

Effect of Linear and Ring-like Co-units on the Temperature Dependence of Nucleation and Growth in II-I Phase Transition of Butene-1 Copolymers

Ya-Hui Lou, Yi-Long Liao, Li Pan, Bin Wang, Yue-Sheng Li, and Zhe Ma*

Tianjin Key Laboratory of Composite and Functional Materials and School of Materials Science and Engineering, Tianjin University, Tianjin 300072, China

 Electronic Supplementary Information

Abstract The phase transition from tetragonal form II to hexagonal form I was studied for the butene-1/ethylene and butene-1/1,5-hexadiene random copolymers, which have comparable molecular weight but distinct linear ethylene and ringlike methylene-1,3-cyclopentane (MCP) structural co-units, respectively. It is known that this solid phase transition follows the nucleation-growth mechanism, so the stepwise annealing protocol was utilized to investigate the influences of co-units on the optimal nucleation and growth temperatures. Compared with optimal nucleation and growth temperatures of -10 and 35 °C, respectively, in polybutene-1 homopolymer, two butene-1/ethylene copolymers with 1.5 mol% and 4.3 mol% co-units have the slightly lower optimal nucleation temperature of -15 °C but much higher optimal growth temperature of 50 °C. Clearly, the effect of ethylene co-unit is more significant on varying optimal temperature for growth than for nucleation. Furthermore, when the incorporated co-unit is ringlike MCP, the optimal nucleation temperature is -15 °C for 2.15 mol% co-units, the same with above BE copolymers, but -13 °C for a very low concentration of 0.65 mol%. Interestingly, the optimal growth temperature of butene-1/1,5-hexadiene copolymers with 0.65 mol%–2.15 mol% MCP co-units increases to 55 °C, which is also independent on co-unit concentration. These obtained values of optimal temperatures provide crucial parameters for rapid II-I phase transition.

Keywords Butene-1 copolymer; Co-unit type; Phase transformation; Nucleation; Crystal growth

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INTRODUCTION

The butene-1 homopolymer and copolymers are one class of typical polymorphic semicrystalline polymers, of which chain segments can adopt various conformations and arrange into different types of unit cell. The different crystalline modifications include hexagonal form I/I' with 3_1 helix, tetragonal form II with 11_3 helix, and orthorhombic form III with 4_1 helix^[1–6]. The hexagonal phase is thermodynamically stable, which has two origins, that is, form I/I'. Form I is obtained by the solid-solid phase transition from initial form II^[7] and form I' directly crystallizes from melt or solution^[2, 8, 9]. However, due to the kinetic reason, melt crystallization often first generates tetragonal form II, which is metastable from thermodynamic point of view. Then, the crystallized form II can transform into the stable form I. This II-I transition can happen spontaneously, resulting in the substantial change in physical properties of material. The II-I transition is often slow, for example, the complete transition

in polybutene-1 homopolymer needs weeks. As a consequence of II-I phase transition, dimension shrinkage and warpage occur in the products even during the storage at room temperature, which limits the application of these butene-1 polymers^[10]. Therefore, how to accelerate the II-I phase transition is a crucial issue for both academic and industrial communities.

It has been reported that phase transition can be strongly accelerated by high pressure^[11], pressured CO_2 ^[12–14], shear or tensile stress^[15–17], and the chemical modification^[18–20]. Jones summarized the influences of a number of linear and branched α -olefin co-units on the phase transition of copolymers^[21]. It was found that the linear α -olefins capable of accelerating phase transition of butene-1 copolymer include ethylene, propylene, and pentene, but other linear α -olefins with more than five carbon atoms and branched comonomers hinder phase transition. Moreover, our recent work demonstrated for the first time that the methylene-1,3-cyclopentane (MCP) is a unique structural co-unit to accelerate phase transition^[22].

It is known that the II-I phase transition is a two-step process that undergoes nucleation and growth. Just based on this mechanism, a novel stepwise annealing method was

* Corresponding author: E-mail zhe.ma@tju.edu.cn

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applied recently by Qiao *et al.*, which decomposes the whole II-I phase transition into separate contributions of nucleation and growth^[23]. In this protocol, the regular annealing at a single temperature was decomposed into two annealing processes at a relatively low temperature (T_{low}) and a relatively high temperature (T_{high}) subsequently, where the former mainly facilitated nucleation due to shrinkage-induced internal stress and the latter benefited growth because rapid segmental diffusion improved. For a polybutene-1 homopolymer with the weight-average molecular weight of 7.11×10^5 g/mol, a maximum transition after annealing at a single temperature was found at 0 °C. The application of stepwise annealing revealed that the aforementioned maximum transition rate was caused by the fact that nucleation and growth had distinct optimal temperatures of -10 and 40 °C, respectively. Moreover, these two optimal temperatures for nucleation and growth can be used in turn to achieve the most rapid transition from forms II to I.

In present work, the stepwise annealing was utilized to investigate the II-I phase transition in two distinct series of butene-1/ethylene and butene-1/1,5-hexadiene copolymers, which are incorporated by the linear ethylene and ringlike methylene-1,3-cyclopentane (MCP) co-units, respectively. The experimental results showed that the introduction of ethylene and MCP co-units in the polybutene-1 main chain had substantial effect on increasing the optimal growth temperature, but their influence on the optimal nucleation temperature was not obvious. Moreover, the raised optimal growth temperature was mainly dependent on co-unit type, not on the co-unit concentration.

EXPERIMENTAL

Materials

The materials studied in present work include a polybutene-1 (PB-1) homopolymer and two series of butene-1 random copolymers, which are butene-1/ethylene (BE) and butene-1/1,5-hexadiene random copolymers. The homopolymer and two butene-1/1,5-hexadiene random copolymers with 0.65 mol% and 2.15 mol% methylene-1,3-cyclopentane (MCP) co-units, were synthesized using dimethylpyridylamido hafnium catalyst, which has been described before^[22, 24]. The two butene-1/ethylene random copolymers with 1.5 mol% and 4.3 mol% ethylene co-units were

provided by Lyondell Basell Industries, which have grade names of PB8640 and PB8220, respectively. For all polymers studied, detailed molecular characteristics and physical properties are summarized in Table 1.

To be compared with the synthesized polymers, the commercial BE copolymers obtained were also purified with the following procedure similar with the synthesis operation. The granules of butene-1/ethylene copolymers were first dissolved in toluene at 110 °C for 1 h. Then, the homogeneous solution was poured into the excessive ethanol and the precipitated materials were collected by filtration. After drying in the vacuum at 50 °C for 24 h, polymers were made into films of about 0.5 mm thick by compression molding at 180 °C for the further analysis.

Methods

The stepwise annealing protocol was employed to explore temperature dependences of nucleation and growth, which is illustrated by Fig. 1. Polymer was first molten at 180 °C for 10 min to erase all preparation histories and then cooled to the desirable temperature for isothermal crystallization to prepare form II crystallites for solid phase transition. Next, the obtained form II was annealed at the relatively low temperature (T_{low}) to nucleate form I and the subsequent annealing at the relatively high temperature (T_{high}) for growth of the transformed form I. The annealing durations were chosen as 30 and 120 min for the low and high temperatures, respectively. The T_{low} and T_{high} were varied separately to find the optimal temperature for nucleation and growth, respectively. According to the different crystallization abilities, the isothermal temperature to prepare form II was

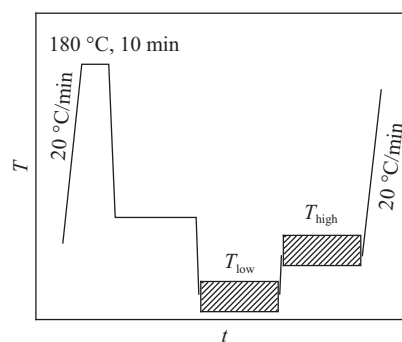


Fig. 1 Illustration of thermal protocol applied

Table 1 Molecular characteristics and properties of the butene-1 homopolymer and random copolymers

Sample code	Structural formula	Co-unit (mol%)	M_w (kg/mol)	T_c (°C)	$T_{m_form\ II}$ (°C)
PB-1		0	435 ^[22]	67	110
BE1.5		1.5	470 ^[19]	44	96
BE4.3		4.3	400 ^[19]	25 ^a	82
MCP0.65		0.65	426 ^[22]	32	85
MCP2.15		2.15	441 ^[22]	17 ^a	69

^a BE4.3 and MCP2.15 do not crystallize during cooling at -10 °C/min, but they exhibit cold crystallization during the subsequent heating process. For BE4.3 and MCP2.15, the crystallization temperatures given in Table 1 correspond to the peak temperature of cold crystallization during heating at 10 °C/min.

chosen at 65 °C for PB-1, which was lowered to 55 and 40 °C for BE1.5 and BE4.3 respectively, and to 55 and 25 °C for MCP0.65 and MCP2.15, respectively. It has been demonstrated by Qiao *et al.* that variation of the form II preparation temperature does not change the optimal temperatures for both nucleation and growth^[23].

Differential scanning calorimetry (DSC) measurements were carried out with DSC Q2000 (TA instrument). To ensure good comparability between different experiments, sample weight taken was always approximately 5 mg. After phase transition, a subsequent heating was performed to examine the fractions of residual form II and transformed form I. The DSC melting curves were analyzed with the peak fitting procedure to quantify the amounts of forms II and I (see Fig. 2a). The degree of the phase transition can be assessed using the equation $f_I = \frac{A_I/\Delta H_I}{A_I/\Delta H_I + A_{II}/\Delta H_{II}}$, where A_I and A_{II} are melting enthalpies obtained from DSC melting peak areas for forms I and II, ΔH_I and ΔH_{II} are the melting enthalpies of ideal crystals in forms I and II with the values of 141 and 62 J/g, respectively^[25].

Wide angle X-ray diffraction (WAXD) measurements were performed with a D8 Discover X-ray diffractometer. The X-ray wavelength was 0.154 nm and the distance from sample to detector was 84.7 mm. For each WAXD frame, the exposure time was 25 s and saving time was 5 s. The diffraction peaks observed at $2\theta = 9.9^\circ$, 17.3° , and 20.5°

correspond to crystallographic planes of (110), (300), and (220)+(211) of form I, respectively. Differently, the diffraction signals at $2\theta = 11.9^\circ$, 16.9° , and 18.5° are attributed to the (200), (220), and (213)+(311) planes of form II, respectively. The (200) diffraction peak at 9.9° and (110) diffraction at 11.9° were used to represent forms II and I, respectively. From the one-dimensional (1D) WAXD curve (see Fig. 2b), the fraction of form I in total crystals can

be calculated with $f_I = \frac{A_{(110)I}}{A_{(110)I} + R \times A_{(200)II}}$, where $A_{(110)I}$ and $A_{(200)II}$ are the integrated areas of form I (110)_I diffraction peak and form II (200)_{II} diffraction peak, respectively, and a correction factor $R = 0.67$ ^[26].

RESULTS AND DISCUSSION

Accelerated Phase Transition Kinetics in Butene-1/Ethylene Random Copolymers

The acceleration effect of ethylene co-units phase on transition kinetics is first explored for the annealing at the single temperature (T_{single}). Fig. 3(a) shows the DSC melting curves of homopolymer PB-1 and the BE copolymers with 1.5 mol% and 4.3 mol% co-units, which were annealed with the regular single-annealing method at 0 °C for 150 min. In each melting curve, there are two endothermic peaks. The melting peak at relatively low temperature results from the original form II and that at elevated temperature indicates

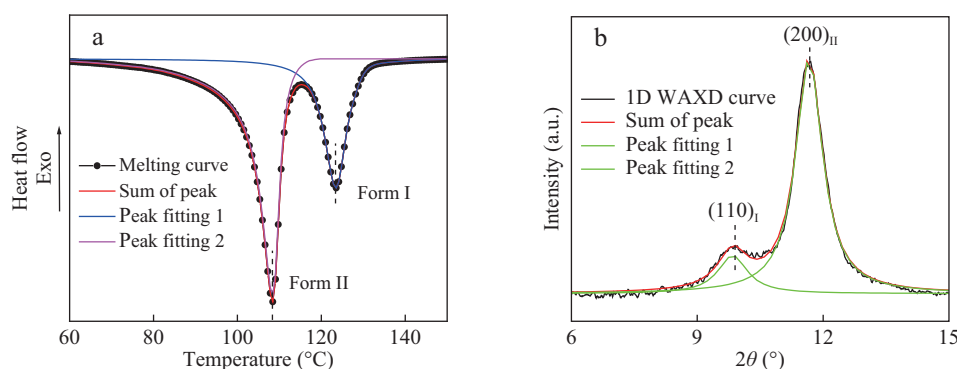


Fig. 2 Examples of peak fitting analysis of (a) DSC melting curve and (b) 1D WAXD curve to estimate the fraction of transformed form I

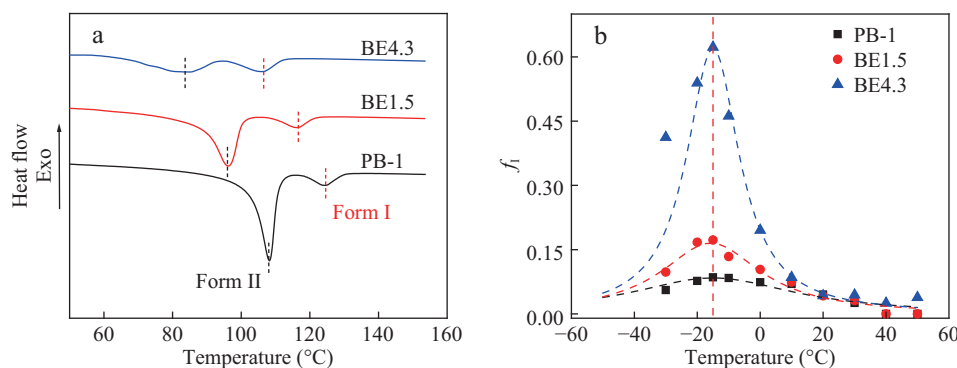


Fig. 3 (a) The DSC melting curve of PB-1 and butene-1/ethylene random copolymers after 150-min annealing at 0 °C; (b) The fraction of transformed form I after annealed at different single annealing temperatures (T_{single})

appearance of form I transformed. Obviously, II-I phase transition happens in all PB-1 and BE copolymers under conditions of 0 °C and 150 min. With increasing concentration of ethylene co-units, the relative area of form I melting peak increases at the expense of form II melting peak. This demonstrates an increased fraction of form I in the total crystallites with increasing ethylene concentration, which confirms that ethylene co-units effectively accelerate the phase transition from forms II to I.

The II-I phase transition kinetics is strongly dependent on temperature. As temperature changes, the different thermal expansion coefficients between crystalline and amorphous domains cause the internal stress and as a consequence, accelerate II-I phase transition. Fig. 3(b) quantitatively compares the temperature dependence of phase transitions, between PB-1, BE1.5 and BE4.3. First, for all annealing temperatures studied, BE4.3 always has the highest fraction of transformed form I, while PB-1 has the least form I. Acceleration effect of ethylene co-unit on II-I phase transition is observed for a broad temperature range from -30 °C to 50 °C. Second, for PB-1 and BE copolymers, the phase transition has a maximum rate at the same temperature of -15 °C. This means that the ethylene co-unit does not vary the optimal temperature for global phase transition, although incorporation of ethylene co-units does accelerate phase transition kinetics. Such bell-shape dependence of phase transition kinetics on temperature is often associated to the mutual effects between nucleation and growth of new form I within original phase of form II. The stepwise annealing protocol will be further employed to decompose the global phase transition of random copolymers into specific nucleation and growth steps.

Note that for the PB-1 homopolymer studied in present work, the identified maximum transition rate of -15 °C is in the range between -20 and 0 °C, which has been reported in the literature for the fast-transition temperature of polybutene-1 homopolymer. Concerning the difference in optimal transition temperature, one possible reason is due to various molecular weights. The homopolymer PB-1 used in present work has a weight-average molecular weight of 4.35×10^5 g/mol, which is slightly higher than that of 3.47×10^5 g/mol showing -20 °C, but much lower than that of 7.11×10^5 g/mol possessing 0 °C maximum transition. The

influence of molecular weight on the optimal temperature of homopolymer is out of the scope of the present work, which has been systematically studied by Qiao *et al.*^[27]. In present work, the comparable molecular weights of all materials minimize the potential influence from molecular weight difference between different materials.

Decomposition of Phase Transition into Nucleation and Growth Steps

To further identify the correlations between nucleation and temperature, the stepwise annealing protocol was employed, which has the fixed high temperature for growth but varying low temperatures for nucleation. Taking BE1.5 as a representative, Fig. 4(a) shows the DSC melting curves of sample after annealing at different low temperatures ranging from -50 °C to 20 °C, where a higher temperature of 20 °C was employed to allow for growth to magnify the nucleation effect. The significant change of form I melting peak area demonstrates a strong dependence of phase transition on nucleation temperature. Also with stepwise annealing approach, the correlation of growth with temperature can be examined by varying the high annealing temperature, where a low temperature was fixed for nucleation. Fig. 4(b) gives the DSC melting curves of BE1.5 that was first annealed at $T_{\text{low}} = -10$ °C to nucleate and subsequently annealed at various T_{high} for growth. It is obvious that growth varies significantly with temperature.

Fig. 4(c) further summarizes the quantified fractions of transformed BE1.5 form I as a function of nucleation and growth temperatures. It can be seen that for nucleation, a maximum rate is located at around -15 °C. Interestingly, the maximum growth temperature is much higher, 50 °C. Considering the fact that the maximum rate of global phase transition with the single annealing is also at -15 °C, it seems that the above temperature dependence of global transition kinetics is dominated by nucleation. This is consistent with the results of Di Lorenzo *et al.* for a comparable annealing duration^[28]. This nucleation-dominant temperature dependence still follows the nucleation and growth mechanism. The observed difference in whether one step or both steps dominates temperature dependence of global phase transition is due to their specific dependence, which can be indicated by peak position and width.

For BE1.5 copolymer, Di Lorenzo *et al.* also found that

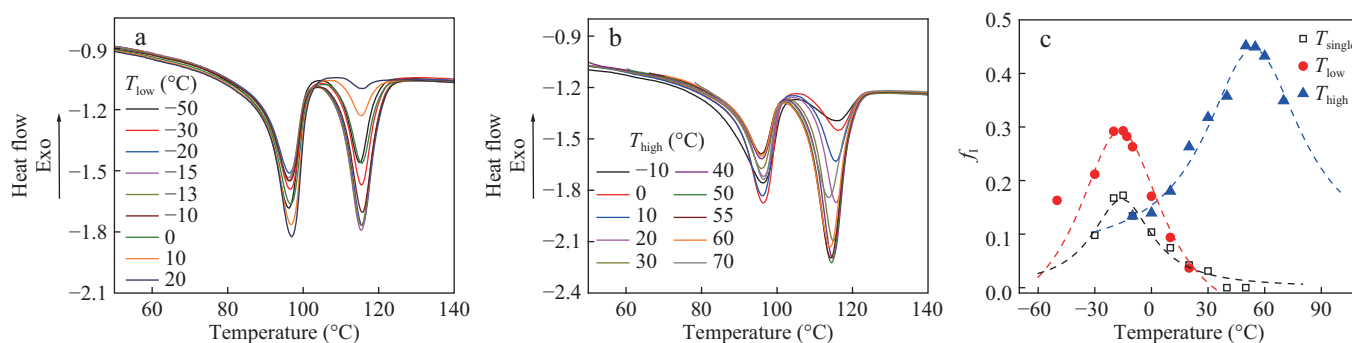


Fig. 4 The DSC melting curves of BE1.5 samples (a) annealed at different nucleation temperatures (T_{low}) for 30 min with subsequent annealing at 20 °C for 120 min, (b) annealed at different growth temperatures (T_{high}) for 120 min with a prenucleation at -10 °C for 30 min, (c) fraction of transformed form I as a function of annealing temperatures

when the duration of annealing at the single temperature was elongated, a maximum transition was observed at 20 °C^[28]. This elevated optimal growth temperature indicates that growth is also possible to dominate the global phase transition. Our results of Fig. 4(c) reveal that actually the maximum growth occurs at 50 °C, which is higher than 20 °C as the optimal temperature for growth-dominant global transition. This obtained value of the maximum growth rate provides more precise annealing temperature for rapid transition kinetics.

Figs. 5(a) and 5(b) show the decomposition of phase transition for PB-1 and BE4.3, respectively. For these two polymers, the temperature dependence of global phase transition is also dominated by nucleation, similar with aforementioned BE1.5. For PB-1, the upper temperature limit for nucleation is around 40 °C, above which, phase transition does not happen just due to non-occurrence of nucleation (see the absence of transformed form I after annealing at the single temperatures of 40 °C and higher). In other words, above the upper limit temperature of nucleation, growth does not vary the phase transition due to no nucleation, no matter how large it is. Compared with nucleation, the growth of form I can occur in a much broader temperature range, leading to still available growth at low temperatures comparable to the fast nucleation temperature range. In this case, nucleation and growth both happen, and as a consequence, phase transition at a single annealing

temperature is possible to develop for detection.

It should be pointed out that the growth of BE4.3 is so fast that it is easy to reach 100% transition within stepwise annealing for 150 min (see Fig. S2 in the electronic supplementary information, ESI), so the annealing durations were shortened to 10 and 40 min for the fixed $T_{\text{low}} = -10$ °C and different T_{high} , respectively. However, the total annealing duration was still 150 min for the single annealing experiment. Thus, as shown in Fig. 5(b), the comparable fraction of form I transformed within different time indicates the transition of stepwise annealing is much faster than the single annealing experiment.

Effect of Ethylene Concentration on Nucleation and Growth

Now it is clear that for II-I phase transition, the temperature of kinetics can be understood by looking at the separate correlations of nucleation and growth. The effect of ethylene co-units on the nucleation and growth is now discussed by comparing PB-1 and BE copolymers with different co-unit concentrations. As shown in Fig. 6(a), the optimal temperature of the maximum nucleation rate is -10 °C for PB-1 and reduces to -15 °C for BE1.5. However, as the concentration of ethylene co-units further increases to 4.3 mol%, the optimal temperature for nucleation remains -15 °C. This means that ethylene is indeed a type of comonomer to effectively lower the optimal nucleation

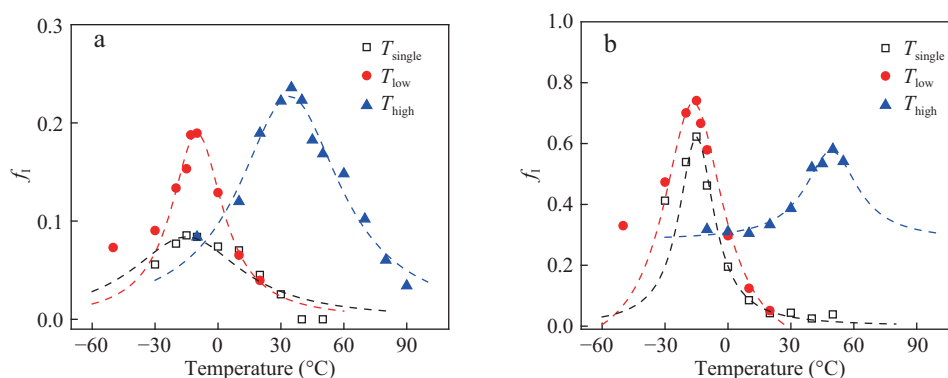


Fig. 5 Fraction of transformed form I in (a) PB-1 and (b) BE4.3 after annealed with different annealing protocols

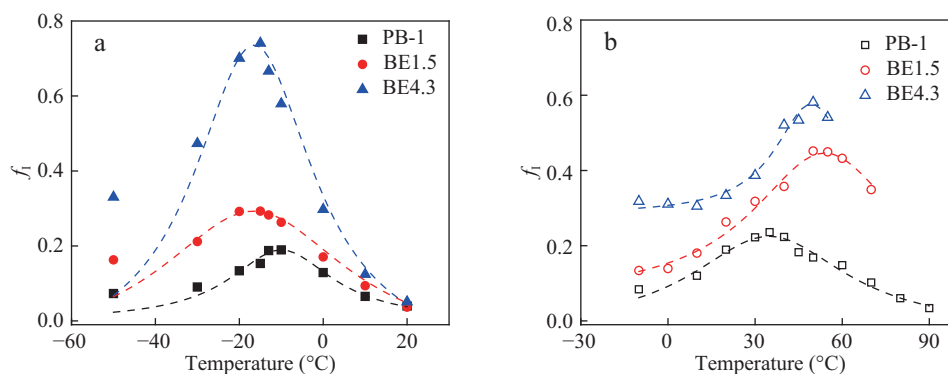


Fig. 6 Fraction of transformed form I in PB-1 and BE copolymers (a) after annealing at different nucleation temperatures (T_{low}) with a followed growth at 20 °C for 120 min, (b) after annealing at different growth temperatures (T_{high}) with a prenucleation annealing at -10 °C for 30 min

temperature and the changing amplitude does not depend on the co-unit concentration, at least for 1.5 mol%–4.3 mol%.

Growth exhibits a distinct change in BE copolymers compared with nucleation. When the polybutene-1 main chain includes ethylene co-units, the optimal temperature for growth is elevated, in contrast with lowered nucleation temperature. Furthermore, addition of 1.5 mol% ethylene co-units raises the optimal growth temperature to 50 °C, much higher than 35 °C of PB-1. This optimal growth temperature remains 50 °C with further increasing the ethylene concentration to 4.3 mol%. Obviously, the maximum growth temperature elevation of 15 °C by 1.5 mol%–4.3 mol% ethylene co-units is much larger than corresponding variation of 5 °C for nucleation. Ethylene co-units have larger influence on the optimal temperature for growth than for nucleation. Since the annealing temperature cannot exceed temperatures of melting region (see Fig. S1 in ESI), no further higher temperature was investigated for growth.

Effect of Ringlike MCP Co-units on Nucleation and Growth

Our recent work demonstrates that methylene-1,3-cyclopentane (MCP) is also a type of effective co-unit to significantly accelerate the transition kinetics of copolymers, which introduces the special structural unit containing five-carbon rings into the main chain. Using stepwise annealing protocol, the influence of such five-carbon ring structural unit on phase transition nucleation and growth was also

explored for two butene-1/1,5-hexadiene random copolymers with 0.65 mol% and 2.15 mol% MCP co-units, named MCP0.65 and MCP2.15, respectively. For MCP2.15, DSC melting curve has multiple melting peaks, which therefore cannot be used to quantify the amounts of forms II and I. In this case, WAXD measurements were carried out to quantify the progress of phase transition in MCP2.15.

Fig. 7(a) shows the one-dimensional WAXD curves of MCP2.15 sample after annealing at T_{low} from –50 °C to 20 °C for 30 min followed by annealing at 40 °C for 120 min. The distinct diffraction peaks of each sample were observed at $2\theta = 9.9^\circ$, 17.3° and 20.5° corresponding to the crystallographic planes of (110), (300) and (220)+(211) of form I. Clearly, the broad temperature range from –50 °C to 20 °C is able to trigger nucleation of form I within original form II crystallite. Fig. 7(b) displays the temperature dependence of growth step. It can be found that after nucleation at the identical low temperature of –10 °C, the amount of form II grown strongly depends on the growth temperature. The highest amount of form I transformed is generated by the growth at 55 °C, as indicated by the largest (110) diffraction area with respect to that of (200) diffraction.

Fig. 8 shows the quantified fractions of transformed form I as a function of nucleation and growth temperatures. For MCP0.65, the maximum nucleation of transformed form I is found at –13 °C. As the concentration of MCP co-units

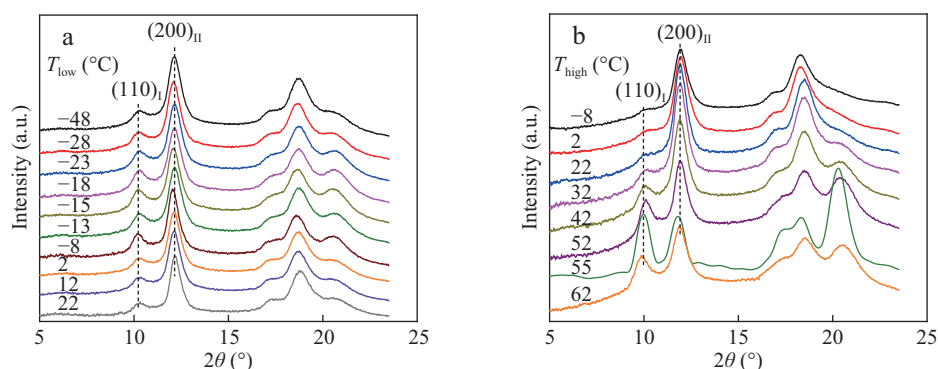


Fig. 7 One-dimensional WAXD patterns of MCP2.15 samples (a) annealed at different T_{low} for 30 min and (b) annealed at different T_{high} for 120 min

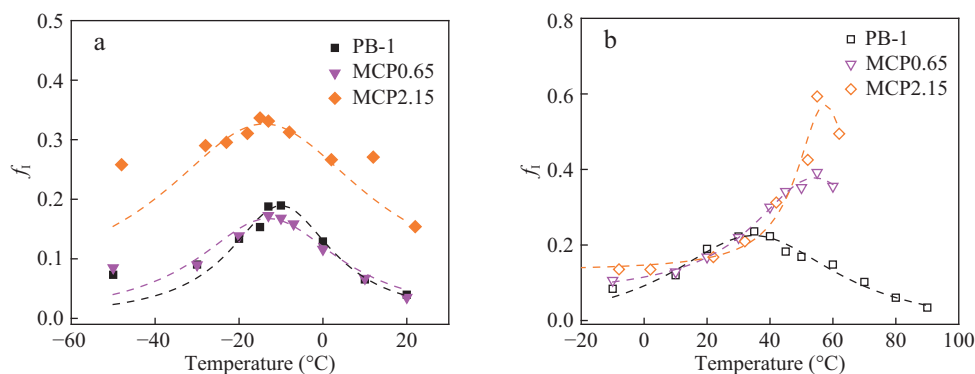


Fig. 8 Fraction of transformed form I in PB-1 and MCP copolymers (a) after annealing at different nucleation temperatures (T_{low}) with a followed growth at 20 °C for 120 min, (b) after annealing at different growth temperatures (T_{high}) with a prenucleation annealing at –10 °C for 30 min

increases to 2.15 mol%, the fast nucleation shifts to a lower temperature of around -15°C , which is the same with BE copolymers. Fig. 8(b) shows the temperature dependence of growth. For MCP0.65, the fast growth rate shifts to 55°C . Obviously, the influence of 0.65 mol% MCP co-units on the growth is also much more obvious than that on nucleation. However, with increasing MCP concentration to 2.15 mol%, the optimal growth temperature of MCP2.15 remains at 55°C .

MCP co-unit introduces one extra unit of five-carbon ring structure into the main chain than ethylene comonomer. It was interesting to investigate the influence of co-unit type on nucleation and growth steps for phase transition. The co-unit type mainly affects the optimal temperature for growth. Knowing the maximum growth of PB-1 at 35°C , the optimal growth temperature is 50°C and 55°C for ethylene and MCP co-units. Furthermore, these varied optimal temperatures are independent on co-unit concentration. However, for nucleation, there is no difference in the optimal temperature between linear and ringlike co-units when co-unit concentrations are in the same range. For example, the optimal nucleation temperature of MCP2.15 with 2.15 mol% co-units is identical with those of BE1.5 and BE4.3 which have 1.5 mol% and 4.3 mol% co-units, respectively. It seems that different types of linear ethylene and ringlike MCP co-units cause the same optimal nucleation temperature, except for the too low co-unit concentration as in MCP0.65.

CONCLUSIONS

The butene-1 based polymer often crystallizes into tetragonal form II due to the kinetic reason. However, form II is metastable thermodynamically, which afterwards transforms into hexagonal form I. The transition kinetics can be significantly accelerated by incorporating linear ethylene or ring-like MCP co-units into main chain. In present work, the stepwise annealing method was applied in the PB-1 and two series of butene-1/ethylene and butene-1/1,5-hexadiene copolymers, to investigate influences of distinct co-units on nucleation and growth using DSC and WAXD methods. The decomposition process was shown for the butene-1/ethylene copolymers containing 1.5 mol% and 4.3 mol% co-units, which demonstrates that the temperature for the fastest transition is dominated by the nucleation step. With the stepwise annealing method, the optimal temperatures of nucleation and growth are found at -15°C and 50°C , respectively, for BE copolymers. First, the optimal nucleation temperature is 5°C lower than that of PB-1, whereas the optimal growth temperature is much higher than that of homopolymer PB-1 by around 15°C . Second, the optimal growth temperature of 50°C does not change with increasing ethylene concentration from 1.5 mol% to 4.3 mol%. Furthermore, for the butene-1/1,5-hexadiene copolymers with 0.65 mol% and 2.15 mol% ringlike MCP co-units, the optimal nucleation temperatures are -13°C and -15°C , respectively. Interestingly, the optimal growth temperatures are identical at 55°C for these two copolymers. Clearly, the effect of linear ethylene and ringlike MCP co-units is more significant on the optimal growth temperature

than on the optimal nucleation temperature. Moreover, the raised optimal growth temperature seems to be determined by co-unit type instead of concentration.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://dx.doi.org/10.1007/s10118-018-2135-6>.

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