

Mechanism of Polymorph Selection during Crystallization of Random Butene-1/Ethylene Copolymer*

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Abstract Starting from an initial sample of butene-1/ethylene copolymer with stable form I', we examined the nucleation of different crystalline polymorphs (here metastable form II and stable form I') at different isothermal crystallization temperatures after being melted at different melt temperature (T_{melt}). When T_{melt} was just above the melting temperature (T_{m}) of the crystallites, self-seeding took place. There, residue crystallites served as nuclei leading to the crystallization of the same crystalline phase. When T_{melt} was a few degrees above the T_{m} , self-seeding was disabled due to complete melting of the initial crystals. Upon crystallization, the selection of the different polymorphs in this random copolymer was found to depend on an interplay between the domain size of segregated long crystallizable sequences and the size and energy barrier of the critical nucleus of the respective crystalline forms. Our results provide a clear understanding of the polymorphs selection during crystallization of a random copolymer as well as homo-polymers under confinement.

Keywords: Crystallization; Random copolymer; Polybutene-1; Polymorphism.

INTRODUCTION

In the molten state, long chain semicrystalline polymers, widely used in many fields of application, consist of a random coil structure of interpenetrating molecules. Such entangled polymer melts generally crystallize into a semicrystalline state with layer-like lamellar crystallites stacking together with entangled amorphous chain segments in between^[1]. The lamellar crystals usually have a thickness of a few up to tens of nanometers and a lateral size of some micrometers, while the amorphous region is assumed to consist of highly entangled polymer chains^[2]. The morphology of such crystalline structures is complex and directly affects the final properties of polymer materials. Accordingly, the process of crystallization of semicrystalline polymers has been investigated for many decades^[1–6]. However, despite of these intense efforts, polymer crystallization is still one of the major unresolved problems of polymer science. In particular, the resulting morphology and properties of polymer crystals depend upon previous thermal history and often exhibit a memory of previously undergone crystallization processes. When polymer crystals are melted at temperatures just above the nominal melting temperature, but below the equilibrium melting temperature, the molten state of the random copolymer may contain domains consisting of segments having sequence-lengths larger than some value. This segregation of long sequences can result in higher crystallization rates, smaller spherulites, or even in polymorphic modifications^[7–12]. Especially this last phenomenon was attributed to a reduction in free energy change of nucleation due to entropic considerations^[10].

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The process of (re)crystallization may be further complicated when various polymorphs can be nucleated. Polymorphism, *i.e.* the ability of a substance to crystallize into different crystal structures, is a ubiquitous phenomenon in semicrystalline polymers^[13]. Polymorphism in polymer crystals may result from different packing modes of macromolecular chains possessing identical regular conformation, or from the possible existence of several low-energy conformations for a given polymer^[14]. Since polymorphs have different physical properties, it is crucial with respect to many applications to control which polymorphic phase forms during crystallization. Polybutene-1 (PB-1) is a typical polymorphic semicrystalline polymer. Upon solidification from the molten state, PB-1 usually crystallizes into metastable form II characterized by loosely tetragonally packed chain segments having a 11_3 helical conformation. Crystallites in form II normally transform into stable form I having densely hexagonally packed chain segments of 3_1 helical conformation *via* a solid-solid transition at room temperature. A direct formation of stable form I crystalline structure has been also reported in ultrathin film and copolymers^[12, 15]. In this case, the resulting crystallites have been termed as form I' although it has exactly the same crystallographic structure as form I. Recently, we observed that the formation of polymorphic crystalline phase in the butene-1/ethylene copolymer was influenced by status of the molten state, independent of the polymorph of the original crystalline phase, which was molten^[12]. In general, at high enough temperatures, a melt of a random copolymer is homogeneous and consists of a random distribution of crystallizable sequences of various lengths. Crystallization from such a molten state of a butene-1/ethylene copolymer favored the formation of crystallites of the metastable form II. However, just above the equilibrium melting temperature, a heterogeneous melt state may exist (at least for some time) which may favor nucleation of stable form I' crystallites. Thus, the volume fraction of form I' and II crystallites can be controlled by changing the amount of heterogeneities in the length-distribution of crystallizable sequences in an otherwise homogeneous melt^[12]. However, the underlying mechanism for such a polymorphic crystallization is still under debate, since selection of the individual polymorphs results from a complex phenomenon of interplay between thermodynamics and kinetics^[16, 17].

In this study, we thus explored and clarified this phenomenon in random copolymers by establishing a map of the form II and I' crystallites of a butene-1/ethylene copolymer as a function of melt temperature T_{melt} and crystallization temperature T_c . Our results indicated that the inhomogeneous distribution in length of crystallizable sequences induced by previous crystallization of the random copolymer was preserved, even when the crystals were melted. The domain size became smaller with increasing T_{melt} . Form I' or II crystals were nucleated and formed in a competitive process, which depended on the respective nucleation barrier potential and the critical size of the respective nucleus. When the size of a domain consisting of long crystallizable sequences was larger than the critical size of the nucleus of any of the crystalline phases, then the crystalline phase with lower barrier potential of nucleation was favored.

EXPERIMENTAL

In our study, we used a random butene-1/ethylene copolymer, consisting of random sequences of butene-1 and ethylene (9.88 mol%) co-units. For simplicity, the material is termed as PBcoE10 in the following discussion. The polymer PBcoE10 was kindly provided by BASSELL Polyolefins, had a weight-averaged molecular weight (M_w) of 153 kg/mol and a dispersity (D) of 2.2. Butene-1/ethylene copolymer is a typical polymorphic polymer. At certain processing conditions, it can crystallize from the melt either into crystals of form I' or of II. Based on our previous study^[12], we used pure form I' crystals as a starting material, which were isothermally crystallized at a constant temperature. Mostly, we used a melt temperature of 130 °C followed by an isothermal crystallization of the system at 50 °C or 68 °C which yields a complete formation of form I' crystalline structure in the sample. The samples were then melted at different temperatures above the melting temperature, up to a temperature of the melt (T_{melt}) of 180 °C, followed by crystallization at various constant temperatures.

To follow the evolution of the crystalline structures during the corresponding thermal protocols, wide-angle X-ray scattering (WAXS) measurements were carried out in a modified Xeuss system of Xenocs France with the

aid of a semiconductor detector (Pilatus100K, DECTRIS, Swiss) attached to a multilayer focused Cu $K\alpha$ X-ray source (GeniX^{3D} Cu ULD, Xenocs SA, France), generated at 50 kV and 0.6 mA. A piece of PBcoE10 sample was tightly wrapped with a thin aluminum foil in order to promote thermal conductivity, and the temperature was controlled by a portable heating device (TST350, Linkam, UK) installed at the setup. The wavelength of the X-ray radiation was 0.154 nm. The sample-to-detector distance was 178 mm, and the effective range of the scattering angle 2θ was 5° – 25° . Each WAXD pattern was collected within 10 min, background corrected and normalized using the standard procedure.

RESULTS AND DISCUSSION

Figure 1 shows the selected WAXS curves and the relative content of form II in PBcoE10 after the sample, which initially contained only form I' crystals, achieved by previous isothermal crystallization at 50°C , was melted at elevated temperatures T_{melt} , followed by recrystallization at a constant temperature T_c . These initial form I' crystals had an ultimate melting temperature around 95°C ^[12]. Interestingly, the ratio of the volume fraction of form II and I' crystals showed a complex dependence on T_{melt} and T_c . In particular at $T_c = 50^\circ\text{C}$, the evolution of the WAXS curves and the relative content of form II crystals were rather peculiar. Pure form I' crystals were re-generated when the initial form I' crystals were melted at $T_{\text{melt}} = 95^\circ\text{C}$. With increasing T_{melt} , the amount of form II crystals increased sharply, reaching a maximum at about $T_{\text{melt}} = 100^\circ\text{C}$, followed by a reduction and its disappearance at about 108°C . Only form I' crystals existed when the copolymer was crystallized from a melt, which had been at T_{melt} between 108 and 125°C . Then, the amount of form II crystals increased and that of form I' crystals decreased gradually. Form I' can be hardly generated from a melt at $T_{\text{melt}} = 180^\circ\text{C}$. Furthermore, the content of form II crystals increased with decreasing T_c , independent of T_{melt} , reflecting that a lower T_c favored the generation of form II crystals. These results indicate that the formation of a given polymorphic phase strongly depended on the melt temperature T_{melt} and crystallization temperature T_c .

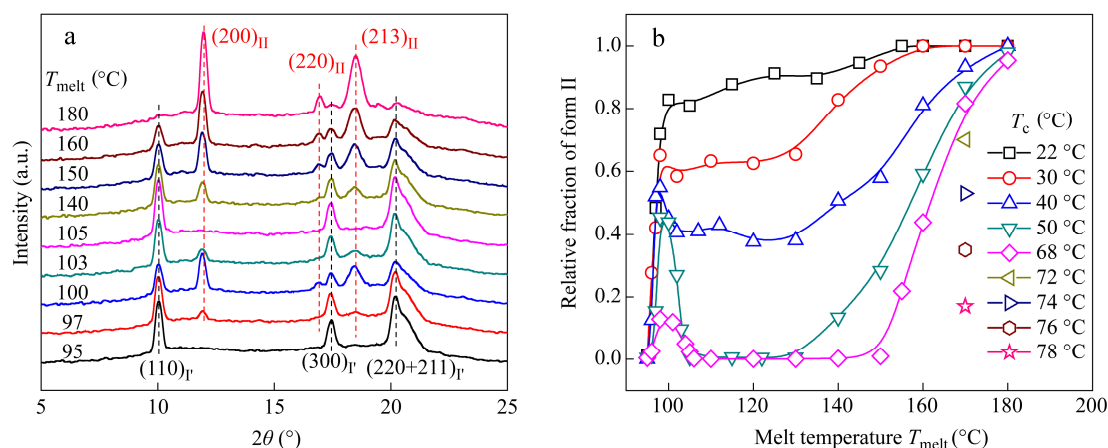


Fig. 1 Selected WAXS curves (a) and the relative amount of form II crystals (b) for the starting samples with form I' crystals after melting for 10 min at T_{melt} and then recrystallization at T_c . In these WAXS curves, the peaks at 11.8° , 16.9° and 18.4° correspond to the crystallographic lattice planes of (200), (220), and (213) of form II crystals, while the peaks at 9.9° , 17.3° and 20.5° correspond to the crystallographic lattice planes of (110), (300), and (220 + 211) of form I' crystals. The relative fraction of form II crystal is given by the ratio of the amount of form II crystals with respect to the total crystallinity of the sample.

Based on our results, a temperature map of relative content of form II to form I' crystals in PBcoE10 was established as a function of T_c and T_{melt} , shown in Fig. 2. Here, the initial conditions were determined by crystallization at 50°C , generating exclusively crystals of form I'. When this sample was brought to T_{melt} only slightly above the nominal melting temperature of 95°C and re-crystallized at lower temperatures, form I' crystals were re-generated due to self-seeding^[18], indicating that the melt around T_m contained residual form I'

crystals serving as nuclei which led to re-formation of the original crystals. When T_{melt} was increased to 100 °C, form II crystals were generated at low T_c while form I' appeared at high T_c . This indicates that the melt lost the helix conformation but kept some memory resulting from the separation of crystallizable sequences according to their length^[9, 10], leading to the formation of domains of certain sizes. De Rosa has observed that for form I' crystals the minimum lamellar thickness required for growth was lower than that for form II crystals^[19]. In addition, it is reasonable to assume that the nucleation probability of both polymorphic crystalline phases depends on the domain size of segregated long crystallizable sequences. At low T_c , the size of the critical nucleus of form II crystals was smaller than the size of such domains, and thus generation of form II crystals was favored. At high T_c , the average size of such domains was larger than the size of the critical nucleus of form I' crystals, but smaller than that of form II crystals. Consequently, form I' crystals were nucleated. In between these limiting cases, a mixture of form II and I' crystals was generated as the size distribution of the domains of segregated long crystallizable sequences allowed nucleation of both polymorphs. With increasing T_{melt} , the average size of domains of segregated long crystallizable sequences became gradually smaller as a result of polymer chain diffusion leading to a homogenization of the melt which kinetically favored the formation of form II crystals. However, at high T_c , only form I' can be generated from the homogeneous melt because the existence of ethylene co-units did not allow establishing form II crystals of the thermodynamically required lamellar thickness. Thus, at high T_c , nucleation of form II crystals was hindered because the required size and thickness of the critical nucleus exceeded the length of crystallizable polybutene-1 sequences in the copolymer. In this case, due to a smaller size of the critical nucleus, form I' crystals were formed almost exclusively. From our temperature map, we can predict the generation of form II and I' crystals for given melt and crystallization temperatures.

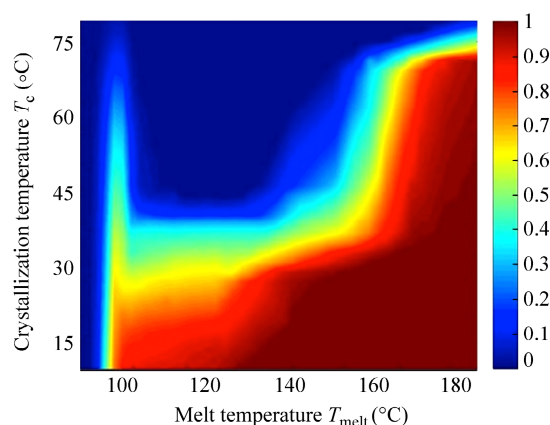


Fig. 2 Temperature map of the ratio of the amount of form II with respect to form I' crystals in PBcoE10 (indicated by the colors) as a function of crystallization temperature T_c and melt temperature T_{melt} . Red (value "1") indicates the 100% of form II crystals; Blue (value "0") reflects that only pure form I' crystals existed; all other colors (0–1) refer to mixtures of form II and I' crystals.

The peculiarities observed for polymorphic crystallization in butene-1/ethylene copolymer provided a clue for a general understanding of the nucleation mechanism of semicrystalline polymers. To achieve the thermodynamically stable size of a crystal, a primary nucleus must be formed *via* a path with a positive free energy difference ΔG ^[3]. The maximum value of ΔG corresponds to the nucleus of critical size. Nuclei smaller than the critical one are called subcritical nuclei or embryos whereas nuclei larger than the critical one are called supercritical when ΔG is still positive. Nuclei with negative ΔG are called stable nuclei or small crystals. As mentioned before, the whole crystallization process can be divided into a nucleation step and a subsequent growth process. The free enthalpy barrier for nucleation can only be overcome by local random fluctuation of the local order of crystallizable sequences. It has been observed that the critical size of form II nucleus was much

bigger than the one of form I' nucleus, while the corresponding nucleation barrier ΔG for form II crystals was much lower than the one for form I' crystals^[20]. Therefore, from a homogeneous melt of polybutene-1 homopolymers, form II crystals are preferentially generated^[15]. To present the underlying mechanism for the direct formation of different crystalline forms in the random copolymer, we present a schematic of the free energy landscapes of nucleation of form II and form I' crystals in Fig. 3. For simplicity, we consider in Fig. 3 the free energy landscapes for the two extreme cases of nucleation of form I' and II crystals in homo-polymers (curves B and D) and in copolymers (curves A and C) of polybutene-1. Clearly, for both types of material, the nucleation barrier for form I' crystals is larger than that for form II crystals. Both nucleation barriers for form I' and II for the copolymer are larger than their corresponding values for the homo-polymer. In addition, the critical size for a stable nucleus is larger for form II compared to form I' crystals. Based on above considerations, we may understand the temperature map presented in Fig. 2. Clearly, all the observed peculiar nucleation behaviors in this copolymer are the result of an interplay between the size of domains of segregated long crystallizable sequences (circled in Fig. 3a) and the size of the critical nucleus, which is not the same for the two crystalline forms. At high T_c , constraints introduced by comonomers prevent the development of a stable nucleus of form II (the length of sequences of crystallizable chain segments is too short) so that much thinner crystallites of form I' were generated, regardless if the melt was homogeneous or contained domains of segregated long crystallizable sequences. For crystallization of samples from such a heterogeneous melt state, the nucleation probability of the two crystalline forms depends thus on the ratio of the size of the critical nucleus of form II crystals to the size of domains of segregated long crystallizable sequences. When the domain size is smaller than the size of the critical nucleus of form II crystals, but larger than that of form I' crystals, form I' nuclei develop according to curve B in Fig. 3. At this condition the nucleation of form II would follow curve C that has a higher free energy barrier than B. All other cases in the temperature map present in Fig. 2 can be easily understood following analogous considerations.

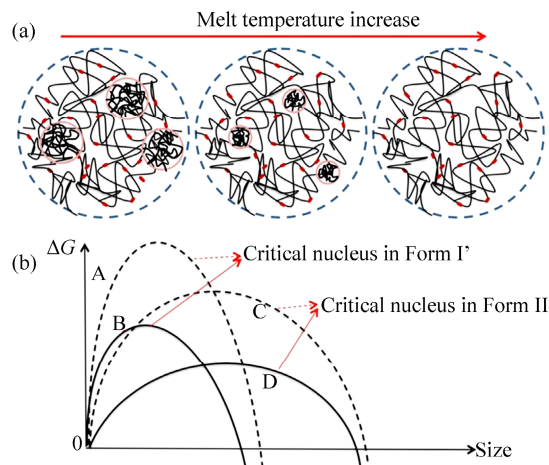


Fig. 3 (a) Schematic representation of the melt state as a function of temperature with solid circles representing domains of crystallizable chain segments segregation; (b) Change of free enthalpy ΔG as a function of size illustrating the nucleation process of Form I' and Form II in butene-1/ethylene copolymer at certain T_c . The dotted lines and solid lines represent the nucleation free energy landscapes for form I' and form II crystals in copolymers and homo-polymers, respectively.

Support of above considerations on nucleation of different crystalline forms can be found in the literature where the direct formation of form I' crystals in thin spin-coated polybutene-1 homo-polymer films was observed^[15]. In such thin films, the nucleation of form II crystallites would be strongly suppressed due to the fact that the film thickness might be much thinner than the required lamellar thickness for the formation of form II crystals. Clearly, when the formation of form II is constrained, a much thinner but normally kinetically slower

form I' would develop. To verify above considerations concerning the mechanism of polymorphic crystallization in copolymers, additional experiments were carried out. Initial samples with pure form I' crystals were prepared by isothermal crystallization at 50 and 68 °C, respectively. These crystals were then melted at T_{melt} which was increased up to 180 °C. These molten samples were then re-crystallized at 50 °C. In parallel, the evolution of the crystalline structures was followed by WAXS measurements. The corresponding results are presented in Fig. 4. These two samples consisted both initially only of form I' crystals of differing lamellar thickness. The sample initially crystallized at 68 °C is expected to consist of larger domains containing longer crystallizable sequences than the one crystallized at 50 °C. Thus, when these two samples were melted at the same temperature, the first one had a higher probability to grow form II crystallites after re-crystallization at 50 °C. Indeed, our results shown in Fig. 4 exhibit such behavior.

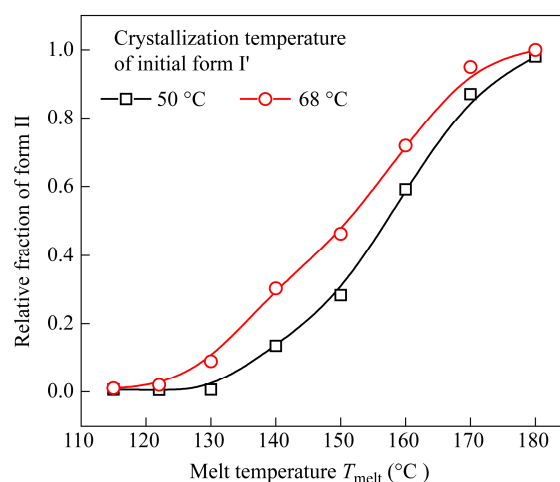


Fig. 4 Relative amount of form II crystals for samples consisting initially of form I' crystals grown at 50 and 68 °C, respectively, after melting at different temperatures and then recrystallization at 50 °C

CONCLUSIONS

In summary, we have elucidated the influence of domain size and length of segregated crystallizable sequences on the polymorphic crystallization of butene-1/ethylene copolymer. We identified an effective route for the formation of a particular polymorphic phase in the semicrystalline polymer by controlling the processing conditions. The formation of a polymorphic crystalline phase results from a competitive process, determined by the nucleation size and barrier potential of the respective crystalline phases. When the initial crystals were melted, the sequence-length segregation may persist, with the corresponding domain size decreasing with increasing the temperature T_{melt} of the melt. Thus, T_{melt} decides the domain size of segregated long crystallizable sequences. When such a molten sample is crystallized at temperature T_c the respective size of the critical nucleation and barrier potential of the individual crystalline phases decide which polymorphic phase will be formed. The phase will be generated, which has a nucleation size smaller than the domain size and a lower corresponding barrier potential.

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