

# Strain-induced Stereocomplex Formation from the Initially Amorphous Poly(L-lactic acid)/Poly(D-lactic acid) Samples

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 Electronic Supplementary Information

**Abstract** The strain-induced crystallization behaviors of ultrasonic micro-injection molded poly(L-lactic acid)/poly(D-lactic acid) (PLLA/PDLA) samples from an amorphous state were investigated by stress-strain relations and *in situ* wide angle X-ray diffraction (WAXD) measurements. The formation of direct strain-induced stereocomplex (SC) was evident. In samples molded at 50 and 80 °C, this phenomenon can be attributed to the acceleration of the ordered structures due to the existence of a large number of SC nuclei. The SC nuclei are assumed to serve as the transient physical cross-links to initiate the strain-induced crystallization. The onset of strain-induced crystallization is analogous to the heating induced structural reorganization. Consequently, the observed strain-induced SC process can be considered a pseudo process, which is actually thermally induced. Upon further stretching, the actual strain-induced crystallization occurs with the exclusive formation of the homocrystallite (HC), while the preceding formed SC crystals undergo slight fragmentation during subsequent tensile deformation. At 120 °C, due to the reduced number of SC nuclei within the sample, the occurrence of cold crystallization during stretching plays a more significant role than SC nuclei with respect to the strain-induced SC process, as demonstrated by *in situ* WAXD measurements upon annealing in both the static and stretched states.

**Keywords** Amorphous PLLA/PDLA blend; Strain-induced crystallization; Strain-induced SC formation

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## INTRODUCTION

Strain-induced crystallization (SIC) is a frequently observed phenomenon during the practical processing of polymers or their subsequent application in products, such as in the case of rubbers.<sup>[1]</sup> The formation of new crystals can be induced during the stretching of a polymer,<sup>[2]</sup> with the crystallization kinetics accelerating by several orders of magnitude.<sup>[3]</sup> The deformation process during stretching involves a multistep structural evolution due to the hierarchical structures of a semi-crystalline polymer. For instance, the inter- and intralamellar slip mechanisms are observed at low strains, followed by crystallite fragmentation and fibril formation at moderate strains, and chain disentanglement occurs at large deformations.<sup>[4,5]</sup>

Poly-lactide (PLA) is a widely used biodegradable thermoplastic polymer due to its favorable biocompatibility, optical and thermal properties.<sup>[6,7]</sup> The stereocomplexes (SCs) formed by mixing the enantiomeric pairs of poly(L-lactide) (PLLA) and poly(D-lactide) (PDLA) demonstrate a melting temperature 50 °C higher than that of homocrystallites (HCs). The hydrolysis resistance and thermomechanical properties of SCs are also

significantly enhanced,<sup>[8,9]</sup> paving the way for the utilization of PLA-based materials into the field of engineering plastics.<sup>[10,11]</sup>

The strain-induced crystallization behaviors of PLLA (or PLA) have been investigated comprehensively. Both amorphous and crystalline samples are considered prior to deformation.<sup>[6,12–18]</sup> For the amorphous sample, the strain-induced crystallization occurs without the concomitant presence of the lamellar macromorphology during the drawing of PLLA.<sup>[14]</sup> Stoclet *et al.* identified a disorder-order transition for strains over 130% upon tensile stretching of amorphous PLA.<sup>[19]</sup> In addition, Jiang *et al.* observed that the cohesive mesophase is generated when molecular chains approach their finite extensibility, triggering the strain-induced crystallization during stretching of glassy PLA.<sup>[20]</sup> Zhang and colleagues revealed that elevating the strain rate yields an increase in the crystallinity, orientation and cavitation of the deformed PLA.<sup>[21]</sup> With respect to the crystalline sample, it was found that the initial crystallites undergo slippage and partial destruction, in parallel with the formation of cavitation and voiding within the low strain range at low deformation temperatures.<sup>[6]</sup> Zhang *et al.* demonstrated that the stress and stretching temperature exert a significant influence on the formation of cavitation upon stretching PLLA samples in the  $\alpha$  form.<sup>[22]</sup> Moreover, the high orientation induced by strain is

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particularly evident at lower draw temperatures because of the slower chain relaxation within PLLA.<sup>[23]</sup> Renouf-Glauser *et al.* pointed out that craze is the primary mechanism governing the deformation of amorphous materials, whereas both cavitation and fibrillated shear dominate the deformation of crystalline counterparts.<sup>[24]</sup>

In comparison with PLLA, only a limited number of studies have been conducted on the strain-induced structural evolution of PLA stereocomplexes (or PLLA/PDLA blends). A previous study was conducted on fibers with respect to PLLA/PDLA blends. It was demonstrated that only the  $\alpha$  form of HC can be induced during drawing from initially amorphous fibers composed of a racemic blend at a draw temperature between 60 and 120 °C.<sup>[25]</sup> Additionally, Stoclet pointed out that the SC is unable to be strain-induced from the initially amorphous PLLA/PDLA blend below 120 °C.<sup>[26]</sup> Furthermore, he observed that the PLLA/PDLA blend with initial SC crystals exhibits superior resistance to stretching than its counterparts with the presence of  $\alpha$  form.<sup>[26]</sup> Pan *et al.* examined the structural evolution of the PLA with initial SC, HC and SC/HC mixtures upon deformation. The improved mechanical resistance of SC-PLA over HC-PLA is partially attributed to the more effective stress transfer within the SC-PLA structure.<sup>[27]</sup> The findings of their study again indicate that the new SC crystallites cannot be generated during stretching at lower temperatures.<sup>[27]</sup> It is generally accepted that the direct strain-induced SC is only generated at a stretching temperature between the melting temperatures of HCs and SCs.<sup>[26]</sup> For example, Chang *et al.* discovered that when the PLLA/PDLA were stretched to a specific strain and subsequently annealed at designated temperatures (180–215 °C), orientation-induced crystallization resulted in an increase in SC formation.<sup>[28]</sup> However, Huang *et al.* prepared amorphous as spun fibers composed of high-molecular-weight PLLA/PDLA blends with a new transesterification catalyst of sodium in masterbatch (MB). The stereo-block PLA copolymers were *in situ* formed through the transesterification reaction, which restricted the phase separation and further promoted the relatively weak CH<sub>3</sub>...O—C hydrogen bonding interactions, along with the exclusive formation of SCs in the PLLA/PDLA/MB blend fibers drawn at low temperatures ( $\leq 102$  °C).<sup>[29]</sup>

Nevertheless, a comprehensive understanding of the deformation mechanism involved during tensile stretching of PLLA/PDLA blends, particularly when the initial state is amorphous, remains elusive. This kind of study is essential for gaining insights into the superior mechanical resistance of SC crystallites compared to their HC counterparts, which is a key area of research. Ultimately, this knowledge can be utilized to regulate and control the final physical properties of PLA-based products.

In this study, PLLA/PDLA blends were processed by ultrasonic injection molding, yielding initially amorphous tensile bars. The strain-induced structural evolution during tensile stretching of the samples was investigated through the analysis of stress-strain relations in conjunction with *in situ* WAXD measurements. As will be illustrated in the following, the direct strain-induced SC crystallites were observed, and the resulting structural evolution was subjected to comprehensive analysis.

## EXPERIMENTAL

### Materials

The PLLA was obtained from Zhejiang Hisun Biomaterial Co., Ltd. (Taizhou, China), while the PDLA with the trade mark of Luminy D070 was purchased from Total Corbion PLA (Thailand) Limited. The molecular information of these two materials is presented in Table 1.

**Table 1** The molecular weight information of the two PLA materials.

| Sample | $M_w$ ( $10^4$ g/mol) | $M_n$ ( $10^4$ g/mol) |
|--------|-----------------------|-----------------------|
| PLLA   | 4.93                  | 1.98                  |
| PDLA   | 4.14                  | 2.98                  |

### Sample Preparation

The PLLA/PDLA blend with a mass ratio of 1:1 was prepared using the solution method. The initial step involved the dissolution of PLLA and PDLA in dichloromethane, obtaining solutions with a concentration of 50 mg/mL. Subsequently, the PLLA and PDLA solutions were mixed followed by stirring for 6 h. The mixed solution was then evaporated for 24 h at room temperature, resulting in the formation of the bulk PLLA/PDLA blend. The PLLA/PDLA blend was subjected to ultrasonic microinjection molding in a Sonorus 1G machine (UltraSion S.L., Spain) to yield a tensile bar with an effective dimension of 24 mm (length)  $\times$  1.3 mm (width)  $\times$  0.5 mm (thickness). During the molding process, the energy of the ultrasonics is transformed into fast mechanical vibrations with the aid of a converter, which facilitates the melting of the sample. The ultrasonic vibration was continued for 1 s, and the melt temperature was determined to be 250–280 °C using a previously established estimation method.<sup>[30–32]</sup> The short duration of the melting process and rapid cooling rate (more than 100 K/s) allow for the reservation of a large number of PLLA/PDLA clusters (SC nuclei).<sup>[30]</sup> The processing filling speed was set at 50 mm/s, and the cooling time was 5 s. The mold temperature was varied from 50 °C (slightly lower than  $T_g$  ~60 °C) to 80 and 120 °C in order to potentially modify the microstructure. The mold temperature of 120 °C is selected to be considerably higher than  $T_g$ , but lower than the melting point of HCs (~170 °C). For the purposes of comparison, the PLLA samples were also prepared under identical processing conditions for ultrasonic microinjection molding.

### Uniaxial Tensile Test

The uniaxial tensile tests were carried out on a tensile machine (Linkam, UK) with a tensile rate of 0.02 mm/s to ensure a quasi-static process during stretching. The tensile temperature was selected to be 70 °C, which is slightly higher than  $T_g$  to achieve a large deformation, but lower than the critical temperature for heating induced structural reorganization (~80 °C),<sup>[30]</sup> thus ensuring that the samples were stretched from the amorphous state.

A camera was employed to capture the images of the sample during tensile deformation, thereby enabling the calculation of the true strain as follows:

$$\varepsilon_H = 2 \ln \frac{b_0}{b} \quad (1)$$

where  $b_0$  and  $b$  are the original and instantaneous widths of the sample, respectively, in the course of tensile stretching.

## DSC Measurements

The thermal properties of the ultrasonic microinjection molded sample were investigated by differential scanning calorimetry (DSC), utilizing a DSC1 Star<sup>e</sup> system (Mettler Toledo, Swiss). The sample was sealed in aluminum pans under a N<sub>2</sub> atmosphere and was heated from 0 °C to 260 °C at a rate of 10 K/min.

## In Situ X-Ray Experiment

In order to conduct the annealing experiments, a custom-made HCS412W hot stage (Instec, America) equipped with a water pump was employed to secure the samples. Subsequently, the *in situ* wide angle X-ray diffraction (WAXD) experiments were conducted during annealing on a modified Xeuss micro-focused system (Xenocs, France) with a wavelength of the X-ray beam being 0.154 nm.

The new samples were mounted onto a tensile machine (Linkam, UK) for tensile stretching. The *in situ* WAXD experiments upon uniaxial tensile stretching were carried out on the aforementioned system upon uniaxial tensile stretching. The X-ray spot size at the sample position is ca. 40 μm × 60 μm, and the distances from the sample to the detector are 41.8 and 59.3 mm during annealing and stretching, respectively. Each WAXD pattern is recorded using a Pilatus 1K detector (resolution of 487 × 195 with a pixel size of 172 μm × 172 μm) within 180 s. All patterns are calibrated with respect to the background before further analysis.

## RESULTS AND DISCUSSION

### In Situ WAXD Measurements during Annealing at 70 °C

Despite the absence of heating induced structural reorganization at the beginning of tensile stretching, the possibility of cold crystallization arises over time since the stretching temperature remains above the glass transition temperature ( $T_g \sim 60$  °C) of the sample. In order to investigate the kinetics of the cold crystallization, *in situ* WAXD measurements were carried out during annealing at 70 °C. Fig. 1 illustrates the WAXD patterns during annealing at varied times. As can be seen, all WAXD patterns exhibit halo patterns, at the earlier stage indicating the amorphous state of samples. This can be attributed to an extremely high cooling rate that occurs during the ultrasonic microinjection molding process. With increasing annealing time, Debye-

Scherrer rings are observed due to the occurrence of the cold crystallization. The three most prominent Debye-Scherrer rings from inner to outer are attributed to SC (110) (12.0°), HCα (110)/(200) (16.5°) and HC α (203) (16.5°) crystal planes, respectively. It is evident the onset of crystallization is reduced as the mold temperature is increased. The cold crystallization occurs at ca. 57, 51 and 21 min for the samples molded at 50, 80, and 120 °C, respectively. This behavior indicates that the total number of crystal nuclei increases with an increase in the mold temperature.

Moreover, one-dimensional WAXD curves were obtained by integrating the WAXD patterns over an azimuthal angle range of 0°–180°. Fig. 2 depicts the resulting one-dimensional WAXD curves during the annealing process. At the initial stage, only a broad peak is observed. As the annealing time is extended, the diffraction peaks emerge as a consequence of the cold crystallization with both SCs and HCs. The intensity of diffraction peaks increases with further increasing time due to the gradual perfection of the newly formed crystals.

In order to perform a quantitative evaluation of the variation in the fraction of SC and HC crystallites during annealing, the WAXD curves were decomposed into the crystalline and amorphous components. This procedure enables the calculation of the overall crystallinity  $X_C$ , as well as the degree of crystallinity for HC crystallites  $X_{HC}$  and for SC crystallites  $X_{SC}$ . The variation of these parameters during annealing is depicted in Fig. 3. Several facts can be observed from Fig. 3. First, the onset of the cold crystallization is delayed at a lower mold temperature due to the reduction in the number of crystal nuclei. An elevated mold temperature facilitates increased HC nucleation due to the enhanced chain mobility. Conversely, the reformulation of SC nuclei is challenging because of the necessity of a longer diffusion distance for PLA molecules. Second, the highest levels of  $X_C$  and  $X_{HC}$  are observed in the sample molded at 120 °C, while  $X_{SC}$  remains low and almost constant for three samples at the late stage of annealing. It can be concluded that HC crystals are the primary contributors to the observed crystallinity during the cold crystallization process.

### True Stress Strain Curves

After figuring out the cold crystallization kinetics at 70 °C, we now turn to investigate the strain-induced crystallization of the sample. Initially, tensile stretching of ultrasonic microinjection

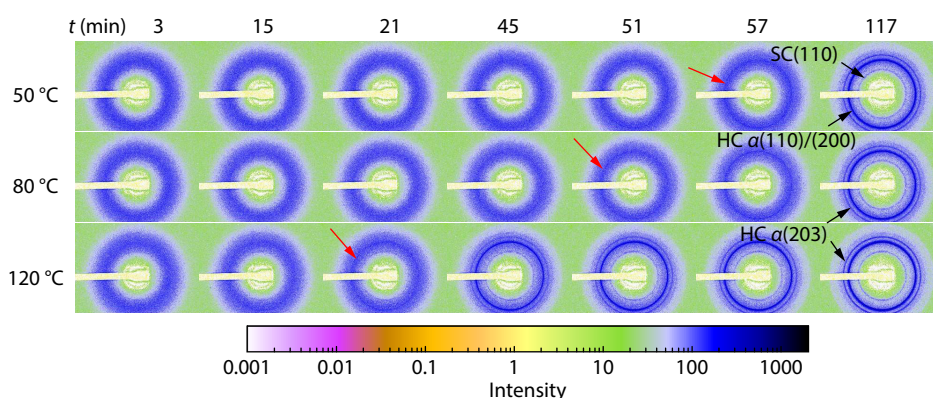


**Fig. 1** Selected two-dimensional WAXD patterns for ultrasonic microinjection molded PLLA/PDLA samples molded at different mold temperatures (50, 80 and 120 °C) during annealing at 70 °C at varied time. The red arrows represent the initiation of the cold crystallization.

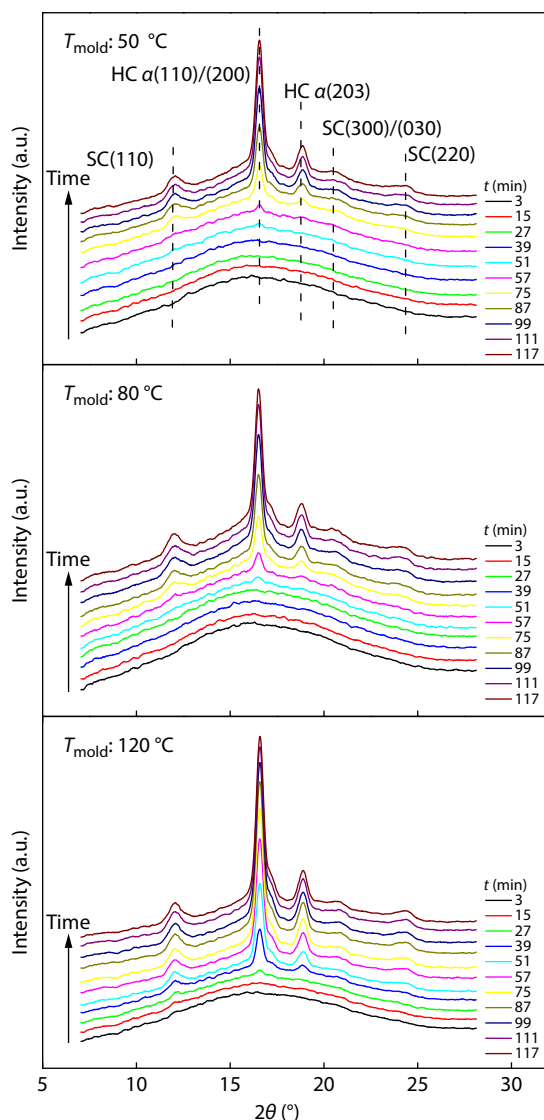


**Fig. 2** One-dimensional WAXD intensity distribution profiles of three ultrasonic microinjection molded PLLA/PDLA samples during annealing at 70 °C. The curves have been vertically shifted for the purpose of clarity.

molded PLLA/PDLA samples was carried out, and the resulting true stress strain curves are illustrated in Fig. 4. Clearly, the stress increased steadily throughout the tensile stretching process. It can be noted that the initial stress below the strain of ca. 0.2 remains almost constant for three samples. Over the strain of 0.2, the stress exhibited a decline with an increase in mold temperature at the same strain. This phenomenon can be attributed to the varying degrees of strain-induced crystallization.

### DSC Measurements

The thermal behaviors of the sample before and after stretching were determined by DSC, which can be used to assess the strain-induced crystallization of samples. Fig. 5 illustrates the resultant DSC melting curves. Before stretching, all samples underwent the glass transition (~60 °C), the cold crystallization, and the melting of HCs and SCs upon heating. In contrast, the cold crystallization process is almost absent after stretching,

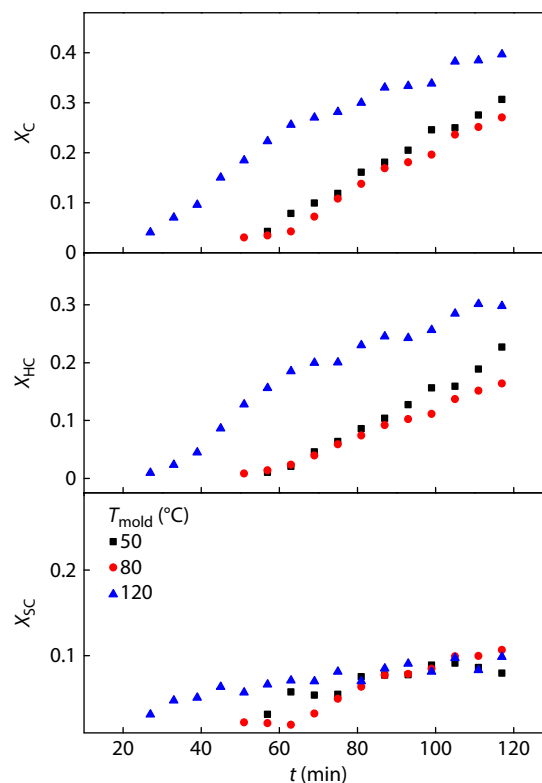


**Fig. 3** The evolution of overall crystallinity  $X_C$  (top), the degree of crystallinity for HCs  $X_{HC}$  (middle) and for SCs  $X_{SC}$  (bottom) of three ultrasonic microinjection molded PLLA/PDLA samples during the annealing process.

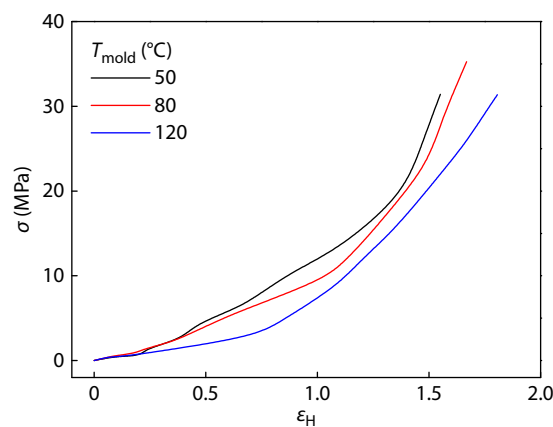


**Fig. 4** The true stress strain curves of ultrasonic microinjection molded PLLA/PDLA samples. The stretching temperature is 70 °C.

which indicates the formation of ordered structures.

The cold crystallization peak, the melting point of HCs and SCs, the enthalpy for cold crystallization, and the melting enthalpies of HCs and SCs are assessed from DSC curves and are presented in Table 2. Before stretching,  $\Delta H_{m,CC}$  demonstrates a positive correlation with the mold temperature, which can be attributed to the formation of a larger number of crystal nuclei with an increase in the mold temperature. As the mold temperature is increased, the value of  $\Delta H_{m,HC}$  rises while  $\Delta H_{m,SC}$  declines. This evidence suggests that HC nuclei are preferred at an elevated temperature, whereas SC nuclei are

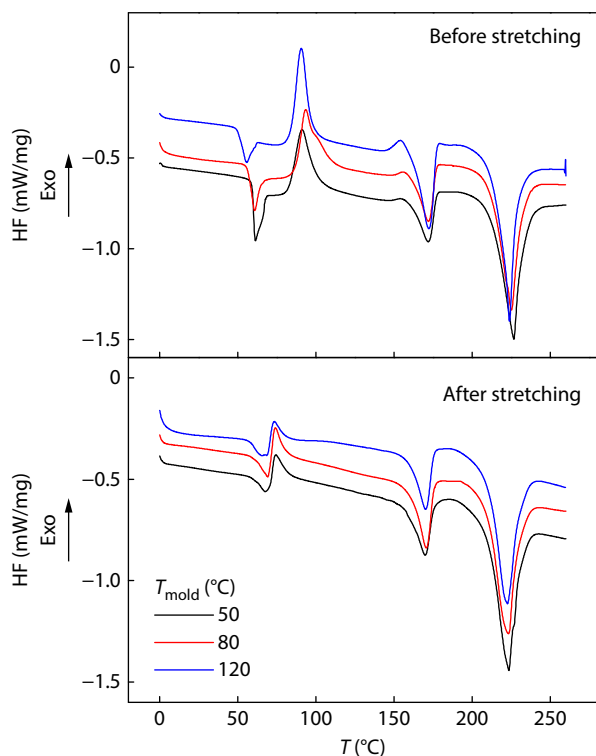


**Fig. 5** DSC melting curves of the samples before and after stretching. The heating rate is 10 K/min.

avored at a lower mold temperature. The value of  $\Delta H_{m,SC}$  remains nearly unchanged for the sample before and after

**Table 2** The cold crystallization peak ( $T_{cc}$ ), the melting point of HCs ( $T_{m,HC}$ ) and SCs ( $T_{m,SC}$ ), the enthalpy for cold crystallization  $\Delta H_{m,cc}$  and the melting enthalpies for HCs ( $\Delta H_{m,HC}$ ) and SCs ( $\Delta H_{m,SC}$ ) of the samples before and after stretching.

| Sample            | $T_{mold}$ (°C) | $T_{cc}$ (°C) | $T_{m,HC}$ (°C) | $T_{m,SC}$ (°C) | $\Delta H_{m,cc}$ (J/g) | $\Delta H_{m,HC}$ (J/g) | $\Delta H_{m,SC}$ (J/g) |
|-------------------|-----------------|---------------|-----------------|-----------------|-------------------------|-------------------------|-------------------------|
| Before stretching | 50              | 91.2          | 171.9           | 226.8           | 23.3                    | 16.2                    | 63.7                    |
|                   | 80              | 93.5          | 172.0           | 225.1           | 27.1                    | 17.5                    | 55.6                    |
|                   | 120             | 90.7          | 172.4           | 223.9           | 29.5                    | 29.3                    | 55.4                    |
| After Stretching  | 50              | –             | 169.9           | 223.5           | –                       | 20.5                    | 65.0                    |
|                   | 80              | –             | 170.6           | 223.2           | –                       | 19.6                    | 60.5                    |
|                   | 120             | –             | 170.2           | 222.6           | –                       | 17.2                    | 56.6                    |

stretching, which indicates that total number of SC nuclei is relatively stable throughout the stretching process.

### In Situ WAXD Measurements during Tensile Stretching

The strain-induced crystallization was further probed by *in situ* WAXD measurements, and the resulting two-dimensional WAXD patterns are presented in Fig. 6. As can be seen, all samples show a halo pattern before stretching, indicating their amorphous nature. Moreover, nearly no preferential orientation is observed from the initial pattern.

This may be attributed to the proximity of the mold gate to the cavity, which suggests that the melt may have already entered the mold cavity during the melting process. During stretching, the Debye-Scherrer diffraction rings appear in the WAXD pattern, which serve to indicate the commencement of strain-induced crystallization. This crystallization process involves the formation of both SCs and HCs. It is notable that the initial formation of SC is accompanied by an almost homogeneous distribution, which indicates that the SC is more likely induced by heating rather than stretching. This can be attributed to the fact that the sample is in a "stretching pause" state during exposure, which allows for the possibility of heating-induced SC formation. It can be hypothesized that stretching may serve to accelerate the crystallization process. This manner will be clarified in more detail in the Discussion section. As the strain was further increased, the diffraction intensity exhibited a gradual concentration in the meridional direction, resulting from molecular orientation along the stretching direction. The diffraction from the SC (110) reflection is markedly weak for the sample molded at 120 °C, indi-

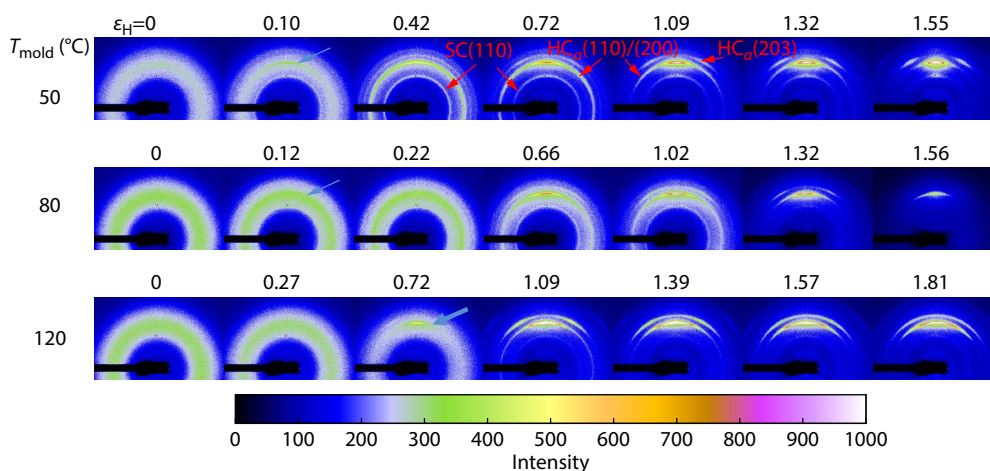


**Fig. 6** Selected two-dimensional WAXD patterns during tensile deformation of three samples. The tensile direction is horizontal. The true strain is indicated above each pattern. The blue arrows indicate the onset of strain-induced crystallization.

cating a low content of SCs.

By integrating the WAXD patterns over the azimuthal angle range of  $0^\circ - 180^\circ$ , one-dimensional WAXD intensity distribution profiles were derived. Fig. 7 displays the WAXD curves for three samples. Prior to stretching, a broad amorphous halo is evident for all samples. During stretching, the crystalline peaks emerge with the presence of both SCs ( $2\theta = 12.0^\circ$ ,  $20.8^\circ$  and  $24.0^\circ$ ) and HCs ( $2\theta = 16.7^\circ$  and  $19.0^\circ$ ). Further stretching leads to a notable alteration of the intensity of diffraction peaks from HCs and SCs, which suggests a variation in the fraction of HC and SC crystallites.

Furthermore, the overall crystallinity  $X_C$ , as well as the degree of crystallinity for HC crystallites  $X_{HC}$  and for SC crystallites  $X_{SC}$  were derived in order to quantitatively evaluate the variation in the content of SC and HC crystallites during stretching. The evolution of these parameters with strain is

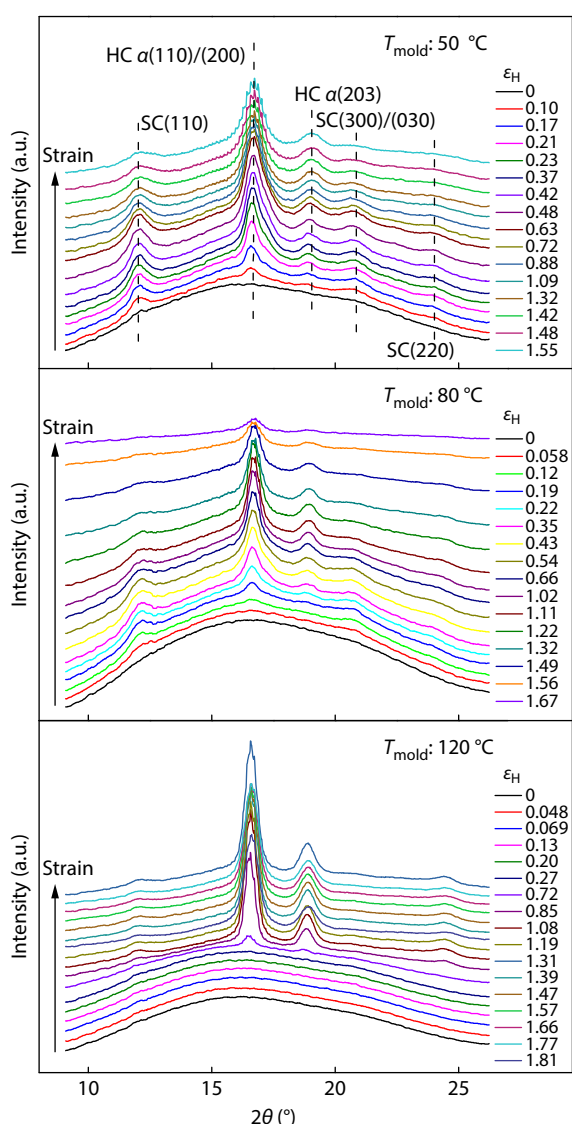


**Fig. 7** One-dimensional WAXD intensity distribution profiles during tensile deformation of samples molded at different temperatures. The curves have been vertically shifted for the sake of clarity.

depicted in Fig. 8. Several significant findings can be seen in Fig. 8. First, the onset of strain-induced crystallization is observed at a relatively low strain for samples molded at 50 and 80 °C, with both instances occurring at a strain of *ca.* 0.1. As the mold temperature is raised to 120 °C, the onset of strain-induced crystallization is markedly delayed to *ca.* 0.7. Second, for samples molded at 50 and 80 °C,  $X_{SC}$  is larger than  $X_{HC}$  at the initial stage of tensile stretching, with  $X_{HC}$  approaching nearly 0. This finding indicates that SC crystallites are the dominant factor at the onset of strain-induced crystallization for these two samples. In the case of 120 °C, both  $X_{SC}$  and  $X_{HC}$  are low at the beginning of strain-induced crystallization. Third, in samples molded at 50 and 80 °C,  $X_C$  and  $X_{HC}$  exhibit a notable increase with the strain, whereas  $X_{SC}$  shows a modest decrease during the tensile stretching. This evidence indicates that SC crystallites are only initiated at the beginning of strain-induced crystallization, followed by the slight fragmentation during the subsequent stretching process. The formation of SC is unlikely to be induced by stretching. Otherwise, the value of  $X_{SC}$  would be expected to increase during stretching.

In contrast, HC crystallites are generated throughout the entire stretching process. Therefore, it can be concluded that the strain-induced formation of HC crystallites is the primary contributor to the overall crystallinity. In the case at 120 °C,  $X_{SC}$  demonstrates a slight increase with strain, which can be attributed to the occurrence of cold crystallization during the tensile stretching process. Fourth,  $X_C$  and  $X_{HC}$  is higher in the

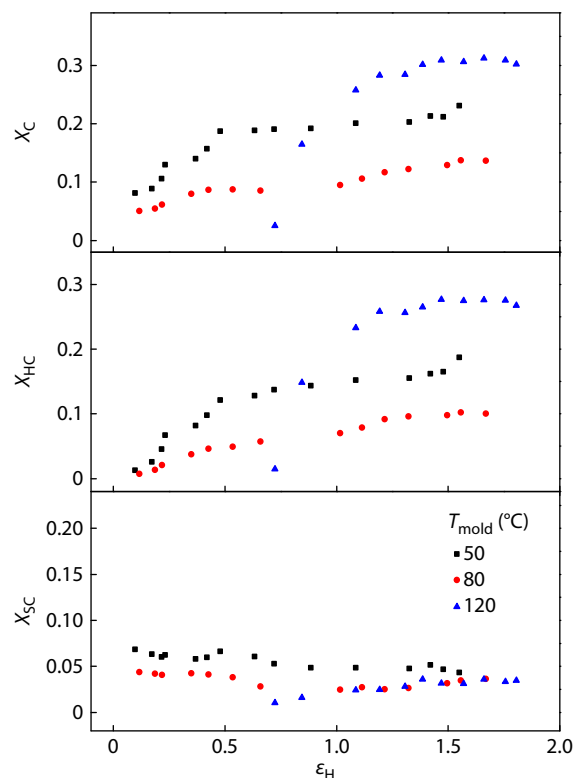


**Fig. 8** The evolution of overall crystallinity  $X_C$  (top), the degree of crystallinity for HCs  $X_{HC}$  (middle) and for SCs  $X_{SC}$  (bottom) of three ultrasonic microinjection molded samples during tensile deformation.

sample molded at 50 °C than that in the sample molded at 80 °C across the tensile deformation, which is in line with the annealing results in Fig. 3. This fact can be attributed to the different amount of SCs formed initially. The sample at 50 °C contains more SC nuclei, which results in the formation of more SC crystals. The SC crystals can act as a nucleation agent, facilitating the formation of HCs upon the subsequent annealing or stretching process.<sup>[33–35]</sup>

Furthermore, the sample molded at 120 °C exhibits the highest crystallinity beyond a strain of *ca.* 1.0 due to the occurrence of cold crystallization. A system with a high crystallinity is typically associated with favorable mechanical properties. However, the tensile stress exhibited by the sample molded at 120 °C is inferior in comparison to the other two samples molded at 50 and 80 °C, as illustrated in Fig. 4. This behavior can be tentatively explained as follows. The *in situ* WAXD tests were performed in a discontinuous manner, with the expectation that cold crystallization would occur during stretching, resulting in a marked increase in the crystallinity. Nevertheless, the true stress-strain curves are obtained on a continuous basis. The tensile test takes *ca.* 15 min, during which time cold crystallization has not yet occurred. It is anticipated that the crystallinity resulting from strain-induced crystallization will be relatively low, which consequently results in an inferior tensile stress. The following sections will provide further clarification regarding the cold crystallization during tensile stretching of the sample.

In order to quantify the orientation of molecular chains during stretching, the degree of orientation is employed, which is calculated by Hermans equation:<sup>[36]</sup>

$$S_{hkl} = \frac{3 \langle \cos^2 \varphi_{hkl} \rangle - 1}{2} \quad (2)$$

and  $\langle \cos^2 \varphi_{hkl} \rangle$  is expressed as:

$$\langle \cos^2 \varphi_{hkl} \rangle = \frac{\int_0^{\pi/2} I_{hkl}(\varphi) \sin \varphi \cos^2 \varphi d\varphi}{\int_0^{\pi/2} I_{hkl}(\varphi) \sin \varphi d\varphi} \quad (3)$$

and  $\cos \varphi$  was calculated using Polanyi equation:<sup>[37]</sup>

$$\cos \varphi = \cos \theta_{hkl} \cos \mu \quad (4)$$

where  $\varphi_{hkl}$ ,  $\theta_{hkl}$  and  $\mu$  represent the angle between the draw direction and the normal vector of the lattice plane  $hkl$ , the Bragg diffraction angle and the azimuthal angle, respectively, and  $I_{hkl}(\varphi)$  is the azimuthal intensity profile along the lattice plane  $hkl$ .

The degree of orientation for three PLLA/PDLA samples is presented in Fig. 9. For samples molded at 50 and 80 °C,  $S_{HC(110/200)}$  decreases steadily during the whole stretching process. There exists a one-to-one correspondence between  $S_{HC(110/200)}$  and strain, indicating that the newly formed HC crystallites undergo a gradual orientation towards the stretching direction as the strain is increased. The value of  $S_{SC(110)}$  is close to 0 and remains largely unaltered below the strain of 0.5, suggesting that the formed SC crystals, which feature a low orientation, are not significantly oriented at the earlier stage of tensile stretching. Further stretching leads to the elongation of the entire molecular network, thereby forcing the SCs to assume a particular orientation. This manner results in a decrease in the value of  $S_{SC(110)}$ . It is worthy not-

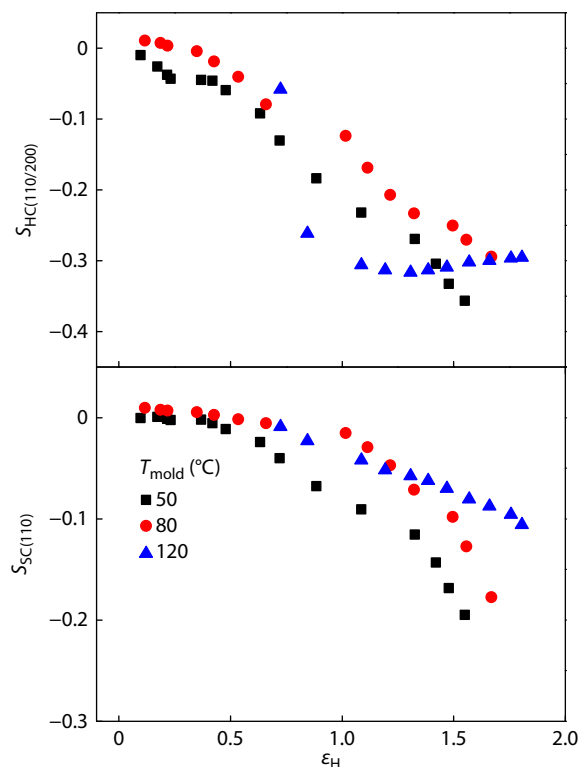


**Fig. 9** The degree of orientation for HC (110/200) lattice plane (top) and SC (110) lattice plane (bottom) as a function of strain for three ultrasonic microinjection molded PLLA/PDLA samples.

ing that the sample molded at 50 °C displays a higher degree of molecular orientation that one molded at 80 °C throughout the tensile deformation. This can be attributed to the fact that the molecular orientation is rapidly frozen at a lower mold temperature during the ultrasonic microinjection process. In the case of 120 °C,  $S_{HC(110/200)}$  exhibits a fast decrease until *ca.* 1.3 followed by a modest increase with further stretching. This behavior can be ascribed to the dominating chain relaxation over chain orientation within HC crystals.<sup>[27]</sup> Additionally, the phenomenon of cold crystallization occurring during the stretching process may also contribute to the observed decrease in molecular orientation. It can be assumed that a proportion of the newly formed crystals resulting from cold crystallization comprise freely molecules and are randomly oriented, which will result in a reduction in the overall degree of orientation. This also provides an explanation for the slight increase in  $X_{SC}$  with strain, as illustrated in Fig. 8. The increase in SCs from cold crystallization exceeds the destruction of SCs, leading to a slight increase in  $X_{SC}$  with strain. With respect to  $S_{SC(110)}$ , it exhibits a progressive decrease due to the elongation of the entire molecular network.

## DISCUSSION

We now switch our attention to the strain-induced SC crystallites. The direct observation of strain-induced SC crystallites can be tentatively explained as follows.

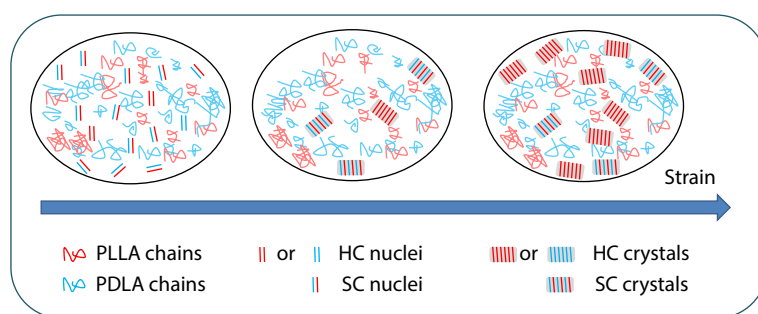
As the tensile temperature (70 °C) is in close proximity to the critical temperature of heating induced ordered structural reorganization ( $\sim 80$  °C),<sup>[30]</sup> it can be hypothesized that

the tensile stretching at the earlier stage provides the requisite energy to accelerate the formation of ordered structures, which are in fact thermally induced. This acceleration process is achieved *via* the presence of SC nuclei. The ultrasonic microinjection molded samples possess a high concentration of SC nuclei due to the survival of PLLA/PDLA clusters, and a lower mold temperature favors the formation of SC nuclei due to the reduced degrees of demixing of PLLA/PDLA.<sup>[30]</sup> As is known, SC nuclei are composed of an alternative packing of L- and D-chains, which enables them to retain strong inter-chain H-bonding with more compact chain packing even in the amorphous state.<sup>[38,39]</sup> It can therefore be postulated that SC nuclei exhibit greater rigidity than the surrounding matrix, and may be regarded as local constraints. Such local constraints can act as transient physical cross-links at the beginning of the tensile stretching, initiating strain-induced crystallization. Thereafter, the newly formed crystals function as physical cross-links, thereby promoting the subsequent strain-induced crystallization process. This process is illustrated in Scheme 1. In addition, the formed SC crystallites enable more effective stress transfer than HCs.<sup>[27]</sup> Consequently, HCs are subjected to larger stress and thus elongated, whereas SCs are almost not oriented at the initial stage. This leads to the observation that the molecular orientation within SCs remains unaltered at low strains, as illustrated in Fig. 9.

The samples molded at 50 and 80 °C follow the mechanism mentioned above as these two samples contain a relatively high content of SC nuclei.<sup>[30]</sup> The earlier formation of SCs for these two samples can therefore be attributed to a melt memory effect, whereby the residual PLLA/PDLA clusters serve as self-seeds to reduce the crystallization barrier energy.<sup>[40–42]</sup> The sample molded at 50 °C exhibits a slightly earlier onset of strain-induced crystallization than that molded at 80 °C due to a slightly larger number of SC nuclei. Since the ordered structures observed initially are in fact thermally

induced, both SCs and HCs are present when the apparent strain-induced crystallization occurs. The direct strain-induced formation of SCs at the initial stage, therefore, can be regarded as a pseudo strain-induced crystallization process. Upon further stretching, only HC crystallites continue to be generated, while the preceding SCs are destroyed to a slight extent. These findings indicate that the actual strain-induced crystallization process is characterized by the exclusive formation of HC crystallites.

For the sample molded at 120 °C, a notable delay in strain-induced crystallization is observed, which may be attributable to a reduction in the SC nuclei number. On the other hand, the total duration of the sample at the occurrence of strain-induced crystallization, including the time required for tensile stretching and X-ray measurements, is *ca.* 25 min. This duration coincides with the onset of the cold crystallization (*ca.* 21 min, as indicated in Fig. 1). It is therefore unclear whether cold crystallization plays a role in initiating strain-induced crystallization. In order to elucidate the contribution of the cold crystallization to the strain-induced crystallization during stretching, the sample was pre-stretched to a true strain of *ca.* 1.2, and held at this state for the annealing treatment. The *in situ* WAXD measurements were conducted during the annealing process. The WAXD patterns as a function of annealing time are presented in Fig. 10. As can be seen, even at a strain exceeding the beginning of crystallization (*ca.* 0.7, as observed in Fig. 6), the crystallites remain undetectable initially. After an annealing time of 21 min, the crystallization was observed. This means that the onset of strain-induced crystallization is triggered by the ordered structure resulting from cold crystallization. Therefore, the presence of SC nuclei is not a crucial factor in the onset of strain-induced crystallization in the sample molded at 120 °C. The crystallites resulting from the cold crystallization serve as the physical cross-links to facilitate the subsequent strain-induced crystal-



**Scheme 1** The strain-induced SCs formation from the amorphous PLLA/PDLA sample.

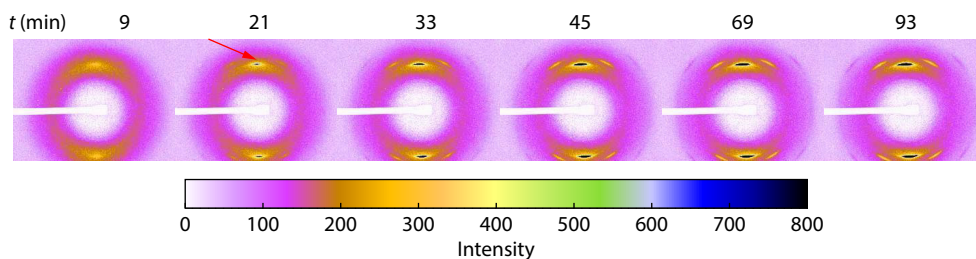


**Fig. 10** Selected two-dimensional WAXD patterns for the ultrasonic microinjection molded PLLA/PDLA samples molded 120 °C prior to stretching to a true strain of *ca.* 1.2 followed by annealing at 70 °C. The red arrows represent the emergence of the cold crystallization.

lization process. Furthermore, the occurrence of cold crystallization accounts for the highest degree of crystallinity at the large strains than those molded at 50 and 80 °C, as illustrated in Fig. 8. The increase in crystallinity resulting from cold crystallization is more pronounced in the sample molded at 120 °C, as evidenced by Fig. 3. It can therefore be inferred that cold crystallization plays a pivotal role in the formation of the majority of the ordered structure during stretching.

In addition, the resulting WAXD curves are demonstrated in Fig. 11(a), and the values of  $X_C$ ,  $X_{HC}$  and  $X_{SC}$  derived from the WAXD curves are presented in Fig. 11(b). As demonstrated in Fig. 11(b), the ultimate values of  $X_C$  and  $X_{HC}$  are ca. 0.13 and 0.09, respectively, which are evidently below those observed at the late stage of stretching (ca. 0.32 and 0.28 for  $X_C$  and  $X_{HC}$ , respectively) as shown in Fig. 8. This fact means that the formation of HCs is not only caused by the cold crystallization, but also induced by stretching. However,  $X_{SC}$  remains almost constant (ca. 0.04), indicating that the formation of SCs occurs *via* a thermal-induced mechanism only.

In order to gain further insight into the role of SC nuclei in the strain-induced crystallization, we prepared ultrasonic micro-injection molded PLLA samples. The WAXD patterns and curves during annealing at 70 °C are presented in Figs. S1 and S2 (in the electronic supplementary information, ESI), respec-

tively. Comparing with three of the PLLA/PDLA samples, a notably elevated proportion fraction of HCs is observed during annealing as indicated in Fig. 2, which can be attributed to the fact that the newly formed SCs can act as nucleation agents, promoting the growth of HCs.<sup>[33–35]</sup>

Subsequently, the strain-induced crystallization of the PLLA samples was investigated by *in situ* WAXD measurements. The results were illustrated in Figs. S3 and S4 (in ESI). In comparison with the PLLA/PDLA samples with a relatively high concentration of HCs, as presented in Figs. 7 and 8, it can be concluded that SCs formed at the beginning of the strain-induced crystallization can serve as nucleation agents, which facilitate the growth of HCs upon the subsequent stretching process.<sup>[33–35]</sup>

What's more, it is of interest to ascertain whether SCs can be induced during stretching in the injection-molded PLLA/PDLA samples. To provide a comparable investigation, the micro-injection molded PLLA/PDLA samples with the same dimensions (24 mm × 1.3 mm × 0.5 mm) were prepared using a Battenfeld Microsystem 50 machine (Wittmann, Austria). The structural evolution during annealing and stretching at 70 °C was investigated by *in situ* WAXD measurements, and the results are presented in Figs. S5 and S6 (in ESI), respectively. Fig. S6 (in ESI) shows that the SCs can also be generated during stretching of the micro-injection molded PLLA/PDLA sample, but only at large strains. This can be attributed to the occurrence of cold crystallization, which is actually a thermal process. Furthermore, this observation indicates that SC nuclei can be reserved in the micro-injection molded system, but the concentration is notably lower than that observed in the ultrasonic micro-injection molded sample. Another possible reason for the formation of SC is the degradation of PLA molecules during the microinjection molding process, which results in the formation of lower molecular weight species with higher mobility. These species are more likely to be paired to form SC nuclei during annealing, ultimately facilitating the development of SC crystals.

## CONCLUSIONS

Strain-induced crystallization of ultrasonic microinjection molded PLLA/PDLA samples from an initially amorphous state was investigated. Direct strain-induced SC formation was observed. For the samples molded at 50 and 80 °C, this behavior can be attributed to the presence of considerable SC nuclei. It is anticipated that SC nuclei act as physical cross-links, initiating strain-induced crystallization. This process can be understood as an acceleration of the heating-induced structural reorganization, whereby the energy provided by the initial strain contributes to the transformation of the sample from an amorphous state to a crystalline phase. Direct strain-induced SCs at the beginning of stretching are thus regarded as a form of pseudo strain-induced crystallization. During the subsequent stretching process, true strain-induced crystallization takes place characterized by the exclusive formation of HCs, whereas the formed SCs undergo slight fragmentation. In the case at 120 °C, the occurrence of the strain-induced SCs can be attributed in part to the cold crystallization, as confirmed by the *in situ* WAXD measurements conducted during annealing in both the static and stretched states. The crystallites resulting from cold crystallization act as physical

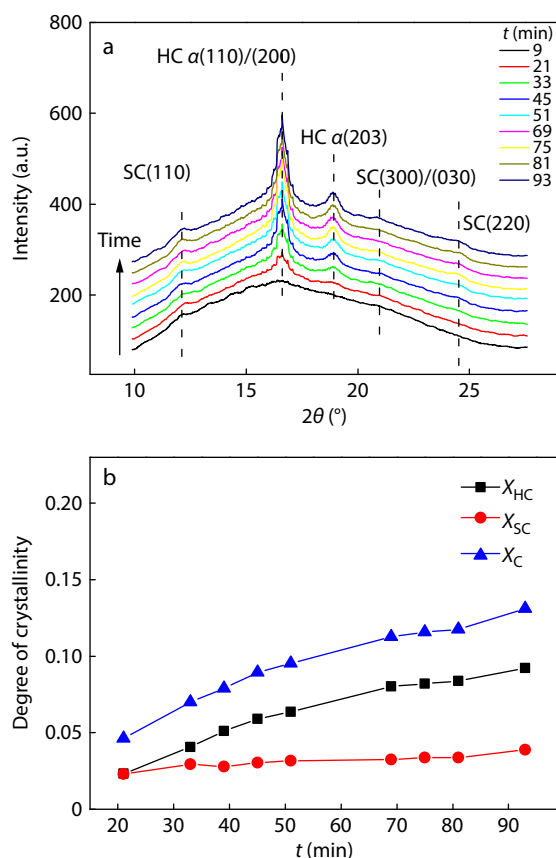


**Fig. 11** One-dimensional WAXD intensity distribution profiles (The curves have been vertically shifted for the sake of clarity.) (a) and the calculated  $X_C$ ,  $X_{HC}$  as well as  $X_{SC}$  (b) of the ultrasonic microinjection molded PLLA/PDLA samples molded at 120 °C prior to stretching to a true strain of ca. 1.2 followed by annealing at 70 °C.

cross-links, promoting the subsequent strain-induced crystallization process.

## Conflict of Interests

The authors declare no interest conflict.

## Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-025-3298-6>.

## Data Availability Statement

The related data (CSTR: <https://cstr.cn/31253.11.sciencedb.j00189.00035>) for this paper is available in the Data Repository of China Association for Science and Technology (<https://www.scidb.cn/c/cjps>).

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