. At the yield point, the boundary of region I/II, \( \sigma \) and \( L_m \) increase to ca. 2.6 MPa and ca. 34.1 nm, while \( \chi_c \) and \( L_e \) drop to ca. 52.9% and ca. 25.7 nm, respectively. In region II (0.36<\( \varepsilon <1.25 \)), \( \sigma \) drops to ca. 1.9 MPa and in the former part (0.36<\( \varepsilon <1.00 \)) \( L_m \) cannot be obtained while \( \chi_c \) and \( L_e \) keep decreasing to ca. 42.9% and ca. 21.0 nm, respectively. Compared to that at 80 °C, in the later part of region II, periodic structure along the equatorial direction still exists (\( L_m \) reduces to ca. 17.4 nm). \( L_m \) reappears from ca. 29.1 nm with slightly decreasing to ca. 28.6 nm at the end of region II. In region III, \( L_e \) disappears while the other three values remain almost constant in this necking part.

**DISCUSSION**

The structural evolutions of LLDPE-LMW/HMW film during uniaxial deformation coupled with the high time-resolution synchrotron radiation X-ray scattering at 80 and 120 °C were...
investigated in this work, which is aimed at revealing the deformation mechanisms in the stretching process. Herein, the following topics will be addressed in the discussion part: (i) lattice plane splitting phenomenon in the whole stretching process; (ii) evolutions of the lateral crystallite size and lattice spacing distance; and (iii) structural evolution of PE film during stretching at various temperatures.

**Lattice Plane Splitting Phenomenon during the Whole Stretching Process**

As shown in Fig. 4, the obvious splitting of the (110) plane could be found in the deformation process. Fig. 7 exhibits the azimuthal integration of the (110) plane at 80 and 120 °C. At 80 °C, two obvious peaks are found at, for example, ε=0.53. The onset strain of the two peaks is ca. 0.39 (pink line in Fig. 7a), just after the yield point. The two peaks gradually converge and finally form one single peak. It is hard to distinguish the offset strain of the two peaks, but one certain result is that splitting of the (110) plane occurs in region II and only one peak is found in region III (necking part). However, at 120 °C, the formation of the two peaks is before the yield point. At ε=1.25, only one peak is shown in Fig. 7b. The splitting of the (110) plane indicates that the formation of the twisting lamellae is accompanied by the crystal melting. And the difference of onset strain between 80 and 120 °C accords with the d-spacing results. This result coincides with our previous work[35] that lamellae rotation toward the stretching direction occurs before strain hardening and the onset of lamellae rotation occurs even earlier (near the yield point) using this kind of low molecular weight PE.

**Evolutions of the Lateral Crystallite Size and Lattice Spacing Distance**

Figs. 8(a) and 8(b) show the variations of the lateral crystallite size estimated from the (110) and (200) reflections based on the Scherrer equation (Eq. 1) at 80 and 120 °C, respectively. At 80 °C, before stretching, \( L_{110}=ca.\) 34.9 nm and \( L_{200}=ca.\) 26.0 nm. In region I, a slight decrement is found in both \( L_{110} \) and \( L_{200}. \) At the yield point, \( L_{110} \) and \( L_{200} \) decrease to ca. 33.1 nm and ca. 25.2 nm, respectively. After the yield point, \( L_{110} \) and \( L_{200} \) decrease sharply to ca. 18.1 nm and ca. 14.9 nm at \( \varepsilon=1.43. \) And both these two values would remain almost constant after \( \varepsilon=1.43. \) In order to compare the above data, the boundary lines between each region are also added in Fig. 8(a). The turning points coincide with the boundary lines very well.

In Fig. 8(b), before stretching at 120 °C, the initial values of \( L_{110} \) and \( L_{200} \) are ca. 38.6 nm and ca. 28.5 nm, respectively, which are much larger than those at 80 °C. Considering that the crystallinity calculated by SR-WAXS is the statistical average result in the sample, some small and unstable crystallites might be melting after heating at 120 °C. At the yield point, \( L_{110} \) and \( L_{200} \) slightly decrease to ca. 36.2 nm and ca. 27.3 nm (still larger than the initial values at 80 °C), respectively. Further deformation leads to a sharp decrease in \( L_{110} \) and \( L_{200} \). At \( \varepsilon=1.25, \) \( L_{110} \) and \( L_{200} \) decrease to ca. 26.1 nm and ca. 21.4 nm. After that, the values would keep almost constant. The evolution trends of \( L_{110} \) and \( L_{200} \) are similar to each other at two different temperatures. No matter at the same strain or at the boundary line, the values of \( L_{110} \) and \( L_{200} \) at 80 °C are smaller than those at 120 °C. It is difficult to determine the reason why the lateral crystallite size increases with the increase of temperature in that the initial sizes are different at different temperatures. Referring to the actual example of PE processing, reannealing at a higher temperature than the original does lead to a further increase in the thickness of the lamellae (recrystallization process).[56] Thus, this result indicates that stretch-induced recrystallization might be related to the temperature.

Besides the lateral crystallite size, another important factor reflecting microscopic structure evolution is the lattice spacing distance. Figs. 8(c) and 8(d) show the variation of crystalline lattice spacing with strain at different temperatures. At 80 °C, the values of \( d_{110}=ca.\) 4.15 Å and \( d_{200}=ca.\) 3.81 Å remain almost constant before the yield point. Further stretching leads to a sharp increase of d-spacing with \( d_{110}=ca.\) 4.16 Å and \( d_{200}=ca.\) 3.82 Å, respectively. Though the difference is not significant, the evolution trend could well support the structural evolution mechanism of PE film as shown above. In region I, the bearing force unit is the amorphous molecular chains and PE crystal changes little. However, the melting of lamellae occurs in region II and leads to the increment of d-spacing. As mentioned above, the microscopic structural information would not change in region II. At 120 °C, \( d_{110} \) changes little (\( \Delta d=ca.\) 0.004 Å). The evolutions in region II and III are similar to that at 80 °C; however, in the initial region, d-spacing also increases. This phenomenon indicates that crystal melting may occur at the beginning of deformation at higher temperatures.

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Fig. 7 The azimuthal intensity distribution of (110) plane at different strains with an interval of 0.132/0.125 at (a) 80 and (b) 120 °C.
Structural Evolution of PE Film during Stretching at Various Temperatures

According to the above quantitative analysis, the structural evolution of LLDPE-LMW/HMW blend can be generally divided into three regions, as schematically illustrated in Fig. 9. The amorphous domain mainly dominates the almost elastic deformation in region I. The crystallinity remains almost constant (Figs. 6b−6d) and the lamellae relocates along the MD owing to the extension of the elastic amorphous molecular chains (the massive decrease of scattering intensities in meridian at the yield point). In region II, after the yield point, the lamellae begin to melt under load and the major difference between 80 and 120 °C also appears in this region. At 80 °C, according to our previous work, due to the heterogeneous stress field, the sequential melting of lamellae at different azimuthal angles is responsible for the appearance of the four-point pattern. At 120 °C, some small and unstable crystals would melt before stretching. Except for the four-point signal, there exist two more points along the meridian direction during the deformation. According to the crystallinity data in Fig. 6, recrystallization has already occurred in region II (Fig. 6d). This indicates that the lamellae melting and recrystallization could occur simultaneously. And this kind of new-formed crystal is linked by the extended chains (streak signal). Further stretching results in the formation of the extended-chain fibrils.

CONCLUSIONS

In summary, the in situ characterization of LLDPE-LMW/HMW during deformation was performed at 80 and 120 °C with the assistance of a specially designed uniaxial tensile machine and SR-SAXS/WAXS. Compared with HDPE, even at 80 °C (lower temperature), no phase transition occurs after the yield point of LLDPE-LMW/HMW. In the stretching process at 80 °C, the amorphous domain mainly dominates the almost elastic deformation before the yield point. After the yield point,
lamellae begin to melt and form the four-point signal. Recrystallization occurs in the final stage of this part and new-formed crystal arranged along the tensile direction. In the stretching process at 120 °C, the initial apparent crystallinity is much lower (27.1%) compared with that at 80 °C (39.4%). Besides the four-point signal in region II, due to the smaller onset strain of recrystallization, crystal signal along the meridian direction together with the four-point signal forms the six-point signal, which means the onset of recrystallization shifts to an earlier strain. The microstructural evolution of these two kinds of SR-SAXS patterns verifies that the sequential melting of lamellae at different azimuthal angles is responsible for the appearance of the four-point pattern because of the heterogeneous stress field. This indicates that the onset of recrystallization at different temperatures is different and controlling this essential parameter is instructive for polyethylene processing.

Electronic Supplementary Information
Electronic supplementary information (ESI) is available free of charge in the online version of this article at http://dx.doi.org/10.1007/s10118-020-2458-y.

ACKNOWLEDGMENTS
This work was financially supported by the National Key R&D Program of China (No. 2016YFB0302500). We would like to acknowledge Prof. Benjamin S. Hsiao (State University of New York at Stony Brook) and SIAM CEMENT GROUP Corporation (Thailand) for their generous supports in raw PE materials and Mr. Wenqiang Hua (SSRF) for his kind help with the operation of detectors.

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