Promotion of self-nucleation with latent Form I nuclei in polybutene-1 and its copolymer

Zefan Wang[1,2], Xia Dong[1,2], Dario Cavallo[3], Alejandro J. Müller*[4,5], Dujin Wang*[1,2]

[1]CAS Key Laboratory of Engineering Plastics, CAS Research/Education Center for Excellence in Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

[2]University of Chinese Academy of Sciences, Beijing 100049, China

[3]Department of Chemistry and Industrial Chemistry, University of Genova, via Dodecaneso, 31 - 16146 Genova, Italy

[4]POLYMAT and Polymer Science and Technology Department, Faculty of Chemistry, University of the Basque Country UPV/EHU, Paseo Manuel de Lardizabal 3, 20018 Donostia-San Sebastián, Spain

[5]Ikerbasque, Basque Foundation for Science, Bilbao, Spain

*Corresponding authors: djwang@iccas.ac.cn and alejandrojesus.muller@ehu.es

ABSTRACT

The formation of Form I nuclei of polybutene-1 (PB-1) and its copolymer with polyethylene (PB1-*ran*-PE) has been studied by means of modified self-nucleation protocols. Even when the self-nucleation temperature was high enough and all Form II crystals melt, re-crystallization can be accelerated if the melt-crystallized sample was annealed at low temperatures (below 60 °C for PB-1 and 75 °C for PB1-*ran*-PE) for just 3 min. These results suggest the formation of latent Form I nuclei within Form II crystals. This hypothesis is consistent with the observed growth of a small amount of Form I crystals during heating, after previous annealing at temperature lower than 20 °C. In addition, a peculiar phenomenon was found in PB1-*ran*-PE, as both Form II and Form I′ can be induced by the presence of latent Form I nuclei, due to cross-nucleation and self-nucleation effects, respectively. The final ratio of the two kinds of crystal Forms is a result of the competition between the two nucleation rates, which strongly depend on crystallization temperature. In this work, we have shown that careful design of novel self-nucleation protocols can yield evidence of the early stages of Form II to Form I transition, even when the degree of transformed crystals is below the limit of detection of conventional techniques sensitive to crystalline order (DSC, WAXD, FTIR).

Keywords: Polybutene-1, Butene-1/ethylene copolymer, polymorphic transformation, self-nucleation, crystalline memory.

INTRODUCTION

Different from small molecules, semi-crystalline polymers with long linear chains can display a relatively wide crystallization and melting temperature range.[1-3] When polymer samples are partially melted, their crystal remains can serve as nucleating agent to accelerate the subsequent crystallization process. This phenomenon is called self-nucleation. Even the orientation of the crystals can be inherited from the initial one (i.e., cloning)[4, 5]. Additionally, after complete melting of polymeric crystals, some memory of the crystalline ordered structure can still survive, and the crystallization of the polymer can be enhanced by melt memory effects.[6-11]

Polybutene-1 is a polyolefin with excellent mechanical properties and complex polymorphic behavior that has attracted much interest from both industry and academia. [12, 13] The tetragonal Form II with an 11/3 helix can be obtained by cooling the sample directly from the melt. The thermodynamically stable Form I, with a 3/1 helix, is usually generated from the kinetically favored Form II by aging the sample at room temperature for 10 days.[14] In addition, another polymorph, Form I′, which has a similar crystal structure to Form I can also be formed[15]. Generally, Form I′ can be obtained by several methods, such as solution crystallization,[16] blending with isotactic polypropylene[15] or copolymerization with other monomers.[17-19]

The transformation mechanism of Form II to Form I has been investigated for several decades. On a molecular level, it has been usually considered that the chirality of the 11/3 helix of Form II does not change when it transforms to Form I, which is made of 3/1 helix. Besides that, both tetragonal Form II and trigonal Form I share a

common (110) plane.[14]

Recently, the precise crystallographic refinement of Form I and Form II have been made by Tashiro et al.[20] A kinetic model was proposed suggesting that a transient hexagonal structure made of 11/3 helices developed first from Form II and then transform to stable Form I by 11/3 to 3/1 helices chain conformational changes. This mechanism can explain the formation of the twin structure of Form I observed by electron diffraction. Another interesting phenomenon is that the solid-solid transformation can be accelerated greatly if PB-1 samples are precooled to -20 °C for several minutes.[12]

Men et al. designed an experiment to quantify the Form II to Form I transformation rate.[21, 22] They demonstrated that a classic nucleation and growth model could be fitted to the Form II to Form I transition using the Tammann's two stage crystal nuclei development method, in analogy with small molecules. In addition, it was proposed that the transition mechanism could be promoted by the internal stress in the sample which is caused by an unbalanced shrinkage of amorphous and crystalline phases. However, the nucleation of Form I at the early stage of the transition has just been indirectly inferred from the acceleration of the overall transformation rate, and not directly evidenced.

Due to the complex polymorphism of PB-1, several researchers have tried to explore the self-nucleation behavior of PB-1 with different crystal modifications. Cavallo et al. [23, 24] found that Form II can be nucleated on the surface of Form I spherulites. This is an example of cross-nucleation. Furthermore, employing

differential scanning calorimetry (DSC) and *in situ* Fourier transformation infrared microspectroscopic imaging, a small amount of Form I′ was found directly inside Form I spherulites, when Form I crystals are partially molten.[25-27] Men et al. investigated the melt memory effect of a butene-1/ethylene sample with high content of ethylene comonomer and found that Form I′ can be formed directly from the heterogeneous melt, in a specific temperature range, as a consequence of melt heterogeneities produced by crystallizable chain sequence segregation coming from previous crystallization. It is proposed that the size of the segregated domains containing long crystallizable sequences is a function of the melt-annealing temperature, and thus the formation of either Form I' or Form II' depends on the interplay between this domain size and the critical nucleus size of the respective polymorph. .[28-30]

In this work, modified self-nucleation (SN) protocols were used as a novel method to detect the early stages of Form II-to-Form I transition in PB-1 and its copolymer. By annealing the melt-crystalized Form II crystals at low temperature for 3 min, an enhanced nucleation was observed during the re-crystallization process, even for SN temperature high enough to completely melt all Form II crystals. These results indicated that a small amount of latent Form I nuclei, undetectable by FTIR and X-ray diffraction, formed during the annealing at low temperature. Different from PB-1, both Form I′ and Form II can be induced by transformed Form I crystals in PB1-*ran*-PE, due to the competition between self-nucleation and cross-nucleation effects. Our work provides a sensitive method to investigate the early stage of the solid-solid transition in polymer crystals and sheds a new light on the understanding the structural change in Form II to

Form I transition of PB-1 and its copolymer.

EXPERIMENTAL SECTION

Materials.

An isotactic polybutene-1 homopolymer (PB-1, trade name: PB0110M) and a butene-1/ethylene statistic copolymer (PB1-*ran*-PE, trade name: PB8340M) were purchased from Lyondell Basell Industries. The physical properties of them are listed in Table 1.

Table 1. Characterization of PB-1 and PB1-ran-PE samples.

	Trade name	Melt flow rate (MFR) (190 °C/2.16 kg)	M_w (kg/mol)	PDI	Content of comonomer (Characterized by NMR)[31]	$T_{m, 1}$ (°C, Form I)	$T_{m, 2}$ (°C, Form II)
PB-1	PB0110M	0.4	65.7	3.52	0	128	117
PB1-*ran*-PE	PB8340M	4	28.1	4.25	4.8%	113	97

Differential Scanning Calorimeter (DSC).

The thermal and the self-nucleation behavior of the PB-1 and PB1-*ran*-PE were characterized by a TA differential scanning calorimeter (Q2000) under nitrogen atmosphere (50 ml/min). The instrument was calibrated with indium.

The thermal protocols applied in this work can be divided in two stages: sample preparation and self-nucleation.

(a) *Sample preparation stage.* As indicated in Figure 1, the samples were first heated to 200 $^{\circ}$C for 3 min to erase thermal history, followed by quenching to $T_{c,1}$ for 90 min ($T_{c,1}$ was set to 85 $^{\circ}$C for PB-1 and 75 $^{\circ}$C for PB1-*ran*-PE). In this way, pure Form II was obtained (see Figure 1a and 1b). In order to investigate the structural changes during the annealing process at low temperatures, some of the samples were cooled to different lower treatment temperatures (T_l) at 10 $^{\circ}$C/min, then they were kept at these low temperatures for 3 min (Figure 1c and 1d).

(b) *Self-nucleation stage.* Two types of SN procedures were designed and implemented:

(b-1) Figure 1a and 1c show standard SN protocols similar to those commonly used in the literature (see for instance ref. 2). Samples were heated to different SN temperatures (or T_s temperatures) for 5 min, and then cooled to 30 $^{\circ}$C for 3 min, followed by heating to 200 $^{\circ}$C. Both cooling and heating rates were 10 $^{\circ}$C/min.

(b-2) In order to investigate the possible competition between self-nucleation and cross-nucleation of PB1-*ran*-PE, another SN experiment was designed and termed ***"isothermal SN"*** (see Figure 1b and d). After the preparation stage (i.e., b-1 above), the samples were heated to a T_s temperature of 118 $^{\circ}$C for 5 min. At this temperature, only Form II can melt but any Form I that could have

formed (by transformation of Form II) will remain. After that, all samples were quenched to different $T_{c,2}$ temperatures for 120 min and finally heated to 200 ºC, also at 10 ºC/min.

According to Lotz et al.[32], three different SN temperature *Domains* can be defined: (1) *Domain I or complete melting domain* occurs when the applied T_s temperatures are high enough to melt all crystals and erase crystalline memory, so that isotropic melts are obtained. In this T_s range, the peak crystallization temperature of the material during cooling from T_s remains constant. (2) In *Domain II*, T_s is high enough to melt all crystals in the sample or most of them, leaving self-nuclei constituted by ordered regions that remember their crystalline state or by small unmolten crystal fragments respectively (see ref. 2). The crystallization temperature of polymer greatly increases as T_s decreases in *Domain II*. (3) In *Domain III*, T_s values are too low and produce partial melting. Unmolten polymer crystals anneal during the 5 min at T_s and a second melting peak is normally observed in the subsequent heating curves after SN.
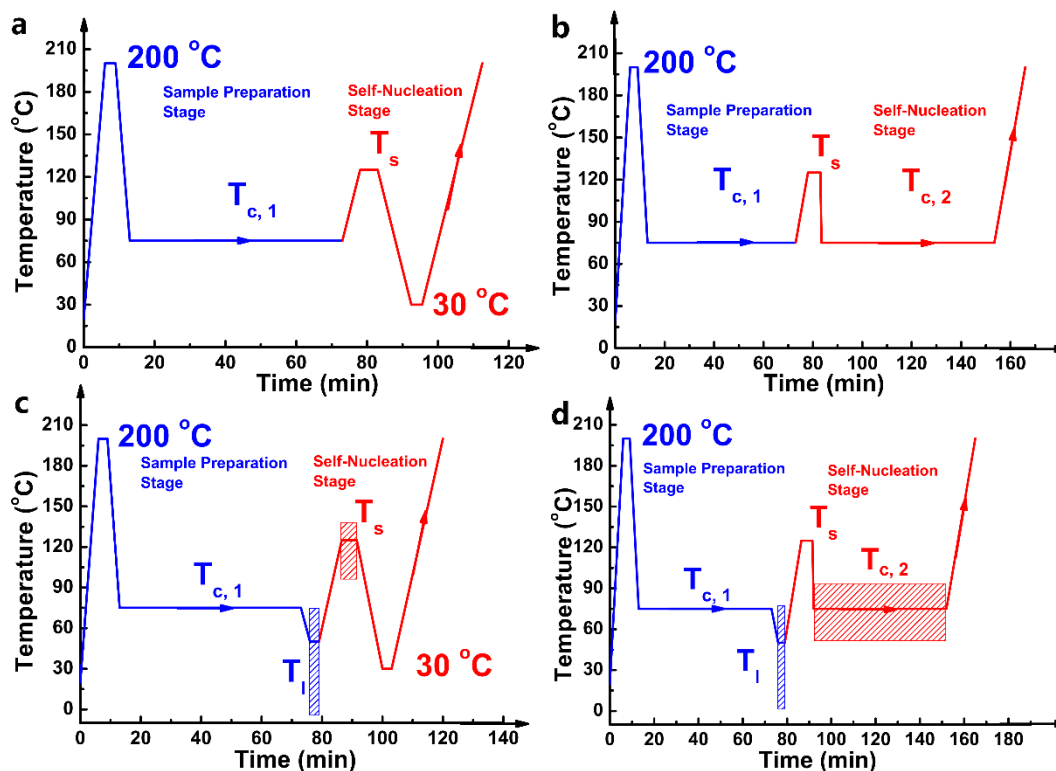
Figure 1. *The non-isothermal (a, c) and isothermal (b, d) SN experimental protocols designed and implemented in this work (see text). Samples with different polymorphic contents are prepared without annealing (a, b) or with an annealing step at low temperatures (c, d).*

Polarized Light Optical Microscopy (PLOM).

The morphology of the self-nucleation and cross-nucleation behavior were observed *in situ* by an Olympus BX51 polarized optical microscopy equipped with a Canon 40D camera system. The thermal treatment was carried out by a calibrated Linkam 600 hot stage. Before the observation, the pellets of PB-1 and PB1-*ran*-PE samples were hot pressed into films with thickness of approximately 80 μm and sandwiched in between two glass slides. Thermal treatments were consistent with the DSC SN protocols.

Wide Angle X-ray Diffraction (WAXD).

The crystal structure of the samples was characterized by wide angle X-ray diffraction (WAXD), using a Xeuss 2.0 system of Xenocs (France) with a Cu Kα source (wavelength =1.54 Å). The sample to detector distance is 140.2 mm. Scattering patterns were collected by a semiconductor detector (Pilatus, 300K DECTRIS, Swiss) with a resolution of 487×619 pixels (pixel size =172 μm^2). Temperature control was applied with a Linkam TST 350 hot stage. Each WAXD pattern was collected for 5 min and the one-dimensional intensity profiles were integrated using the standard procedure with background subtraction. The main reflections at 11.9º, 16.9º and 18.5º are assigned to (200), (220) and (213+311) planes of Form II. Peaks at 10.0º, 17.5º and 20.4º belong to (110), (130) and (220+211) crystal planes of Form I and I' respectively.[24, 28]

Fourier Transform Infrared Spectroscopy (FTIR).

In situ FTIR spectra were obtained by using a Nicolet 6700 FTIR spectrometer equipped with a Linkam FIIR600 hot stage. The films of PB-1 and PB1-*ran*-PE were first heated to 200 ºC for 5 min followed by a quenching to $T_{c,1}$ for 90 min. After that, samples were then cooled from $T_{c,1}$ to 0 ºC for 3 min and heated to 80 ºC again. Both cooling and heating rates were 3 ºC/min. During this process, FTIR spectra were obtained with a resolution of 4.0 cm^{-1} and 16 scans with 1 ºC intervals. The baseline of each spectrum was corrected according to the standard procedure.[33, 34] Two typical strong absorption bands at 923 cm^{-1} and 905 cm^{-1} are usually adopted to differentiate

Form I and Form II crystals respectively.[27, 35, 36]

Results and Discussion

The self-nucleation behavior of PB-1 homopolymer with or without annealing at low temperatures.

Figure 2 shows the non-isothermal SN (i.e., the SN protocol described in Figure 1a, see experimental) results for PB-1 at a T_s=128 ^{o}C, with or without annealing at 0 ^{o}C for 3 min.
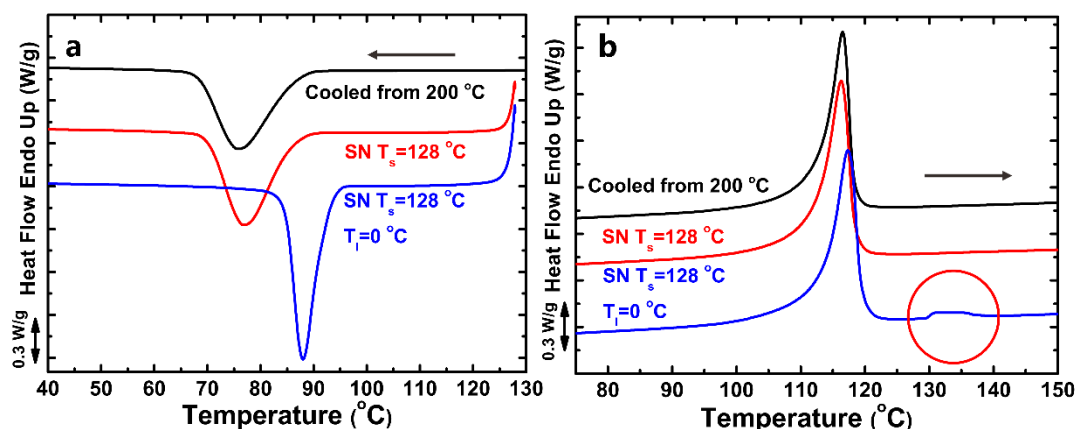

Figure 2. *DSC cooling (a) and subsequent heating (b) curves for the PB-1 samples self-nucleated at T_s temperature at 10 ^{o}C/min. Samples with different polymorphisms were compared: pure Form II crystallized at 85 ^{o}C isothermally (red); Form II with small amount of Form I crystals annealed at 0 ^{o}C for 3 min after isothermal crystallization at 85 ^{o}C (blue).*

In a standard SN protocol, the sample is cooled from T_s down to a temperature low enough to allow the full crystallization of the material. The situation in PB-1 is

complicated by its polymorphic transformations. If the sample is cooled from T_s=128 ℃ (a temperature high enough to completely melt Form II) to 30 ℃, PB-1 Form II can completely recrystallize. Hence, if the sample is kept at 30 ℃ for a short time (3 min) and then reheated, the DSC trace drawn in red in Figure 2 is obtained.

The peak crystallization temperature of the sample self-nucleated at T_s=128 ℃ (without any annealing at 0 ℃) is located at 76 ℃, which is nearly same as that of the sample directly cooled from 200 ℃. In the other words, all the crystals and crystalline memory of Form II are destroyed at this T_s value.[2]

Performing a small modification to the thermal protocol described as standard SN for PB-1 Form II, the sample is cooled to 0℃ and kept at that temperature for 3 min, a very short time, considering that Form II can only completely transformed to Form I after days at room temperature. However, the peak crystallization temperature of the sample, annealed at 0 ℃ for 3 min after SN at T_s=128 ℃, increased to 88 ℃ (from 76 °C), and the crystallization exotherm becomes narrower. This increase in T_c must correspond to a nucleating effect on Form II crystals.

Figure 2b shows that besides the expected melting peak of Form II at 117 ℃, a very small endothermic peak within the 130 ℃ to 136 ℃ range, that corresponds to Form I, can also be appreciated in the heating scan of the sample annealed at 0 ℃. These transformed crystals are then responsible for the nucleation effect caused on the crystallization of PB-1 as Form II crystals during cooling from T_s. Figure S1 shows that both FTIR and WAXD could not detect any Form I crystals during the cooling process. However, when the sample was heated to 80 ℃ again, a slight enhancement of the 923

cm[-1] band was clearly observed, especially in the second derivative spectra (Figure 3).

These results indicate that the small amount of Form I crystals observed by DSC are

actually formed during the heating process, where the growth of Form I crystals within

form II phase is faster.[21] According to Tammann's two-stage nucleation theory and the

classical nucleation and growth theory proposed by Men et al.[21], annealing at low

temperatures can cause an unbalanced shrinkage of amorphous and crystalline phases

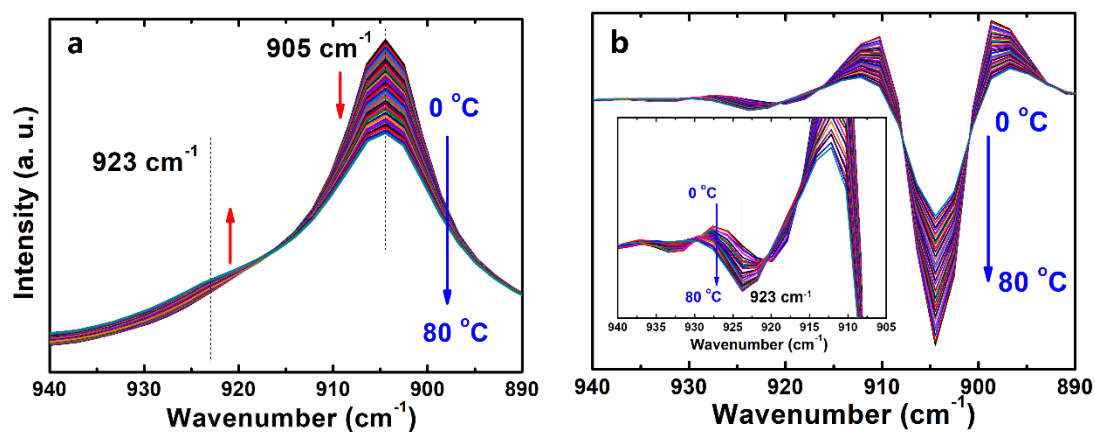which may accelerate the formation of Form I crystals.

Figure 3. Temperature-resolved FTIR spectra (a) and the corresponding second derivative spectra (b) of PB-1 sample during the heating process. The sample was isothermally crystallized from the melt at 85 °C, then it was cooled to 0 °C for 3 min, and finally heated to 80 °C at 3 °C/min while FTIR spectra were recorded.

Similar results were also obtained by PLOM (Figure S2). The morphology of PB-1 spherulites did not change after annealing at 0 °C, as compared to that obtained when crystallizing at 85 °C (Figure S2 a and b). However, when the PB-1 film was heated to 128 °C, all Form II crystals melted but a weakly birefringent template remained at

temperatures above the melting point of Form II crystals. By comparing the PLOM results to the results of DSC measurements (Figure 2), it can be deduced that this template must belong to the small fraction of Form I crystals obtained during the heating process. After that, the sample was quenched to 85 ℃ and PB-1 was able to crystallize very fast, within a few minutes, because of the high nucleation density produced by the Form I crystals that survived. In this situation, only Form II is nucleated by the Form I template, i.e., a cross-nucleation effect.[23]

The effect of annealing at low temperatures: the formation of Form I latent nuclei.

The Form II to Form I transformation mechanism of PB-1 crystals has been investigated for several decades since the introduction of PB-1.[12, 14, 20] According to the literature, the transformation rate at room temperature is faster than at lower or higher temperatures. Precooling at temperatures below 0 ℃ has also been used to accelerate the transformation process. Both FTIR and WAXD were used to attempt the detection of structural changes of Form II during the cooling process (Figure S1a, S1c and S1e). However, no signals corresponding to Form I could be detected, indicating that these techniques are not sensitive to the presence of Form I nuclei, due to their low volume fraction under the applied conditions.

Self-nucleation can be an effective way to detect the presence of active nuclei, even if they are present in small quantities.[2] The results of the non-isothermal SN tests with annealing at different low temperatures (using the protocol outlined in Figure 1c, see experimental) are shown in Figure 4.

According to the applied sample preparation stage protocol (see experimental), the PB-1 sample is first molten at 200 ℃, then isothermally crystallized at 85 ℃ into Form II. Next, the sample is cooled down to a temperature denoted T_l (see Figure 1a), where it is annealed at low temperatures for just 3 minutes, before it is self-nucleated employing a constant T_s=128 ℃. If T_l is higher or equal to 60 ℃, the behavior of the sample is the same to that of a sample cooled from 200 ℃ directly. Therefore, such relatively high T_l temperatures (60 ℃ and higher) do not influence the sample crystal structure, which remains as Form II exclusively.
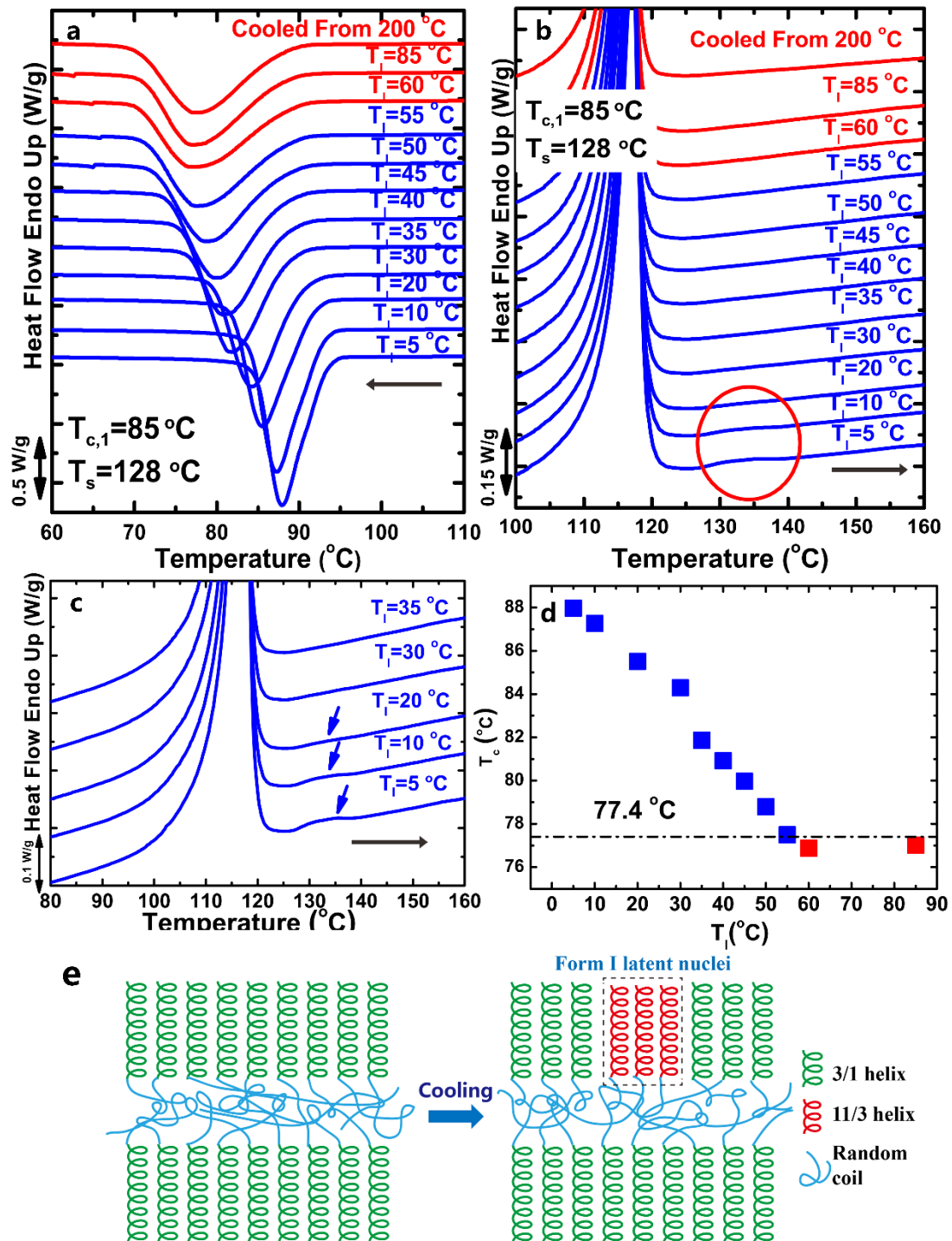
Figure 4. *The effect of annealing at low temperatures on the self-nucleation of PB-1. (a) DSC*

cooling scans from a SN temperature of 128 °C; (b, c) subsequent heating scans. Red and blue

curves demarcate the Region I and Region II, respectively. The DSC curve corresponding to the

crystallization from an isotropic melt (i.e., cooled from 200°C, a temperature at which thermal

When annealing temperatures (i.e., T_l temperature values) lower than 60 °C are employed, the peak crystallization temperature (T_c), after SN at T_s=128 °C, increases with respect to the standard behavior of PB-1 upon cooling from 200 °C, as shown in Figure 4a. As the T_c value is proportional to the nucleation density, this result indicates that the low temperature annealing is producing a nucleation effect. The subsequent heating scans, recorded immediately after the cooling traces shown in Figure 4a, are presented in Figure 4b. When the T_l temperature approaches 20 °C, a small melting peak located between 130 °C and 140 °C can be observed. This additional melting peak at higher temperatures is due to the melting of a small fraction of Form I crystals.

The behavior of the sample after low temperature annealing followed by SN presented in Figure 4a and 4b can be interpreted as follows. When T_l values lower than 60 °C but higher than 20 °C are employed, some Form I nuclei are produced during the 3 min at T_l within the existing Form II crystals. However, their presence can only be detected by the subsequent nucleation effects (the increase in T_c values reported in Figure 4a). In this case, these nuclei are termed "latent nuclei".[37-39] Nevertheless, when T_l is 20 °C or lower, Form I nuclei are able to grow into crystals during the heating process, and they can be detected by their melting endotherm (at 130-140 °C) in Figure 4b. The T_c-T_l relationship is summarized in Figure 4d. According to the T_c value of the

self-nucleated sample, two temperature *Regions* can be defined: *Region I* (above 55 $^{\circ}$C), where only Form II exists in the sample without any Form I nuclei and *Region II* (below 55 $^{\circ}$C), where latent Form I nuclei are generated, thereby nucleating the formation of Form II crystals.

These results confirm earlier work by Men et al.,[21] indicating that the nucleation of Form II by Form I nuclei (and/or crystals) strongly depends on annealing the sample at low temperatures. A simplified scheme is shown in Figure 4e. The loose 11/3 helices in Form II may be transformed to compact 3/1 helices during annealing at low temperatures for a short time, then the packing mode of the polymer chain can change and provide nuclei for the following melt-crystallization of Form II, as shown for fully-transformed Form I samples self-nucleated at relatively high temperatures.[23, 24]

According to the above discussion, even a small amount of Form I crystals (or nuclei) generated at low temperatures can have a large effect on the self-nucleation of PB-1. Therefore, it is necessary to investigate the effect of different T_s values for PB-1 Form II with or without Form I nuclei (Figure 5).

The three standard SN *Domains* can be observed for pure Form II if the sample is crystallized at 85 $^{\circ}$C without low temperature annealing (following the SN protocol described in Figure 1a). When the T_s value reaches 122 $^{\circ}$C, all the ordered structures are destroyed and the melt reaches an isotropic state (*Domain I*). The range of *Domain II* (117~122 $^{\circ}$C) is relatively narrow (see Figure 5e), like in other non-polar homopolymers, such as polyethylene[7] or polypropylene.[32]

In the case that PB-1 samples are annealed at low temperatures to induce the

formation of Form I crystals (annealing at 0 °C for 3 min, using the SN protocol presented in Figure 1c), the situation is more complex. Above 136 °C, all crystals are molten (both Form II and Form I) and the melt becomes isotropic (*Domain I* in Figure 5f).

As the PB-1 samples annealed at low temperature contain both Form I and Form II crystals, the SN Domains can be defined for each polymorph (as their melting points are different). When the T_s value is below 136 °C, PB-1 Form II is nucleated by unmolten Form I crystals by cross-nucleation, see how the T_c values increase in Figure 4b with respect to samples in *Domain I*. Therefore, in the range between T_s temperatures of 136 and 128 °C, a *Domain II (Form II)* can be defined for the cross-nucleation of Form II by Form I crystals. However, in the same temperature range, the 5 min holding time at T_s during SN, also produces annealing of the Form I crystals present in the sample. The annealing that occurs in that temperature range is highlighted with a circle and with a close up with arrows in Figure 5d. Therefore, in the same temperature range of 136 to 128 °C, a *Domain III (Form I)* co-exists with *Domain II (Form II)*, as indicated in Figure 5f.
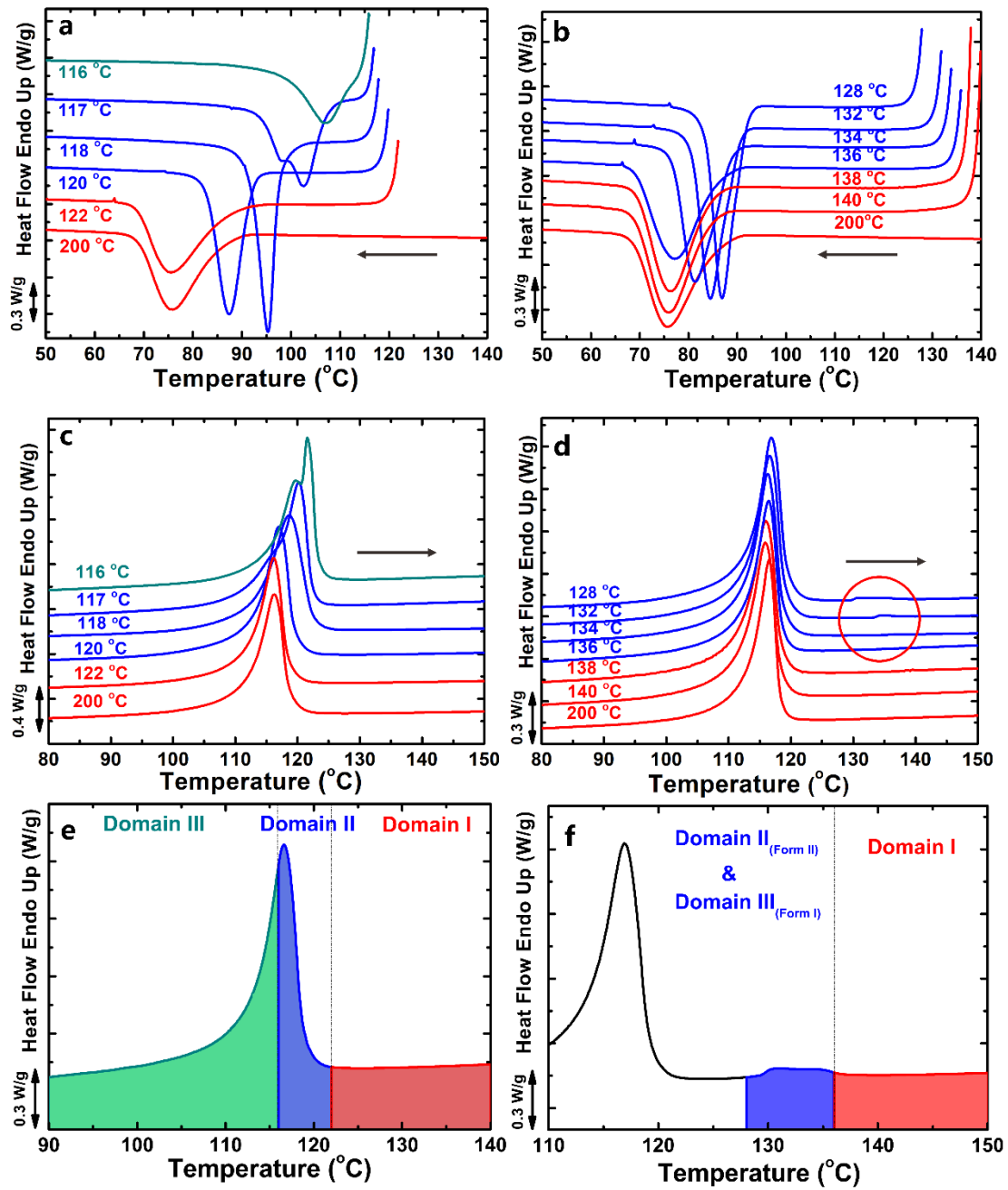
Figure 5. *Self-nucleation behavior of PB-1 containing only Form II (a, c, e) or Form II mixed with a small amount of Form I crystals (or nuclei) (b, d, f). (a, b) DSC cooling scans from different T_s temperatures; subsequent heating process (c, d); (e, f) representations of the SN domains for PB-1 samples with different polymorphic structures.*

Self-nucleation of butene-1/ethylene statistic copolymer: the formation of Form I′

crystals.

Figure 6 shows the self-nucleation behavior results (after application of the SN protocols shown in Figure 1b and d) of PB1-*ran*-PE samples with different thermal histories. For the sample crystallized at 75 ^{o}C without annealing at 0 ^{o}C, all the crystals have completely disappeared at 118 ^{o}C (see the optical micrograph in Figure 6b), which means that the sample contains only Form II crystals. In this situation the DSC heating trace shows a single melting peak at 102 ℃, corresponding to the melting point of Form II crystals (Figure 6a).

Different results are obtained if the PB1-*ran*-PE copolymer is annealed at 0 ^{o}C for 3 min before self-nucleation. A small melting peak corresponding to Form I appears in the DSC heating scan at 120 ^{o}C (Figure 6a, labeled with an arrow). Additionally, when the sample with an identical thermal protocol is observed by PLOM at 118 ℃, a template of Form I crystals can be observed (Figure 6b and S3). Similar to the homopolymer case, the formation of Form I crystals can be attributed to their nucleation at 0 ^{o}C, and their growth during the subsequent heating process, facts that were verified by FTIR results (Figure S1 and Figure S3). The above observations by DSC and PLOM regarding the production of a small fraction of Form I crystals parallel the results obtained in PB-1 homopolymer.

However, a difference with respect to PB-1 homopolymer can be observed in Figure 6a, as a large amount of PB-1 Form I′ crystals and a small quantity of Form II crystals are produced upon re-crystallization at 75 °C (applying the protocol described

in Figure 1d).

The morphology was also observed by PLOM (Figure 6b bottom right). During the isothermal crystallization process at 75 $^{\circ}$C, the birefringence of the Form I template was largely enhanced because of the generation of Form I′ caused by homo-polymorphic self-nucleation. Additionally, some bright spots (signaled with arrows) that belong to Form II were generated by the cross-nucleation effect. These results indicate that Form I′ can be induced when there are residual Form I crystals in PB1-*ran*-PE.
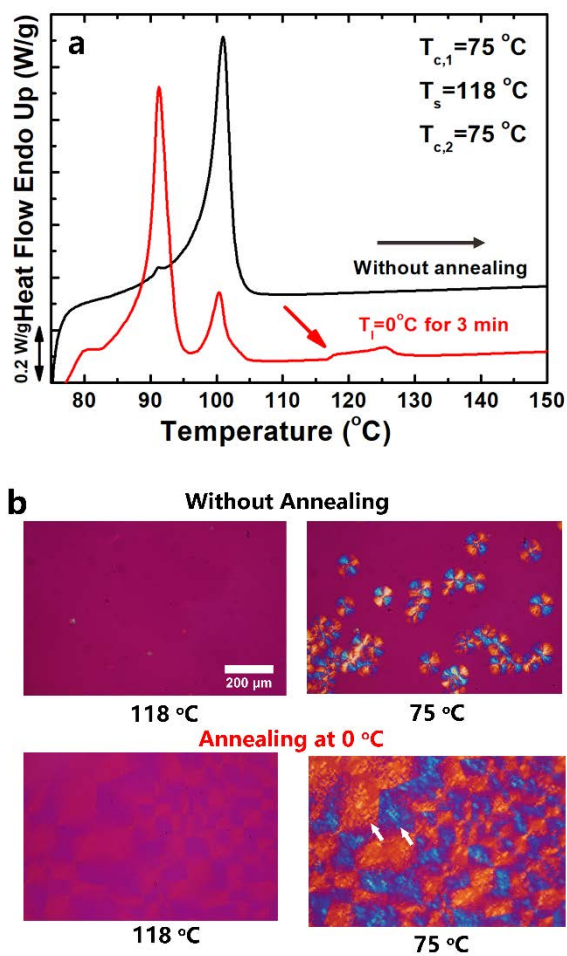

Figure 6. The self-nucleation behavior of PB1-ran-PE sample with or without annealing at 0

^{o}C. The T_s value is 118 ^{o}C. All the samples were first crystallized at 75 ^{o}C after erasing their thermal history. (a) DSC heating scans for the self-nucleated sample at 10 ^{o}C/min; (b) corresponding PLOM micrographs for the samples self-nucleated at 118 ^{o}C (left) and crystallized at 75 ^{o}C isothermally (right).

Comparing to PB-1 homopolymer Form I self-nucleation results by Cavallo et al.[26], it seems that the inclusion of ethylene comonomer enhances the nucleation of Form I′ crystals. According to previous studies,[15] two requirements are needed for the formation of Form I′ crystals in PB-1 homopolymer: a hindrance to the nucleation of the faster-growing Form II polymorph and the presence of an interface to selectively nucleate Form I′ crystals. In PB1-*ran*-PE copolymer, a small amount of Form I crystals can efficiently induce the formation of Form I′ crystals, at the expense of Form II crystals which compete for the crystallization of the amorphous fraction. Therefore, it must be deduced that either the growth rate of the two polymorphs is comparable in the copolymer sample, or that the efficiency and selectivity of Form I crystals towards Form I′ nucleation overwhelm Form II heterogeneous nucleation.
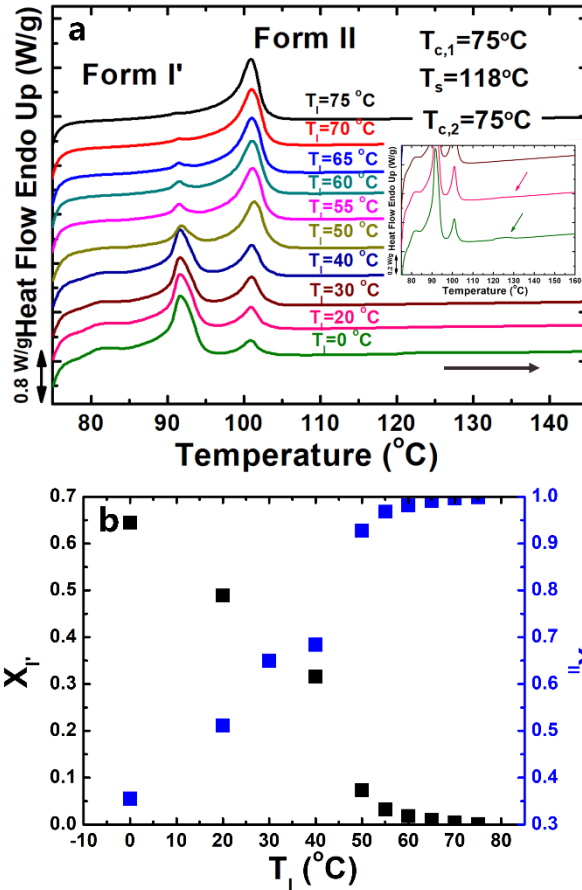
Figure 7. The effect of low annealing temperatures on the self-nucleation of PB1-ran-PE. The SN temperature is 118 °C. All the samples were first crystallized at 75 °C after erasing their thermal history (according to the SN protocol presented in Figure 1d). (a) DSC heating scan of the self-nucleated sample after crystallizing at 75 °C; (b) summary of the content of Form I' and Form II crystals according to DSC results.

In analogy with previous results for the homopolymer sample, the production of Form I latent nuclei by low temperature annealing could not be evidenced by FTIR or WAXD in the copolymer (Figure S1b, S1d and S1f). Therefore, we turned once more to self-nucleation in order to detect the production of Form I' nuclei and crystals.

Instead of the non-isothermal SN procedure used in the homopolymer, a different SN protocol was applied for PB1-*ran*-PE, as described in the experimental section, Figure 1d, due to the strong melt memory effect in the copolymer. The sample was first isothermally crystallized at 75 °C, after erasing its thermal history by heating to 200 °C. Then the sample was cooled to T_l for 3 minutes, to perform the low temperature annealing process. After that, the sample was subjected to a modified SN process: first it was self-nucleated at T_s=118 °C for 5 minutes and then cooled to $T_{c,2}$=75 °C for 70 min to isothermally crystallize. The formation of Form I′ crystals during this isothermal crystallization process can be used to detect the nucleation of Form I within Form II crystals during the low temperature annealing process.

As shown in Figure 7a, even the sample crystalized at 75 °C without annealing displays a minor melting peak at 93 °C in the final heating trace. These results show that some amount of Form I′ can be induced after SN process. Under the assumptions outlined above, i.e., that Form I′ is nucleated in the presence of Form I crystals as a substrate, these results can be interpreted as a consequence of the presence of a small amount of Form I crystals, transformed directly from Form II during the first isothermal crystallization process at 75 °C (i.e., the preparation stage indicated in the protocol outlined in Figure 1d).

When the annealing temperature decreases from 70 °C to 0 °C, a higher content of Form I′ can be induced in the copolymer, while a concomitant reduction of Form II can be observed (Figure 7b). This behavior is indicative of an increased formation of Form I nuclei at lower annealing temperatures, which provides Form I′-selective nucleation

sites during the subsequent re-crystallization. When the annealing temperature is below 20 °C, a small endothermic peak at 125 °C can be observed in the final heating scan, corresponding to the melting of Form I crystals.

Besides the documented Form I′ crystallization induced by suitable substrates, like Form I for PB-1 or iPP α-form,[15, 19, 27] Androsch et al. [17-19] reported the direct generation of Form I′ at large undercoolings in a butene-1/propylene copolymer with 11.4 mol% comonomer. We note that a large amount of Form I was also obtained in this situation because of the simultaneous and fast Form II-Form I solid state transition in that condition. Therefore, it is plausible that the direct melt-crystallization of Form I′ was induced by the earlier presence of Form I crystals by solid state transformation. Using a butene-1/ethylene copolymer, with high content of ethylene comonomer (9.8 %), Men et al.[28, 29, 40] found that the Form I′ crystals can be formed by melt memory effect which is independently from the original crystalline structure present before the melting stage. It was proposed that crystallizable and non-crystallizable chain sequences segregated during the crystallization process, constitute heterogeneities, with sizes that depend on melt temperature,, in which   Form I′ could nucleate. Although our results cannot exclude this mechanism, we note that the extent of segregation should be lower in our case, due to the lower content of ethylene comonomer (4.8 %). On the other hand, it clearly appears that Form I′ can only be obtained in our system, when some Form I crystals (or latent nuclei) are still present in the melt. In conclusion, the mechanism of Form I′ formation in the absence of selective nucleating substrates still needs investigation, and can depend on the comonomer content.

The competition between self-nucleation and cross-nucleation in PB1-ran-PE.

Recently, it has been found that a given form of a polymer crystal can induce the nucleation of a different polymorph. This phenomenon is called cross-nucleation and has been reported in several semi-crystalline polymers, like polybutene-1,[23, 24] polypropylene [41] and polypivalolactone,[42] amongst others.
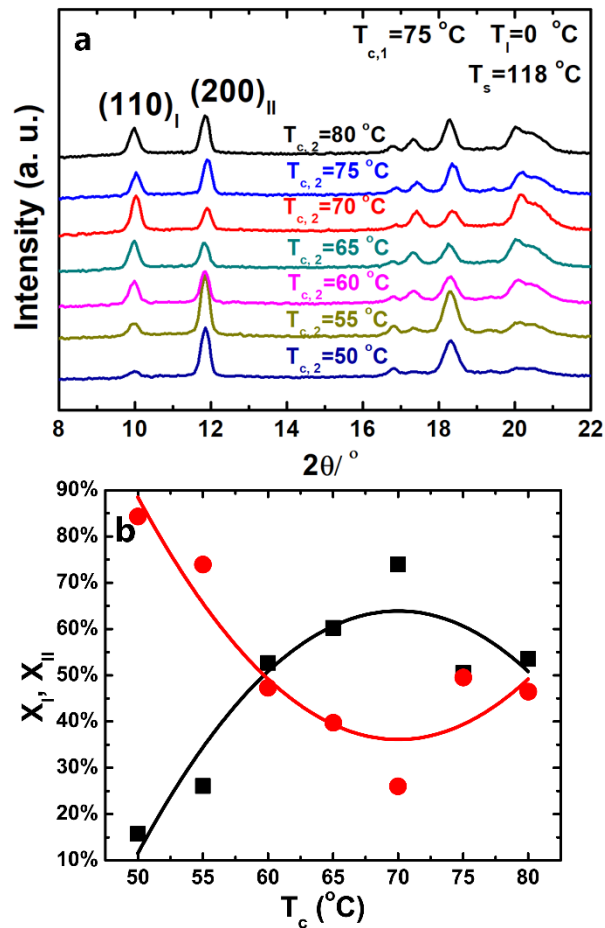

Figure 8. The competition between the cross-nucleation and self-nucleation behavior in PB1-ran-PE. (a) The WAXD patterns of the self-nucleated sample crystallize at different temperatures. The $T_{c,1}$, T_s and T_l values are 75, 118 and 0 °C, respectively (see the protocol in

Figure 1d); (b) the fraction of Form I and Form II calculated by WAXD data.

Figure 8a shows WAXD data for the PB1-*ran*-PE sample after isothermal crystallization process at different temperatures (See experimental part, Figure 1d). All samples were first crystallized at 75 °C and then annealed at 0 °C and self-nucleated at 118 °C respectively. The contents of Form I′ and Form II were estimated by the following equation [43]:

$$X_{I'} = \frac{I(110)_{I'}}{I(110)_{I'} + RI(200)_{II}}$$

where $I(110)_{I'}$ and $I(200)_{II}$ are intensities of the $(110)_{I'}$ and $(200)_{II}$ reflections, respectively. The parameter R in the equation is taken as ~~0.36~~0.67[44, 45], and it is used for correcting the different diffraction power of those crystallographic planes in trigonal and tetragonal crystal structures in Form I′ and Form II. The trend of the polymorphic composition will likely depend on the competition between the nucleation and growth of each polymorph, which is strongly related to the crystallization temperature. In particular, the high growth rate of Form II at high temperatures and the low nucleation density of Form I′ at low temperatures may determine the preference of the two crystal forms. In the intermediate crystallization temperature region (around 70 °C), the maximum in Form I′ content (and relative minimum of Form II) is possibly attributed to the enhanced Form I′ formation by self-nucleation on Form I seeds.

Conclusions

We have investigated the initial stage of the Form II to Form I transition of PB-1 and its PB1-*ran*-PE copolymer, using specially designed SN procedures. Different from other semi-crystalline polyolefins, the melt crystallized Form II can show an enhanced self-nucleation behavior when annealed at low temperatures (T_l) for a short time, before partial melting.

For PB-1, the change in the re-crystallization behavior can be observed when the T_l value is lower than 60 ºC, indicating the formation of "latent" Form I nuclei. If the T_l temperature is lowered than 20 ºC, a clear melting peak of Form I is observed, due to the growth of a small amount of Form I crystals during the subsequent heating process, as verified by temperature-resolved FTIR spectra.

In the copolymer case, Form II and Form I′ can be nucleated due to the cross-nucleation and self-nucleation phenomenon, respectively. The formation of Form I′ can be enhanced when more Form I nuclei are present in the system, i.e., by annealing as decreasing T_l. Furthermore, the crystallization temperature is also found to play an important role in the competition of the formation of Form II and Form I′, i. e., Form I′ is favored by nucleation and growth at around 70 ºC.

AUTHOR INFORMATION

Corresponding Authors

*E-mail: alejandrojesus.muller@ehu.eus, djwang@iccas.ac.cn.

Notes

The authors declare no competing financial interest.

Supporting Information

Figure S1-S3: FT-IR and WAXD spectra of PB-1 and PB1-*ran*-PE samples during the cooling process, PLOM micrographs of PB-1 samples during the self-nucleating process, FT-IR spectra and the corresponding spectra of PB1-*ran*-PE during the heating process.

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