Counts Content and Stretching Temperature-Dependent Critical Stress for Destruction of γ Crystals in Propylene–Ethylene Random Copolymers

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ABSTRACT: Tensile deformation behavior of three random propylene–ethylene copolymers with the same molecular weight and different contents of counit was investigated at different temperatures from room temperature to close to melting point via tensile tests, step-cycle tests, and in situ wide-angle X-ray diffraction techniques. Upon stretching, the original crystalline lamellae must be destroyed, generating new highly oriented ones. A critical stress has been suggested, under which the original crystallites can be destructed. The propylene–ethylene copolymer samples in pure γ-form transformed gradually into α-form during tensile stretching. This crystalline transition proceeded via a destruction (melting) of the original γ-form crystals followed by recrystallization of the freed polymeric chain segments into α-form along stretching direction. This result provides a marker for investigating the critical stress mentioned above. Such critical stresses triggering the destruction of γ-form crystals for the propylene–ethylene copolymer samples of different ethylene counit contents were successfully calculated. It turned out that this critical stress depended on the ethylene counit content and stretching temperature. Samples with less ethylene counits show higher critical stress because of a lower degree of insertion of the ethylene counits into the crystalline unit cell than samples with higher ethylene counit content. The critical stresses remained constant when the samples were stretched at low-temperature region, whereas they decreased significantly at high stretching temperatures close to the melting points due to strong thermal distortion of the crystalline lattices, making the crystallites less stable.

INTRODUCTION

Semicrystalline polymers are normally composed of layerlike crystalline phase and entangled amorphous chains in between.1 Understanding of the microstructural evolution of semicrystalline polymers during tensile stretching is of both scientific and industrial relevance. Upon investigating the macroscopic recovery properties in several typical semicrystalline polymers, it was concluded that a semicrystalline polymer can be regarded as interpenetrated networks of hard crystalline skeleton and amorphous entangled soft network.2–5 Through a so-called “step-cycle” test, a separation of the total strain into elastic part and plastic one can be achieved.6 Surprisingly, the recovery properties of semicrystalline polymers change in a characteristic way at four critical strains (A–D), reflecting microstructural evolution in the systems. Macroscopically, the systems show onset of plastic strain at A, a sudden increase in plastic strain at B, a plateau for elastic strain at C, and finally a decrease in elasticity at D. According to above-mentioned interpenetrated network model, these characteristic critical strains can be understood as a result of isolated intralamellar crystalline block slips (A), a change into a collective block slips (B), crystalline block disaggregation (melting)—recrystallization-induced fibrillation (C), and disentanglements (D), which is also confirmed by true stress–strain relationship investigations and in situ wide-angle X-ray diffraction (WAXD) measurements.6–12 Specially, the position of critical strain C is determined by the interplay between the stability of crystalline blocks and the state of amorphous entangled network.5 Only if the stretched amorphous entangled network reaches certain strain can it generate a critical stress, leading to a destruction of the crystalline blocks followed by recrystallization with polymeric chains aligned along the stretching direction forming crystalline fibrils. This two-phase model explains the mechanical response of semicrystalline polymers with sufficient crystallinity. A change of the position of critical strain at C toward larger value was discovered in a low-crystallinity ethylene/octane copolymers.
copolymer\textsuperscript{13} that led to a more general three-phase model, taking into account the heterogeneity of the distribution of the crystalline phase. In such system, disaggregation (melting)—recrystallization process of crystalline blocks was delayed due to the heterogeneous strain distribution in the system. In addition, an elasticity reinforcement in large-deformation regime at elevated stretching temperature for propylene—ethylene copolymer\textsuperscript{13} in step-cycle test also occurred due to slippage of fibrils after depletion of unoriented crystals.

Isotactic polypropylene (iPP) is a widely used commercial polymer with various polymorphs, including monoclinic (α), trigonal (β), orthorhombic (γ), and one smectic meso-phase.\textsuperscript{14—21} The mechanical behavior of iPP is closely related to that of crystalline polymorphs obtained under specific conditions. However, γ-form can only be generated under some tough conditions, such as crystallization at high pressure\textsuperscript{22} for iPP, leading to the lack of investigation on the deformation mechanism. In fact, iPP samples containing γ-form with the unique nonparallel structure can prevent chain slips within crystals under stress except for the (001) transverse slips.\textsuperscript{23,24} Besides, γ-form prepared under high pressure reveals an enhanced strength and a strongly reduced evolution of the dislocation density compared to the α-form.\textsuperscript{25} For propylene—ethylene random copolymers, crystallization of γ-form can proceed at high temperature under atmospheric pressure because the stereo and regio defects in the chain made forming a low-energy ordered structure by chain tilting in copolymer\textsuperscript{26} at an advantage. De Rosa et al. demonstrated that the amount of γ-form in polypropylene was determined by the concentration\textsuperscript{27} and distribution\textsuperscript{28} of defects. γ-Form tends to develop in the sample with random distribution of defects. They have also investigated\textsuperscript{29} the influence of chain microstructure on the crystallization of polypropylene. The crystallization kinetics increased with increasing the concentration or rr defects and decreasing the molecular weight. Finally, they concluded that the amount of γ-form increased with increasing crystallization temperature, comonomer concentration, and content of rr stereodefects. The influence of catalyst and stereoirregularities on the formation of γ-form has also been studied in previous research\textsuperscript{30—33} and all of them concluded that γ-form was promoted at high temperature and systems with more defects.

The transition from γ-form to α-form under tensile deformation has also been investigated in recent years.\textsuperscript{34—40} Auriemma et al.\textsuperscript{41} proved the existence of a continuum of disordered modifications in oriented γ-form and calculated the fraction of bilayers similar to γ-form or α-form at different stretched ratios. The structural disorder originated from the random succession of bilayers of chains. Some of the bilayers of chains were arranged like γ-form, whereas others like α-form. So, the network was composed of continuum of structural disorder. De Rosa et al.\textsuperscript{30,42} investigated the relationship between the elastic properties and concentration of rr defects. At the same time, they found\textsuperscript{43} that γ-form can transform into mesophase at very high deformation and the mesomorphic phase can transform back to α-form upon releasing the tension only for some elastic samples due to the enthalpical contribution. The orientation mode of γ-form with unique structure during stretching was first named “cross-β” by Auriemma et al.\textsuperscript{44} because the perpendicular orientation of chain axis with respect to the stretching direction was very similar to the configuration of stretched silks.\textsuperscript{45} Actually, the cross-β orientation was first proposed in this system where part of the chains of silk protein oriented perpendicular to the stretching direction. In 2006 and 2007, De Rosa et al. described structural-mechanical phase diagram\textsuperscript{46} for isotactic polypropylene and demonstrated that the mechanical behavior, including the elastic modulus, ductility, toughness, and strength, can be tuned by changing the concentration of rr stereodefects and ethylene counits. Recently, they have investigated\textsuperscript{47} the influence of temperature on the deformation of disordered γ-form and proposed that γ-form transformed into mesophase at room temperature and into α-form at 60 °C, which was due to the increase of mobility of chains in amorphous matrix at a high temperature. In 2006, Hsiao et al.\textsuperscript{48} investigated the elastic behavior of propylene—ethylene copolymer, which was composed of α-form. In addition, Mao et al.\textsuperscript{49} analyzed the transition behavior of γ-form during stretching. The c axis always had a tilt angle with respect to the fiber axis in the cross-β configuration. They also found\textsuperscript{50} that larger lamellar crystals in α-form were generated at higher stretching temperature, whereas stretch-induced mesophase composed of tiny β-form was obtained under larger stress at lower stretching temperature. They investigated\textsuperscript{51} the partial melting and recrystallization behavior of uniaxial stretched γ-form of propylene—butene copolymer and found that the survived crystals could serve as seed. Besides the above work, Boger et al.\textsuperscript{49,50} also studied the phase transition behavior and orientation of elastic polypropylenes.

Despite that a large body of literature reports on the transition of γ-form to α-form in tensile stretched propylene—ethylene random copolymers have been published, the actual micromechanical mechanism of such transition remains not being fully revealed. Of particular interest is the exact quantification of the critical stress for the destruction of the original γ-form crystals during stretching. The purpose of this work is thus to investigate the deformation behavior of pure γ-form in random propylene—ethylene copolymers with different contents of counits with special attention on quantifying the critical stress for the destruction of γ-form crystallites. The fibrillation point (critical point C) shown in step-cycle tests was in correspondence with the transition point of γ-form to α-form verified by WAXD measurements. The critical stress for the onset of the destruction of γ-form crystallites was calculated. It turns out that the transition point and critical stress of destructing the original γ-form during stretching depend on the content of counits and stretching temperature.

# RESULTS AND DISCUSSION

The polymorph of random propylene—ethylene copolymer during isothermal crystallization depends strongly on the crystallization temperature and stereodefects in the samples.\textsuperscript{52—56,59,51} The relationship between the fraction of γ-form (\(f_\gamma\)) and isothermal crystallization temperature is illustrated in Figure S2 in Supporting Information. The formation of γ-form favors high crystallization temperature and high concentration of counits. Figure S2 shows that \(f_\gamma\) increased with crystallization temperature and reached maximum (100%) at the highest temperature. At low temperature, the crystallization of α-form is kinetically favored, leading to a large amount of α-form. At high crystallization temperature, chain folding\textsuperscript{57} of very long sequence-attached noncrystallizable units with rich defects is very difficult. Chain tilting in producing γ-form is an effective way to form a low-energy three-dimensional ordered structure as the critical nucleus sequences increase with temperature. The “defects”\textsuperscript{51,52,53} include the concentration of counits and [rr] stereodefects, which shorten the average length of the
crystallizable sequences and the kinds of counit that lead to different inclusions in the crystal. In this system, the content of γ-form was the highest for iPPcoE16 at the same crystallization temperature, indicating that the amount of defects was the largest for iPPcoE16. According to the isothermal crystallization results, pure γ for iPPcoE6, iPPcoE12, and iPPcoE16 was prepared by isothermal crystallization at 90, 65, and 55 °C, respectively. The WAXD curves of iPPcoE12 in pure α-form and pure γ-form are shown in Figure 1 as an example. As most diffraction peaks of the two polymorphs overlap each other, the only difference is the two specific diffraction peaks, (117)γ at 20.1° and (130)α at 18.8°.

The differential scanning calorimetry (DSC) melting curves for pure γ-form of the three samples are shown in Figure 2. For pure γ-form, one melting peak located near the isothermal crystallization temperature was observed. The melting temperature increased with decreasing content of ethylene counits. The other broader one located at lower temperature was due to the secondary crystallization during cooling from isothermal crystallization temperature down to room temperature.

Because ΔHf (heat of fusion) of γ-form for copolymers differs from its homopolymer counterpart due to the different partitioning levels of ethylene counits in the crystalline structure, the crystallinity was calculated by fitting the one-dimensional WAXD curves into several Gaussian peaks instead of using DSC measurements. To further investigate the difference between the pure γ crystallinity measured by WAXD, lamellae thicknesses (dc) derived from small-angle X-ray scattering (SAXS) data for isotropic samples at different temperatures are shown in Figure 3. The crystallinity continued decreasing during heating because some unstable crystals melted at low temperature. The lamellar thickness dc apparently increased with increasing temperature. The increase of dc can be understood as a result of melting of the thinner lamellae at elevated temperatures. In addition, dc for a sample with high content of ethylene counits was always higher at the same temperature. The relatively higher thickness of the lamellae was due to the participation of continuous long-chain segments of sample with high ethylene content in the crystal during crystallization. The detailed 1D WAXD curves, 1D-SAXS curves, and correlation function curves for iPPcoE12-γ are shown in Figure S3 in Supporting Information.

To investigate the recovery properties of pure α-form and pure γ-form, step-cycle tests have been carried out at different temperatures. The variations of plastic strain and elastic strain with total strain obtained from step-cycle tests at 25 °C for iPPcoE12-α and iPPcoE12-γ are shown in Figure 4 as an example. In the beginning of stretching, both elastic strain and plastic strain increased. The recovery property for iPPcoE12-γ was better because its elastic strain was higher than that of iPPcoE12-α at the same total strain. The orthorhombic unit cell of γ-form contains nonparallel bilayers, which are composed of 31 helices. For stretched γ-form at small strain, crystallized chain segments tended to move toward perpendicular to the fiber axis because chains lay diagonally in ab-plane perpendicularly to the c axis. Such orientation in this configuration was certainly unfavorable so that the elastic property was better in the beginning. The deformation mechanism changed from crystalline block slip to disaggregation (melting)–recrystallization process at critical point C, where elastic strain started to decrease and plastic strain increased at a larger slope. The critical point C for iPPcoE12-α was at around 0.8, whereas for iPPcoE12-γ it was at 0.6, indicating the difference in the deformation mechanism between the two crystalline polymorphs. For a deeper investigation, tensile tests were carried out at different temperatures for the two polymorphs.

Figure 5 shows the critical strain at point C as a function of crystallinity when stretched at 25 and 60 °C for samples possessing pure α-form and pure γ-form crystallites. The critical strain at point C for sample with pure α-form was always located at 0.8 independent of the stretching temperature and content of counits. Similar results reported that critical point C was both 0.7 for form I in two P1B-based copolymers with different contents of counits at room temperature, which was caused by the same interaction between the entanglement amorphous chain and the crystalline blocks. However, the strong dependence of the critical point C for samples with pure γ-form crystallites on the stretching temperature and content of counits has been observed for random propylene–ethylene copolymers. To find the relationship between the critical point C and the onset of destruction of original γ-form crystallites, in

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**Figure 1.** Integrated one-dimensional (1D) WAXD curves of iPPcoE12 in pure α-form (iPPcoE12-α) and pure γ-form (iPPcoE12-γ).

**Figure 2.** DSC melting curves for pure γ-form of iPPcoE6, iPPcoE12, and iPPcoE16.
situ WAXD measurements during stretching for samples with pure γ-form have been carried out.

Selected two-dimensional (2D) WAXD patterns of iPP-coE12-γ stretched at 25 °C are given in Figure 6 as an example. Raw 2D WAXD patterns and 1D WAXD curves during stretching are given in Figures S4 and S5 in Supporting Information. The isotropic diffraction circles transformed into highly oriented diffraction points during tensile tests. In addition, the diffraction point of (130)\(\alpha\) in the meridian was observed at larger strain, indicating the destruction of original γ-form crystallites followed by recrystallization of the freed polymeric chain segments into α-form by drawing. However, it was difficult to precisely judge transition point by the appearance of (130)\(\alpha\), because the intensity of the peak at the starting point. The evolution of strong reflection peak of (008)\(\gamma\) may be regarded as a signature to judge the transition point due to the following reasons. In cross-β orientation mode with c-axis parallel to fiber axis, (008)\(\gamma\) arc orientated along the equatorial direction. For further stretching, the intensity of the (008)\(\gamma\) arc became weaker, whereas the diffraction arc close to meridian in the same plane became stronger at larger strain, indicating that the meridian diffraction arc was not originated from (008)\(\gamma\). Because the transition from γ-form to α-form has already started at larger strain indicated by the diffraction point of (130)\(\alpha\), and content of γ-form continued decreasing, the meridian diffraction arc with increasing intensity observed in (008) plane can only be due to (040)\(\alpha\), because they shared the same diffraction peak, as shown in Figure 1. To quantify the orientation behavior of the plane (008)/(040)\(\alpha\), the orientation degree was calculated using the Hermans orientation equation:

\[
S_{\text{H}} = \frac{3(\cos^2 \theta_{\text{H}}) - 1}{2}
\]

where \(\theta\) denotes the angle between the normal direction of the plane and the reference axis. \(\langle \cos^2 \theta_{\text{H}} \rangle\) derived from azimuthal scattering intensity distribution is defined as:

\[
\langle \cos^2 \theta_{\text{H}} \rangle = \frac{\int_{\theta}^{\pi/2} I_{hkl}(\theta) \cos^2 \theta \sin \theta \, d\theta}{\int_{0}^{\pi/2} I_{hkl}(\theta) \sin \theta \, d\theta}
\]
where $I(\theta)$ is the scattering intensity along angle $\theta$. It is important to note that the orientation degree in the present case assumes values in the range of $-0.5 \leq S \leq 0$. For a perfect orientation of the lattice planes with their normal perpendicular to the stretching direction, the order parameter is $-0.5$, whereas overall random orientation gives 0.

Figure 7 depicts the selected azimuthal scattering intensity distribution curves of (008)$_{\gamma}$/(040)$_{\alpha}$ (left) and degree of orientation of (008)$_{\gamma}$/(040)$_{\alpha}$ as a function of strain (right) for iPPcoE12-\(\gamma\) stretched at 25 °C. At lower strain, the diffraction intensity of (008)$_{\gamma}$ arc in equatorial direction increased, which was in accordance with the cross-\(\beta\)-orientation mode of \(\gamma\)-form. For further stretching, the intensity of the arc close to meridian increased, whereas the arc in equatorial direction decreased. The degree of orientation weakened in the beginning because most crystalline chains oriented perpendicular to the fiber axis. After the occurrence of \(\gamma\)-form to \(\alpha\)-form transition, more chains in \(\alpha\)-form oriented along the stretching direction, leading to a quick increase of the orientation at larger strain. Therefore, the position of the turning point in the plot of orientation degree was chosen to judge when the transition started.

All of the critical strains at point C obtained from step-cycle tests (details in Figures S7–S9) and transition point derived from WAXD data (details in Figure S6) for samples with pure \(\gamma\)-form of iPPcoE6, iPPcoE12, and iPPcoE16 are summarized in Figure 8. One finds a surprising coincidence between the macroscopic critical point in mechanical tests and microscopic transition point from \(\gamma\)-form to \(\alpha\)-form. Macroscopically, critical point C derived from step-cycle tests was defined as the strain at which elasticity reached a plateau value due to change of deformation mechanism from crystalline block slip to disaggregation (melting)—recrystallization. For pure \(\gamma\)-form of...
random propylene—ethylene copolymer, transition from γ-form to α-form can only be achieved by stretching. The recovery property for crystalline block started to decline once the transition occurred because transition from γ-form to α-form was an irreversible process. In addition, the elasticity of the stretching-induced α-form was worse than that of γ-form in cross-β orientation mode. Different from the α→β transition in poly(butylene succinate), which occurred much later than lamellae-to-fibril transition, crystals in γ-form transformed into fibrils in α-form, where chains were oriented along the stretching direction via disaggregation (melting)—recrystallization. Therefore, the critical point C derived from the step-cycle tests was strongly influenced by the destruction of the original crystals in different situations. As shown in Figure 8, larger critical strain was needed at higher stretching temperature, which was similar to the crystal transition behavior of sPP.\(^6^{0}\) Besides, transition process occurred much earlier for samples with less content of counits.

Clearly, destruction (melting) of the original γ-form crystallites during stretching requires a critical stress under which the crystallites are no longer stable. The critical stress cannot be read directly from the true stress—strain curves because the total stress includes contributions from all components in the system, whereas only those acting directly on the crystallites are responsible for the transition. To investigate the critical stress of destruction of the original γ-form crystallites at the transition point, the Gaussian model of Haward and Thackray\(^6^{1,6^{2}}\) was employed. The model (shown in Figure S10 in Supporting Information) was composed of a Hookean elastic spring in a series with an Eyring dashpot and a rubbery spring in parallel, which can effectively describe all basic macroscopic effects occurring during stretching of semicrystalline polymers. The crystalline phase including the lamellar and block coupling was represented by the Hookean elastic spring attached with Eyring dashpot.\(^6^{3}\) The rubbery spring stood for entangled network of amorphous chains. Although the model did not consider three-phase structure in low-crystallinity samples, it can still be applied to our case for the following reason. In a three-phase structure, the above-mentioned coupling can be regarded as the coupling between crystalline lamellar stacks. The rubbery spring can still represent mechanical response of the stretched entangled network. Figure S11 in Supporting Information shows the estimation of the Hookean elastic constant \(E\) and the rubber elastic constant \(G\) on a plot of true stress as a function of \(\lambda^2 - 1/\lambda\) (\(\lambda\) represents the draw ratio). The system was regarded as a rubber filled with crystalline particles. And the effect of crystallinity was reduced by using the Einstein relation.\(^6^{4}\) The critical stress of network at the transition point was defined as

\[
\sigma = \frac{G}{(1 + 2.5\alpha)} \times (\lambda^2 - 1/\lambda)
\]

where \(\alpha\) is the crystallinity measured by WAXD. Thus, the effect of crystallinity on the critical stress was removed. The data of all of the Haward and Thackray plots are shown in Figure S12 in Supporting Information. Recently, Wang et al.\(^6^{5}\) have proposed that the deformation of some copolymers deviated from the model due to the strain-induced crystallization at very large strain. In fact, this effect scarcely occurred in our case, and the deformation behavior abided by this model in the experimental draw ratio is shown in Figure S12. As a comparison, the critical stress of original α-form at the critical point calculated by the Gaussian model of Haward and Thackray will also be discussed in the following part.

Figure 9 shows the critical stress of network for the destruction of α-form, which is a quite stable polymorph as no polymorph transition occurs during tensile tests. The deformation behavior of α-form was not influenced by stretching temperature and content of counits. The destruction of the original crystallites or the fibrillation process was controlled by a constant critical stress of 3.1 MPa, indicating the same interplay between the crystalline blocks and amorphous network in the samples of pure α-form for the three copolymers.

The critical stress of network for samples in γ-form at the transition point as a function of stretching temperature is given in Figure 10. Unlike the deformation behavior of α-form, the critical stress for the destruction of γ-form kept constant at low temperature and declined at high temperature. The critical stresses for the destruction of γ-form for iPPcoE6, iPPcoE12,
and iPPcoE16 were 2.1, 1.8, and 1.7 MPa, respectively. The results indicated that higher critical stress was needed to destruct the crystallites in γ-form for samples with lower count content. Although the chain sequence in the molten state for each copolymer is the same, the deformation behavior for pure α-form and γ-form differs a lot. It has been reported that part of ethylene chain went into crystalline region in propylene–ethylene copolymers, which was confirmed by solid-state CP/MAS $^{13}$C NMR spectra. Besides solid-state NMR technique, the average length of isotactic polypropylene ($L_{\text{avg}} = 2\text{[mm]/[mr]} + 2$) is also related to the different degrees of inclusion of stereodefects and constitutional defects in the crystals of iPP. Even though it is not clear whether the different crystalline polymorph has an effect on the concentration of defects in the lattice, the more extensive crystallization process indeed leads to a higher ethylene concentration in the lattice. Pure α-form was prepared by a rapid cooling process, whereas pure γ-form was prepared by a long crystallization process at high temperature. We may conclude that the different thermal history brought about the variations in the concentration of ethene in the lattice. The level of defects in the crystalline region for pure α-form remains low for all of the three copolymers due to the rapid crystallization. And the critical stress is higher than that for pure γ-form. For pure γ-form, the concentration of defects in crystalline region is highest for iPPcoE16 with the highest content of counits. Samples with more defects in the unit cell were much easier to be destroyed in the cross-β orientation mode during stretching. The critical stress for the transition was lower for samples in pure γ-form with higher content of ethylene counits.

Besides, the deformation temperature had an influence on the phase transition. As shown in Figure 10, for all three samples, the critical stress of the destruction of γ-form during stretching kept constant at low temperature and decreased at high temperature. The decreasing crystallinity was excluded due to the following possible reasons. First, the effect of crystallinity was removed in the calculation of critical stress. In addition, the crystallinity continued decreasing with increasing stretching temperature, which is shown in Figure 3, and only at higher temperature, the critical stress started to decline. This result indicates that the crystallites became less stable, requiring smaller stress to perform the destruction process at high temperature. Temperature-dependent full width at half-maximum (FWHM) of the WAXD diffraction peak of (008), results shown in Figure 10 may help to understand the situation. First of all, all of melting of unstable crystallites with smaller size during heating would result in a decrease in the FWHM as on average the size of the crystallites increases. However, the FWHM of (008)$_{\gamma}$ diffraction peak for iPPcoE6 shown in Figure 11 started to increase at 65 °C. Clearly, at high temperatures, distortion of the crystalline lattice due to thermal motion of the chain segments dominated the diffraction behavior, resulting in a strong peak broadening. And the situations were similar for other samples, including iPPcoE12 and iPPcoE16. We may conclude that destruction of the original γ-form crystallites at high temperature can proceed under lower stress due to the deterioration of the crystalline order of polymer chains during heating.

**CONCLUSIONS**

In summary, stretching-induced destruction of γ-form crystallites in random propylene–ethylene copolymers with the similar molecular weight occurred at the onset of lamellae-to-fibril transition, which was evidenced by the fact that critical strain at point C and onset strain of polymorph transition were located at the same position. The critical stress of network for the destruction of original γ-form crystallites was obtained, which depends strongly on the stretching temperature and content of counits. The critical stress at the transition point was higher for samples with lower count content due to the less partitioning of ethylene counits in the crystalline phase. In addition, high stretching temperature made the critical stress lower because the crystalline structure became less stable due to thermal distortion of the crystallized segments.

**EXPERIMENTAL SECTION**

The random propylene–ethylene copolymers iPPcoE6, iPPcoE12, and iPPcoE16 produced using metallocene catalyst were kindly provided by ExxonMobil Asia Pacific Research and Development Co., Ltd. Those three samples are Vistamaxx performance polymers. The trade names for iPPcoE6, iPPcoE12, and iPPcoE16 are Vistamaxx 3588, Vistamaxx 3980, and Vistamaxx 3000, respectively. The melt flow rate (MFR), molecular weight, and the fraction of ethylene counits of the samples are shown in Table 1.

The pellets were first compression-molded at 180 °C into films with a thickness of 0.5 mm and then held for 5 min to erase the thermal history. Samples with pure α-form were prepared by quenching the melt into water bath at room temperature. Samples with pure γ-form were obtained by quenching the melt into water or oil bath at selected isothermal crystallization temperature for sufficiently long time. Differential scanning calorimetry (DSC), small-angle X-ray scattering (SAXS), and wide-angle X-ray diffraction (WAXD) measurements have been carried out on isotropic films before stretching. Besides, another group of samples in pure γ-form with a different processing method have been prepared for studying the critical stress for destructing original γ-form crystallites of different thickness. The details of preparation method, the raw data, and the final results for the second group of samples are shown in Supporting Information (Figures S13–S16), which provide solid evidence to support our conclusion.

The DSC measurements were carried out with a DSC1 STARE System (Mettler Toledo, Switzerland), which had been
Table 1. Basic Characteristics of the Random Propylene–Ethylene Copolymers

| sample      | MFR (230 °C/ 2.16 kg) (g/10 min) | $M_n$ (g/mol)$^a$ | $M_w$ (g/mol)$^a$ | $M_w / M_n$ | ethylene counits (mol %) |
|-------------|----------------------------------|------------------|------------------|-------------|--------------------------|
| iPPcoE6     | 8                                | $2.1 \times 10^5$ | $9.9 \times 10^4$ | 2.15        | 6                        |
| iPPcoE12    | 8                                | $2.0 \times 10^5$ | $9.4 \times 10^4$ | 2.07        | 12                       |
| iPPcoE16    | 8                                | $1.9 \times 10^5$ | $9.1 \times 10^4$ | 2.11        | 16                       |

$^a$The molecular weight and $M_w / M_n$ of samples were obtained by gel permeation chromatography in 1,2,4-trichlorobenzene.

 calibrated for temperature and melting enthalpy using indium as a standard under N$_2$ atmosphere at a heating rate of 10 K/min.

The SAXS measurements were carried out on a modified Xeuss system of Xenocs, France, equipped with a semiconductor detector (Pilatus 100 K, DECTRIS, Switzerland) attached to a multilayer focused Cu K$_\alpha$ X-ray source (GeniX$^{}\alpha$ Cu ULD, Xenocs SA, France), generated at 50 kV and 0.6 mA. The sample-to-detector distance is 166 mm. A 2D MAR CCD X-ray detector with a resolution of 2048 $\times$ 2048 (pixel size = 79 $\mu$m) was used for calculating the thicknesses of crystalline crystallites. The correlation function $K(z)$ was derived from inverse Fourier transformation of the experimental intensity distribution $I(q)$ as follows

$$K(z) = \frac{\int_0^\infty I(q) q^2 \cos(qz) \, dq}{\int_0^\infty I(q) q^2 \, dq}$$

which was used for calculating the thicknesses of crystalline lamellae ($d_c$), amorphous layers ($d_a$), and the long period ($d_m$) of the samples composed of two-phase layerlike systems. The weight crystallinity measured by WAXD was less than 50%, so the smaller value obtained from the correlation function was assigned to $d_a$ and $d_c$ was then obtained as $d_c = d_m - d_a$.

The “Dog bone” tensile bars with dimensions of 10 $\times$ 5 $\times$ 0.5 mm$^3$ were obtained with the aid of a punch. The tensile tests were carried out using a portable tensile testing machine (TST 350, Linkam, U.K.) at different temperatures. Optical images of the sample were employed to measure the strain of the sample during testing. The Hencky measure of strain $\epsilon_{H}$ is used as a basic quantity of the extension, which is defined as

$$\epsilon_{H} = 2 \ln \frac{b_0}{b}$$

where $b_0$ and $b$ are the widths of undeformed and deformed areas, respectively. In step-cycle experiment, the sample was stretched step-by-step at a constant speed. After each step, inverse movement of the clamps was performed to contract the sample until a stress of zero was achieved. Then, the sample was stretched again at this given speed, until it re-reached the point at which it left the initial curve. A stepwise stretching of the sample with loading–unloading cycles was combined in the process. The imposed strains were therefore decomposed into a quasi-elastic (recoverable) part and a quasi-plastic (irreversible) part. Details of step-cycle tests are shown in Figure S1 in Supporting Information.

In situ synchrotron WAXD measurements during tensile tests at 20 $\mu$m/s were performed at beamline 1W2A, BSRF, Beijing. The wavelength of X-ray radiation is 0.154 nm, and the sample-to-detector distance is 166 mm. A 2D MAR CCD X-ray detector with a resolution of 2048 $\times$ 2048 (pixel size = 79 $\mu$m) is used to acquire 2D WAXD patterns. The primary X-ray beam was first positioned at the middle of the horizontally placed sample strip. All of the WAXD patterns were collected within 100 s after every step under load and background-subtracted.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b01269.

Details of step-cycle tests; isothermal crystallization results; 1D WAXD, SAXS, and correlation function curves at different temperatures for isotropic samples; details of WAXD data during stretching, including 2D patterns, 1D curves, and degree of orientation curves; all of the step-cycle tests; description of the Gaussian model of Haward and Thackray and corresponding results; and the preparation method for second group of pure γ-form and deformation results (PDF)

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#### Notes

The authors declare no competing financial interest.

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