

Deformation Temperature and Lamellar Thickness Dependency of Form I to Form III Phase Transition in Syndiotactic Polypropylene during Tensile Stretching*

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Abstract Phase transition from form I to form III in syndiotactic polypropylene crystallized at different conditions during tensile deformation at different temperatures was investigated by using *in situ* synchrotron wide angle X-ray diffraction technique. In all cases, the occurrence of this phase transition was observed. The onset strain of this transition was found to be crystalline thickness decided by crystallization temperature and drawing temperature dependent. The effect of drawing temperature on this phase transition is understood by the changes in mechanical properties with temperature. Moreover, crystalline thickness dependency of the phase transition reveals that this form I to form III phase transition occurs first in those lamellae with their normal along the stretching direction which have not experienced stress induced melting and recrystallization.

Keywords: Tensile deformation; Phase transition; Syndiotactic polypropylene; WAXD.

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INTRODUCTION

Syndiotactic polypropylene (sPP) shows a very complex polymorphic behavior with four crystalline forms. The $(t_2g_2)_n$ helical conformation are presented in form I and form II^[1–4], chains in form III adopt all trans (ttt)_n planar conformation^[5], and form IV is characterized by chains in $(t_6g_2t_2g_2)_n$ conformation^[6], respectively. Form I is the stable crystalline structure of sPP with typical reflections of crystallographic planes of (200), (020) and (121) at $d = 0.725$, 0.561 and 0.429 nm as observed by X-ray diffraction. It can be obtained under the most common conditions of melt and solution crystallizations^[1, 7, 8]. Additionally, the (211) reflection at $d = 0.47$ nm is presented in a limit ordered model of form I^[1, 7]. Form III is a metastable structure with the characteristic reflections of (020), (110), (021) and (111) planes at $d = 0.545$, 0.488 , 0.375 and 0.345 nm as detected by X-ray diffraction. It can be achieved by stretching highly stereoregular sPP to a high deformation at room temperature^[2, 5, 9].

Abundant investigations about the influences of the stereoregularity^[5, 9, 10], deformation temperature (T_d)^[11, 12] and crystallization temperature (T_c)^[13–16] on phase transition of sPP have been reported in past years.

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The high stereoregularity, low drawing temperature and the ordered initial morphology of *s*PP all contributed to the transition from helical phase to trans-planar one. It has been emphasized that a crystal-crystal phase transition of form I to form III induced by deformation is associated with a critical stress^[10, 17]. The critical stress required for this transition with defined stereoregular *s*PP depends on the deformation temperature. It has been claimed that the critical stress for form I transforming into form III of *s*PP with 78% and 93% stereoregularity is 8–12 MPa at room temperature^[10]. While fibers in stable helical form I stretched at high temperatures (60–80 °C) showed no structural transition^[11], possibly due to the breaking of *s*PP fibers before they reach the critical stress for phase transition^[11]. As the initial morphology of *s*PP can affect the appearance of form III of oriented *s*PP^[18], the original structure of *s*PP relies heavily on crystallization temperature. Sample prefers an ordered structure model of form I at high crystallization temperatures^[2, 8, 19], where a larger stress to activate the transition is needed^[10]. Attributed to this consequence, the critical strains at which phase transition occurs may be not the same among the samples achieved at different crystallization conditions.

In this work, we investigated the phase transition of form I to form III in isotropic *s*PP with a high stereoregularity as a function of deformation temperature and lamellar thickness by using synchrotron wide angle X-ray diffraction (WAXD) technique. The appearance of form III was also observed when *s*PPs were stretched at temperatures higher than 80 °C. The critical strain marking the onset of the phase transition increases at high deformation temperatures. In addition, a larger onset strain of form I to form III transition was obtained for *s*PP samples crystallized at higher temperatures. Moreover, the form III was dominant only if the deformation temperature was below 86 °C.

EXPERIMENTAL

*s*PP was purchased from Aldrich Polymer Products, with a molecular weight $M_w = 174000 \text{ g}\cdot\text{mol}^{-1}$ and a polydispersity $M_w/M_n = 2.3$, its fully syndiotactic pentad content [rrrr] is 93%. The pellets were molded in a hot press at 180 °C, developing films of 0.5 mm in thickness, which were slowly cooled down to room temperature (sample *s*PP-air) or rapidly transferred into an oil bath for isothermal crystallization at 95, 100, 105, and 110 °C (samples *s*PP95, *s*PP100, *s*PP105, *s*PP110) for 24 h. After crystallization, differential scanning calorimeter (DSC) measurements were carried out with a DSC1 of Mettler Toledo Swiss under N₂ atmosphere under a heating rate of 10 K·mol⁻¹. Small angle X-ray scattering (SAXS) measurements on the prepared films were conducted in order to obtain structural details such as thicknesses of crystalline lamellae and amorphous layers. A SAXsess mc² system from Anton-Paar Austria was used during SAXS measurements. The one-dimensional electronic density correlation function by considering the final lamellar stack model was utilized to acquire the parameters mentioned above^[20, 21], which were provided as an inset in Fig. S1 in the Supporting Information.

In situ synchrotron WAXD experiments with a sample-to-detector distance of 155 mm were performed at the beamline BL16B ($\lambda = 0.124 \text{ nm}$) at SSRF, Shanghai, China. We used a stepwise tension at a constant cross-head speed of 20 $\mu\text{m}\cdot\text{s}^{-1}$ at deformation temperatures (T_d) of 30, 70, 86 and 105 °C, respectively. In order to ensure a homogenous heating of the sample, each sample was kept at the drawing temperatures for 10 min before stretching. The WAXD patterns were collected within 100 s after each step. Optical photo images of the samples were employed simultaneously. The Hencky strain was used as a measure for the deformation which is defined as

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

where b_0 and b are the widths of the undeformed and deformed area located at certain spots on the samples.

RESULTS AND DISCUSSION

The DSC curves are depicted in Fig. 1. The main melting peak temperature of isothermal crystallized samples increases with the increasing of the crystallization temperature. For the sample slow-cooled in the air, the higher melting peak temperature is due to a process of melting and recrystallization during heating run. Taking the

melting curve of *s*PP110 as an example, the observed several melting peaks located at 50, 90, 112 and 130 °C can be assigned as follows: the melting of initial crystal lamellae with granular sub-structure (112 °C); the perfect lamellar crystallites (130 °C); the secondary lamellae formed on cooling to room temperature (90 °C) and the imperfect block-like structures formed during storage at room temperature (50 °C)^[22]. In order to give a more intuitive explanation, basic results from DSC and SAXS are listed in Table 1. The higher crystallization temperature leads to a thicker crystalline and a higher melting peak temperature. One may notice the linear crystallinities deduced from SAXS are lower than the weight fraction crystallinities derived from DSC for *s*PPs. Two reasons lead the deviations^[23]. One is caused by a heterogeneous situation, such as spherulites partially filling a sample. The other is that the granular substructures may exist at the borders and in between crystalline blocks. If the thickness of the separating regions is below 2 nm, no scattering could be detected at the small-angle range. Furthermore, the one dimensional WAXD curves of unstretched *s*PPs are shown in Fig. 2. All the samples possess form I crystalline modification, and the crystalline structure prefers the ordered model in *s*PP100, *s*PP105 and *s*PP110, as evidenced by the (211)_{hl} (hl represents the helical form I) reflection^[1, 7]. The above results indicate the initial structure of *s*PP depends deeply on the crystallization conditions. The higher crystallization temperature induces a more ordered and perfect crystal structure in *s*PP samples.

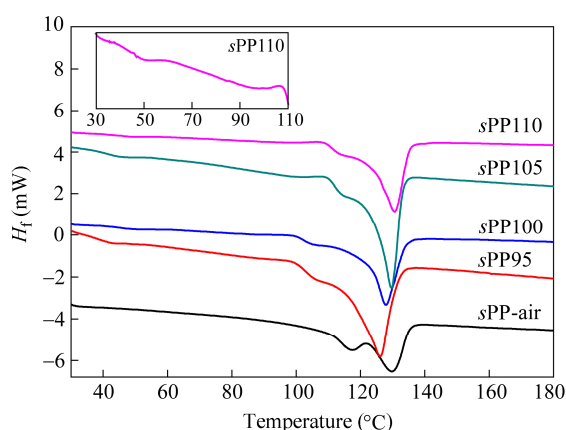


Fig. 1 DSC curves of *s*PPs, crystallized from the melt at different temperatures

The inset represents the melting locus of *s*PP110 at low temperature range. (Heating rate: 10 K·min⁻¹)

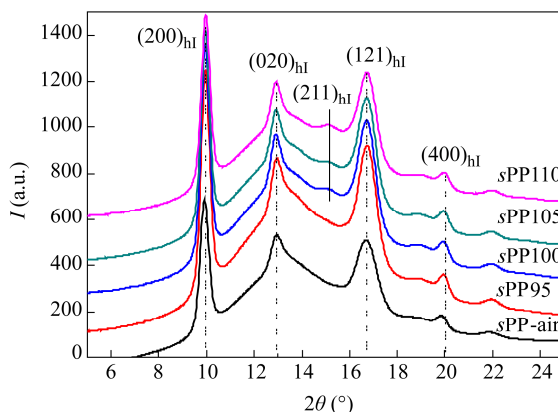


Fig. 2 WAXD profiles of unoriented *s*PPs

Table 1. The thicknesses of crystalline lamellae (d_c) and amorphous layers (d_a), and the long spacing (d_{ac}) of the samples derived from one dimension correlation function of small angle X-ray scattering data, and melting temperature (T_m) and the weight fraction crystallinities (ϕ_w) derived from differential scanning calorimetry (DSC)

Samples	d_c (nm)	d_a (nm)	d_{ac} (nm)	T_c (°C)	T_m (°C)	ϕ_w (%)
<i>s</i> PP-air	4.4	7.1	11.5	—	129.43	24.1
<i>s</i> PP95	5.2	10.1	15.3	95	125.76	29.8
<i>s</i> PP100	5.4	10.4	15.8	100	127.76	27.5
<i>s</i> PP105	5.6	10.5	16.1	105	129.24	33.3
<i>s</i> PP110	5.8	11.6	17.4	110	130.48	31.9

Figure 3 shows selected WAXD patterns taken at different stains for *s*PP-air drawn at 30 and 105 °C. The unoriented *s*PPs are in stable form I with identified reflections of (200), (020) and (121) planes. After the sample underwent a high deformation, the scattering intensity became polarized along arcs, manifesting that the crystallites oriented with chain axes parallel to the tensile direction. For *s*PP-air drawn at 30 °C, WAXD pattern indicates extensive diffractions from form III at a stain of 1.26, which is indicated by the absence of the (200)_{hl} reflection and the presence on the equator of a broad maxima belonging to (020)_t and (110)_t (t represents the trans-planar) reflections of form III^[5]. At a strain of 1.6 of *s*PP-air stretched at 105 °C, although the intensities of

the $(200)_{\text{hl}}$ and $(121)_{\text{hl}}$ reflections are strong, a small quantity of form III are still obtained as evidenced by typical reflections of $(021)_{\text{t}}$ and $(111)_{\text{t}}$. According to the true stress-strain curves shown in Fig. 4, the critical stress for the appearance of form III in sPP-air deformed at 105 °C is 11.5 MPa. This value is almost the same as the critical stress pointed out in reference^[10].

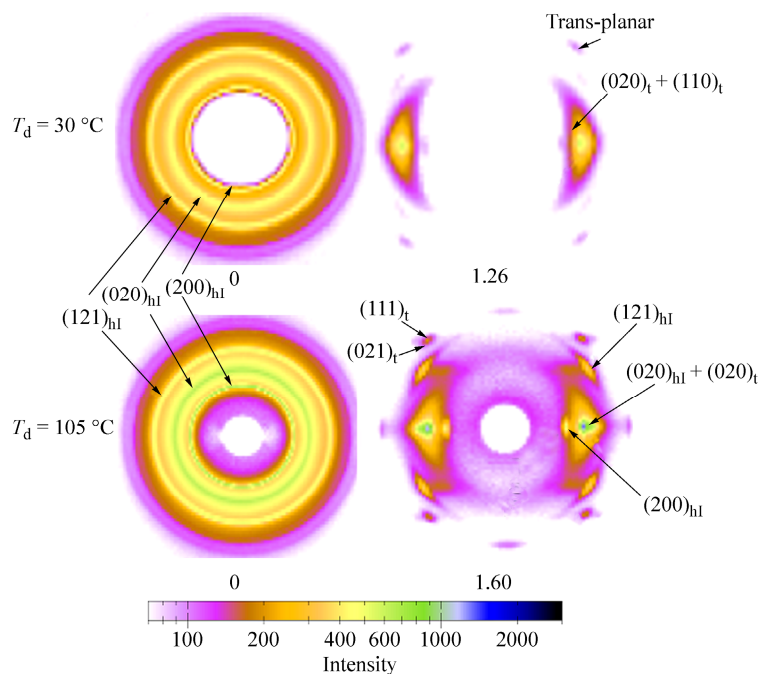
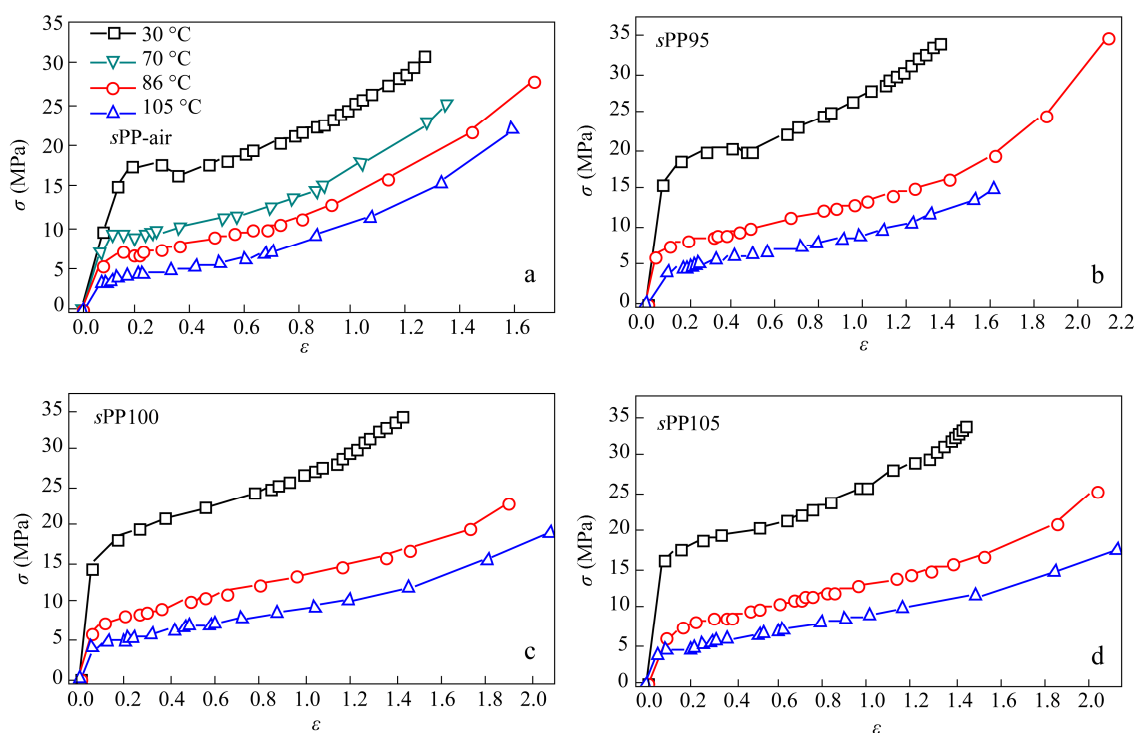


Fig. 3 Selected WAXD patterns of uniaxially drawn sPP-air at 30 °C (top) and 105 °C (bottom) taken at different strains as indicated on the graph (Stretching direction: vertical)



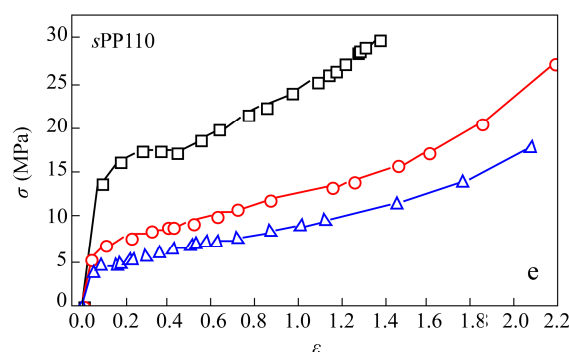


Fig. 4 True stress-strain curves of (a) *sPP*-air, (b) *sPP*95, (c) *sPP*100, (d) *sPP*105 and (e) *sPP*110, measured at the temperatures indicated in the plots

More detailed information about *sPP*-air drawn at four different temperatures is shown in the Supporting Information (Fig. S2). Drawing temperature (T_d) dependency of this form I to III phase transition in *sPP*-air is given in Fig. 5. The first line at low strain indicates the beginning of form I to form III transition at different temperatures; the second line at high strain represents the occurrence of dominant form III in structure. The method used to determine the strain of the occurrence of form III and of form III being dominant is explained in the Supporting Information, and the relevant results are shown in Figs. S3 and S4. As the form III crystalline modification in oriented *sPP* under tension could transform into forms I and II by annealing at high temperatures^[2, 9], form III crystallites are no longer dominant in the system above 86 °C. Therefore, a dotted line is drawn to continue. Obviously, the initial strain of phase transition is almost constant from 30 °C to 60 °C, and then increases with the increasing of T_d . Such phenomenon may be caused by the stress^[10, 17]. In Fig. 4, the stress of *sPP* stretched at high temperatures is sharply decreased compared with the stress produced at the low deformation temperature. Clearly, it is easy to reach the critical stress for phase transformation when the *sPP* sample is drawn at low temperatures, while the material becomes soft at high stretching temperatures. Therefore, in order to reach the critical stress of phase transition, a larger strain is needed when the *sPP* sample is deformed at high temperatures.

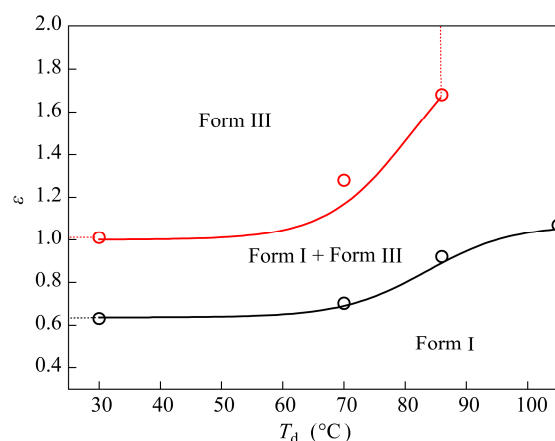


Fig. 5 Phase diagram of stretched *sPP*-air showing the region of the stability of different polymorphic forms as a function of drawing temperature

In Figure 6, we present the relationship between the d_c and the phase transition of *sPP*s from form I to form III at 30 °C. (The corresponding WAXD patterns at different strains are provided in Fig. S5.) The lower line shows the strain values where form III starts to appear during tensile stretching. The higher line signifies the

threshold strain values for form III being dominant in the deformed *s*PP samples. An increase in the onset strain of form I to form III phase transition is observed with the increasing of lamellar thickness (d_c). This implies a crystalline thickness dependency of the phase transition. As the diffraction intensity distribution of the transformed trans-planar form III phase indicates strong orientation of the polymeric chains within the crystallites along the stretching direction, one can conclude that only those crystalline lamellae with their normal along the stretching direction transform into form III. This seems confusing at the first sight when we consider a general scheme of tensile deformation in semi-crystalline polymers. Stretching a semi-crystalline polymer can be regarded as a process of stretching two interpenetrated networks being constituted by the crystalline phase and the entangled amorphous phase^[24, 25]. The result of the tensile deformation in semi-crystalline polymers is transforming the originally isotropic spherulitical structure into a highly oriented fibrillar one with chains preferentially aligned along stretching direction. The transition was found to begin at certain critical strain depending on the state of amorphous network and the stability of crystalline blocks. This critical strain for fibrillation in *s*PP is found to be constant irrespective to the changes in stretching temperature and original crystalline lamellar thickness^[26]. In addition, the thickness of the crystallites in the resulting fibrils depends only on the stretching temperature^[27–30]. The above mentioned crystalline thickness dependency of the form I to form III transition during stretching *s*PP samples clearly indicates that this process is not linked to the newly established crystallites within fibrils where same thickness is observed for the crystallites. Indeed, the aforementioned fibrillation process, although starting at a critical strain, continues over a large range of strain. Lamellae with their normal about 45° with respect to the stretching direction experience the largest shear stress and therefore disaggregate (“melt”) and recrystallize first. Lamellae with their normal along the stretching direction are rather stable at the beginning. They may break down to small blocks with their normal still along stretching direction due to the uneven distribution of tie molecules over two opposite surfaces resulting in uneven distribution of stresses on the respective surfaces^[10, 31]. The lamellar thickness dependency of the form I to form III transition in *s*PP samples can therefore be assigned to these crystallites which still possess their original thickness.

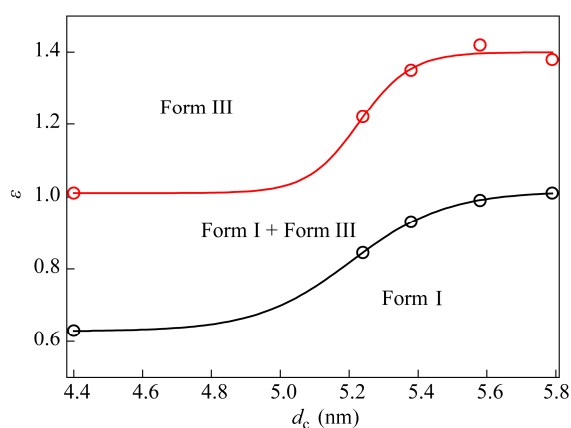


Fig. 6 Phase diagram of stretched *s*PPs showing the region of stability of different polymorphic forms as a function of lamellar thickness (The samples were drawn at 30 °C.)

We also exhibit the WAXD patterns of isothermal crystallized samples drawn at 86 °C (left) and 105 °C (right) in Fig. S6. The occurrence of form III in deformed *s*PP samples is indicated by arrows. In Fig. 7, the d_c dependency of the onset strains for phase transition from form I to form III of deformed *s*PP samples stretched at different temperatures is shown. Clearly, this phase transition is more sensitive to T_d than d_c . This behavior can be understood according to the results of crystalline thicknesses in Table 1 and of true stress-strain curves in Fig. 4. When T_d is increased, the stress reduces rapidly, resulting in a larger critical strain for phase transition.

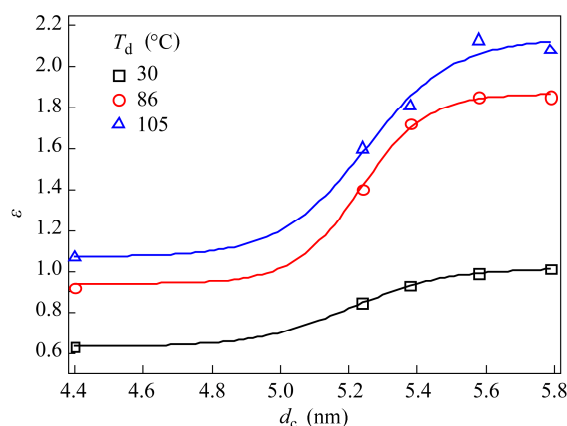


Fig. 7 Phase diagram of stretched sPPs drawn at different temperatures showing strain of onset of form I to form III transition as a function of lamellar thickness

CONCLUSIONS

The tensile deformation-induced phase transition from form I to form III in isotropic sPP films prepared at different crystallization conditions was studied by using *in situ* synchrotron WAXD measurements. It was found that the onset strain of form I to form III transition depends on both crystalline thickness and stretching temperatures. The stretching temperature gives more pronounced effect due to a strong softening of the material at high temperatures. The sample needs to be stretched to a larger strain to reach the critical stress for the phase transition. Crystalline thickness dependency of the phase transition indicates the actual location of this process being linked to the crystallites originated from lamellae with their normal along the stretching direction without experiencing a stress induced melting and recrystallization process during deformation.

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