

Enhanced Phase Transition in Poly(ethylene glycol) Grafted Butene-1 Copolymers

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Electronic Supplementary Information

Abstract In the present work, a series of poly(ethylene glycol) grafted polybutene-1 copolymers (PB-*g*-PEG) were designed and successfully synthesized with reaction intermediate method, of which the branch densities and length could be tuned independently. The branch density varied from 0.39 mol% to 1.23 mol% and the branch length was tuned by employing PEG number-averaged molecular weight (M_n) from 350 Da to 750 Da and 1000 Da. The non-isothermal crystallization and phase transition behaviors of these butene-1 copolymers with varying branches were systematically explored by differential scanning calorimeter. The results first showed that compared with the linear polybutene-1 homopolymer, presence of steric 4-[4-(trimethylsilylalkynyl)-phenyl]-1-butene (TMS) groups suppressed crystallization and phase transition of copolymers. Interestingly, the introduction of long poly(ethylene glycol) (PEG) branches with $M_n=350-1000$ Da not only elevated the peak temperature of the non-isothermal crystallization but also enhanced the II-I phase transition, with respect to copolymers with TMS groups. Furthermore, the quantitative correlations between phase transition kinetics with the branch parameters (density and length) were explored. It was found that the phase transition presents a non-monotonic trend with increasing branch density and branch length. In this case, the optimal branch density and length obtained were 0.77 mol% and 750 Da, respectively. Employing the small angle X-ray scattering and transmission electron microscopy, a direct correlation between the phase transition kinetics and the long periodicity of separated phase was obtained, which may be due to the increased internal stress and facilitated stress transport.

Keywords Polybutene-1 copolymer; Crystallization kinetics; Phase transition; Phase separation

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INTRODUCTION

Isotactic polybutene-1 (PB-1) is one class of interesting polymorphic macromolecules, which can crystallize into various crystallites, including trigonal phase, tetragonal phase, and orthorhombic phase.^[1–7] Because of the kinetic reason, amorphous PB-1 melt prefers to crystallize into the tetragonal modification of form II under the customary conditions.^[8,9] However, the obtained tetragonal phase is thermodynamically metastable and often spontaneously transforms into the most stable trigonal phase form I.^[10–15] Thus, the kinetics of II-I phase transition process has an important influence on obtaining the ultimate product of stable form I crystallites, which possess the elevated melting temperature and good mechanical properties.^[16–21]

There are various physical and chemical methods reported to regulate II-I phase transitions, such as incorporation of designed structural co-units, application of mechanical stress, and the stepwise thermal annealing.^[11,22–29] It was found that

the introduction of structural co-units is one robust approach to regulate the kinetics of phase transition, which is strongly dependent on the designed macromolecular architectures.^[16,22,30,31] The α -olefins provide the suitable copolymerization co-monomers to introduce the well-defined linear branches. As the α -olefin co-monomers of no more than five carbon atoms, including ethylene, propylene and pentene, were randomly copolymerized into the main chain of polybutene-1, the obtained copolymers showed the significantly accelerated phase transition.^[31–35] In addition, those cyclic co-units are also able to largely affect the phase transition kinetics, depending on their sizes and locations incorporated into main chain.^[24,32,36,37]

It is known that II-I phase transition follows the nucleation-growth pathway, of which the former nucleation process is the rate-determining step. For semicrystalline PB-1, the crystalline and amorphous components have different thermal expansion behaviors, so the cooling post to crystallization generates the internal stress and consequently triggers nucleation of the transformed form I within the original form II. Thus, the external stress implemented by mechanical deformation obviously accelerates phase transition. Liu *et al.* showed

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that tensile deformation at low temperatures can facilitate the contraction of interhelix and interplanar distance of (110) crystal planes, thereby accelerating II-I phase transition.^[38] Zheng *et al.* demonstrated that the component stress perpendicular to the *c*-axis is the key to enhancing phase transition in 1-butene/4-methyl-1-pentene copolymers.^[16] Shi *et al.* studied the phase transition under the nano-scale confinement condition by the anodic aluminum oxide (AAO) templates.^[39,40] A large mismatch exists in thermal expansion between PB-1 and AAO templates, while the resulting pronounced internal stresses promote the nucleation of form I, leading to the accelerated II-I phase transition. On the other hand, phase transition was accelerated by enhancing the transport of internal stress into lamellar crystallites. Qiao *et al.* systematically studied the phase transition in PB-1 with various molecular weights and crystallite sizes.^[2] It was clearly demonstrated that the intercrystalline links play the crucial role in transporting internal stress to form II crystallites to be transformed. Then, An *et al.* synthesized the polybutene-1 ionomers to induce the long-chain branch and ionic functional groups. The results showed that the ion aggregates acted as the additional physical cross-links and enhanced the transport of internal stress to crystallites, leading to the significantly promoted II-I phase transition.^[41,42]

On the other hand, the presence of secondary co-units often decreases the regularity of main chain and shortens the average length of the crystallizable sequences, decreasing the crystallization rate of copolymers. To prevent a significant decrease in crystallization kinetics, it was also reported that the introduction of branched structure may accelerate the crystallization.^[43–45] Takamura *et al.* reported that the long chain-branched poly(L-lactide) exhibited a much raised nucleation density.^[46] Wang *et al.* also found that for poly(L-lactide), the introduction of branched structure can shorten the nucleation induction period and enhance the crystallization kinetics.^[44,47] In previous work, the crystallization and phase transition behaviors were studied for the poly(ethylene glycol) grafted polybutene-1 copolymers.^[48] The presence of poly(ethylene glycol) (PEG) branches within molecular weight from 750 Da to 4000 Da increased the crystallization kinetics of copolymers, but how II-I phase transition rate varied was dependent on the length of PEG branch. The quantitative results showed that the relatively short PEG branches with the number-averaged molecular weight $M_n=750$ Da accelerated phase transition, whereas the too long PEG branches with $M_n=4000$ Da caused a slower phase transition with respect to PB-1 homopolymer.^[48]

In this work, the polyethylene glycol grafted polybutene-1 copolymers were prepared by reaction intermediate method, and various PEG branches were successfully introduced into the polybutene-1 main chain. First of all, the incorporation was varied within 0.39 mol%–1.23 mol%, which determines the density of branches introduced. And the branch length can be tuned by varying the PEG molecular weight, which includes the $M_n=350$, 750 and 1000 Da. The results showed that the TMS groups slow down the crystallization, whereas the PEG branches enhance crystallization and elevate the peak temperature of non-isothermal crystallization. More importantly, presence of PEG branches significantly accelerated the solid II-I phase transition. It was found that the phase transition kinetics exhibits the non-monotonic dependence on the graft density and branch length. Based on these results, the optimal density and length of branches could be obtained for the design of macromolecular architecture, in order to most effectively accelerate the II-I phase transition.

EXPERIMENTAL

Materials

The materials studied in this work include polybutene-1 homopolymer, 1-butene/4-[4-(trimethylsilylalkynyl)-phenyl]-1-butene copolymers (PB-TMS) with the steric side groups, and polyethylene glycol grafted polybutene-1 copolymers (PB-g-PEG) with PEG branch. First of all, $\{\text{Me}_2\text{Si}(2,5\text{-Me}_2\text{-3-(2-MePh)cyclopento[2,3-}b\text{]thiophen-6-yl)}_2\}\text{ZrCl}_2/[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ catalytic system was employed to copolymerize 1-butene with 4-[4-(trimethylsilylalkynyl)-phenyl]-1-butene (Ph-TMS), where the obtained copolymers was referred to PB-TMS, see Fig. 1. Then, the tetrabutylammonium was used as the catalyst to remove trimethylsilyl from the PB-TMS copolymers, and the azido-terminated poly(ethylene glycol) was grafted onto the copolymers by the copper(b) bromide/pentamethyldiethyl catalytic system. The methoxy poly(ethylene glycol) is used as the grafting co-units to prevent crosslinking. In this way, the incorporation of branches in PB-g-PEG copolymers is equivalent to that of PB-TMS copolymers, so the density of PEG graft could be regulated by the incorporation degree of the initial Ph-TMS co-units. In this work, the incorporation of TMS groups and PEG branches varied within the range of 0.39 mol%–1.23 mol%. On the other hand, the molecular weight (M_n) of PEG was also varied from 350 Da to 750 Da and 1000 Da, in order to further tune the branch length in PB-g-PEG copolymers. The copolymerization methods have been described in detail previously.^[48–51]

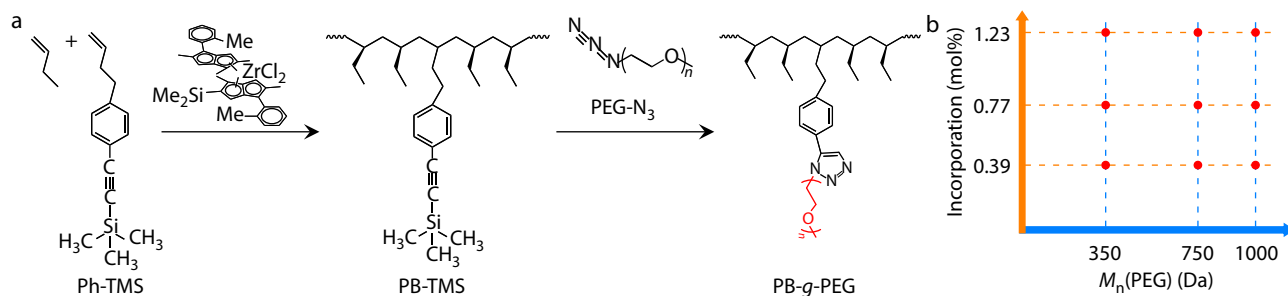


Fig. 1 (a) Synthesis route to PB-g-PEG copolymers; (b) The PB-g-PEG copolymers were prepared with different graft densities and graft lengths.

The incorporation of Ph-TMS co-units and degree of PEG grafting were determined by high temperature ^1H nuclear magnetic resonance (Bruker 400 MHz spectrometer). The molecular weight and distribution were measured by high temperature gel permeation chromatography (PL-GPC 220). The molecular properties of the polymers studied in this work are given in Table 1.

Table 1 Molecular properties of PB-1 homopolymer and PB-TMS copolymers.

Sample	Incorporation of Ph-TMS (mol%)	$M_w (\times 10^3 \text{ Da})$	M_w/M_n
PB-1	0	534	2.8
PB0.39-TMS	0.39	466	2.6
PB0.77-TMS	0.77	340	2.7
PB1.23-TMS	1.23	438	2.7

Differential scanning calorimetry (DSC) measurements were carried out with DSC Q20 (TA Instrument) under a nitrogen atmosphere. The nitrogen flow was kept constant at 50 mL/min. The temperature of DSC was calibrated with indium. The samples were first annealed at 180 °C for 10 min to erase the thermal history and then cooled at 10 °C/min to allow the completion of non-isothermal crystallization. The obtained tetragonal form II was aged at 25 °C to transform into the thermodynamically stable trigonal form I. After various aging durations were designed, polymers were heated again at 5 °C/min to examine the degree of II-I phase transition.

Fourier transform infrared spectroscopy (FTIR) measurements were performed by the IRTTracer 100 (Shimadzu Instrument) with a resolution of 4 cm^{-1} . The spectra were acquired by co-adding 45 scans.

Transmission electron microscopy (TEM) measurements were conducted using a JEOL 2100plus transmission electron microscope operated at acceleration voltage of 200 kV. The samples dissolved into toluene and mixed with a tetrahydrofuran solution of gold nanoparticles with 4-mercaptophenol ligands. The mixed solution was applied dropwise on a copper mesh and left at room temperature for 6 h to allow the solvent to volatilize. The strong hydrogen bond interaction allows gold nanoparticles to be selectively incorporated into the PEG phase, which facilitates the identification of polybutene-1 phase and PEG phase.^[52]

The small-angle X-ray scattering (SAXS) measurements were performed with Xeuss 2.0 X-ray diffractometer. The X-ray wavelength was 0.154 nm and the distance from the sample to the detector was 2460 mm. For each SAXS pattern, the exposure time was 600 s. The periodicity of phase separation was determined from q_{max} of SAXS curves according to Bragg's law.

RESULTS AND DISCUSSION

Influence of Steric TMS Branch on Melt Crystallization and Phase Transition

Fig. 2(a) shows the ^1H -NMR spectra of the prepared copolymers. The characteristic signal peak at 0.38 ppm belongs to trimethylsilyl, while those observed at 7.23 and 7.47 ppm come from phenyl. These results demonstrate the successful incorporation of Ph-TMS co-units into polybutene-1 copolymers. The influences of these incorporated TMS groups

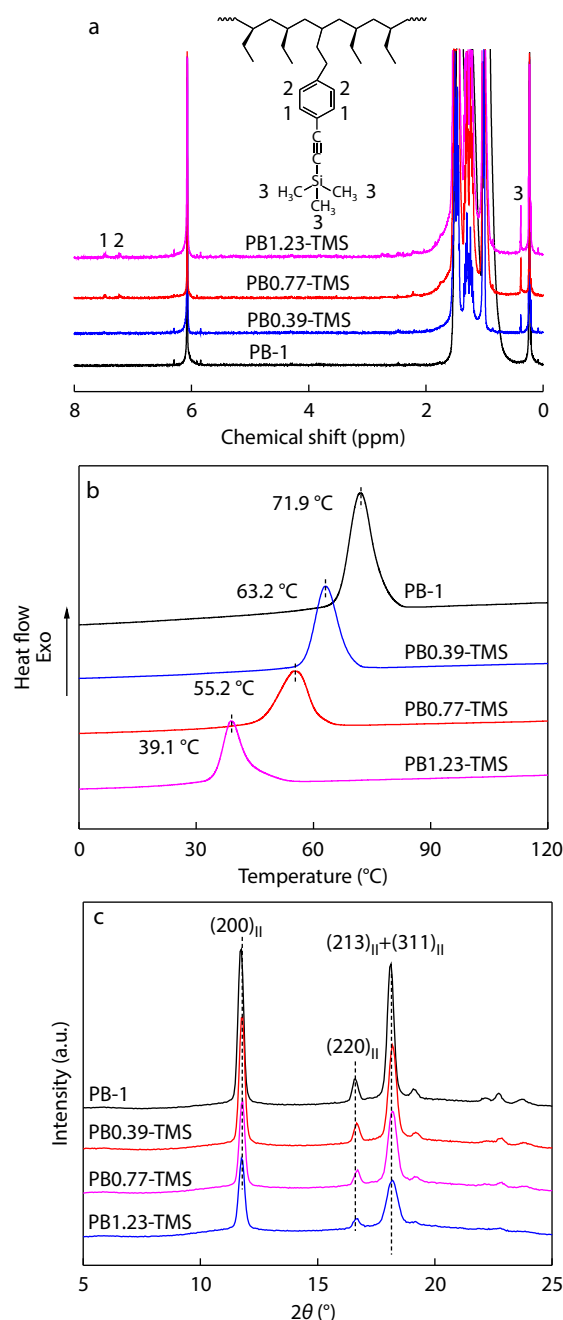


Fig. 2 (a) ^1H -NMR spectra, (b) DSC cooling curves, and (c) one-dimensional WAXD curves of PB-TMS copolymers.

on the crystallization of amorphous melt and the phase transition of tetragonal form II into form I was studied. First of all, it was seen that presence of TMS groups reduces the peak temperature of cooling crystallization (Fig. 2b). The WAXD results demonstrated that there were only the tetragonal crystallites, i.e., form II, generated in the cooling crystallization of Ph-TMS copolymers (Fig. 2c). Then, these kinetically favored form II may transform into the more thermodynamically stable trigonal form I spontaneously.

The DSC measurements were utilized to investigate the solid phase transition from form II to form I at room temperat-

ure. From Fig. 3(a), it can be seen that during aging, an additional melting peak started to appear at 125 °C in PB-1 homopolymer, which was much higher than that of form II (113 °C) and corresponded to the appearance of transformed trigonal form I. As aging proceeds at 25 °C, the melting enthalpy of form I increases, whereas that of form II decreases significantly. The II-I transition seemed to reach the plateau state at an aging time of around 164 h, where the crystallites were nearly pure form I transformed. On the other hand, the II-I phase transition also happened in the copolymers with Ph-

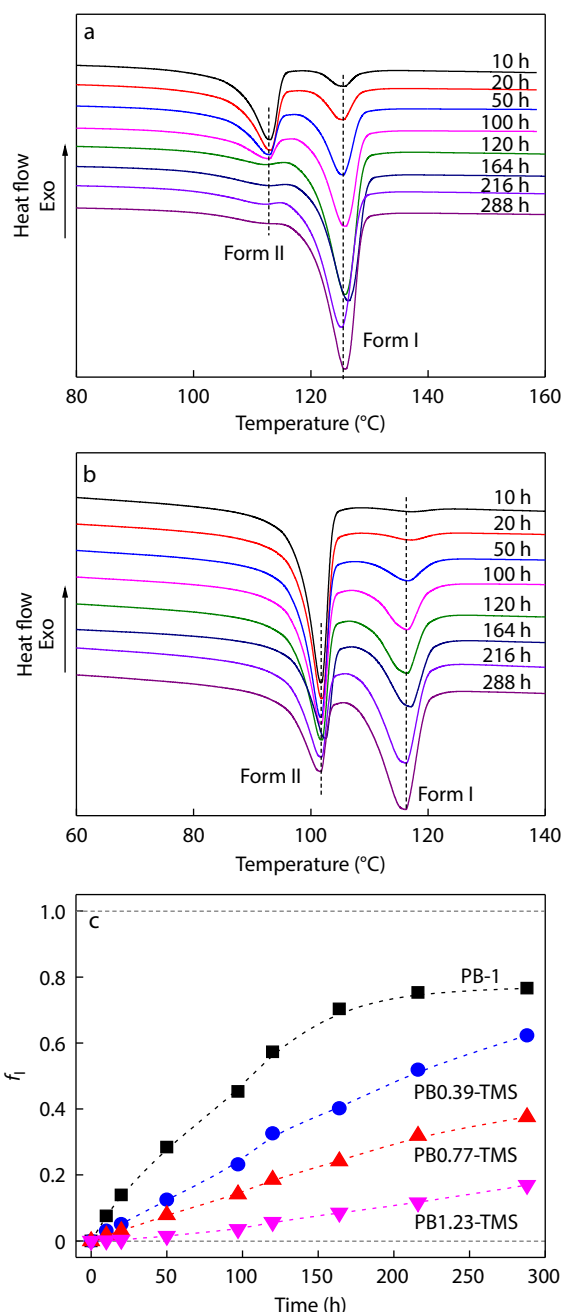


Fig. 3 DSC heating curves of (a) PB-1 and (b) PB0.77-TMS after aging at the room temperature for various durations; (c) The corresponding quantified fraction of transformed form I in total crystallites after aging at the room temperature.

TMS co-units, as demonstrated by the results of PB0.77-TMS as the representative (Fig. 3b). However, transition kinetics of PB0.77-TMS is quite slow compared with above PB-1. The pronounced melting peak of form II at 103 °C indicated that there was a large amount of form II crystallites survived, even the aging duration lasted as long as 288 h.

In order to assess the transition kinetics, the quantitative fraction of transformed form I were assessed by

$$f_I = \frac{\Delta H_I / \Delta H_{I,ideal}}{(\Delta H_I / \Delta H_{I,ideal}) + (\Delta H_{II} / \Delta H_{II,ideal})}, \text{ where } \Delta H_I \text{ and } \Delta H_{II} \text{ are}$$

melting enthalpies of form I and form II, respectively. In this equation, $\Delta H_{I,ideal}$ and $\Delta H_{II,ideal}$ are the ideal (100% crystallite) melting enthalpies of form I and form II, respectively.^[26,30] Fig. 3(c) presents the fraction of form I for PB-1 and all PB-TMS copolymers with 0.39 mol%–1.23 mol% co-units. In PB-1, f_I reached 7.6 % at the aging time of 10 h and reached a plateau value of about 75 % after aging for 216 h. For PB0.39-TMS copolymer, f_I was only 3.1% after aging for 10 h, which indicates that a low incorporation of 0.39 mol% can obviously slow down the phase transition. When the incorporation of Ph-TMS co-unit was increased to 1.23 mol%, II-I phase transition cannot occur within 10 h and led to a low f_I of only 16.9% for 288 h. It is clear that the presence of Ph-TMS co-units largely suppresses the solid phase transition of form II into form I. Although the PB-TMS copolymers have the lower crystallization temperature than PB-1, corresponding to the decreased difference between the crystallization temperature and the phase transition temperature, their suppressed phase transitions are mainly associated to the steric effect of Ph-TMS co-units, consistent with previous reports.^[16,22]

Influence of Long PEG Branch on Melt Crystallization

Fig. 4(a) gives ¹H-NMR spectra of PB-*g*-PEG copolymers with 0.77 mol% branches as the representative. It can be clearly seen that the absence of signal at 0.38 ppm, demonstrating that the trimethylsilyl groups were completely removed. The methylene signal of PEG was observed at 3.76 ppm, indicating that PB-*g*-PEG copolymers were successfully prepared. The excess azido-terminated poly(ethylene glycol) co-units were used and react at 70 °C for 12 h to ensure complete grafting. Moreover, the intensity increase of signal at 3.76 ppm is consistent with the increase of the molecular weight of PEG branches. FTIR results show that the signal at 2160 cm⁻¹ belonging to the alkyne groups is absent in PB-*g*-PEG copolymers (Fig. 4b). The influence of PEG branches on melt crystallization was examined employing the identical cooling rate of 10 °C/min. Interestingly, DSC results of Fig. 4(c) present that PB-*g*-PEG copolymers with PEG branches have the much higher non-isothermal crystallization temperature $T_{c,cooling}$ than PB-TMS copolymers, although their incorporations were the same. Fig. 4(d) summarizes the $T_{c,cooling}$ values for all PB-*g*-PEG copolymers with branch densities of 0.39 mol%–1.23 mol% and branch lengths of $M_n(\text{PEG})=350\text{--}1000$ Da. It is seen that with respect to TMS side group, the PEG branches significantly elevate the peak temperatures of non-isothermal crystallization for the whole graft density range of 0.39 mol%–1.23 mol%. At the same time, it was found that the peak temperatures of non-isothermal crystallization in PB0.39-*g*-PEG350 and PB0.39-*g*-PEG750 are even higher than that of PB-1 homopolymer.

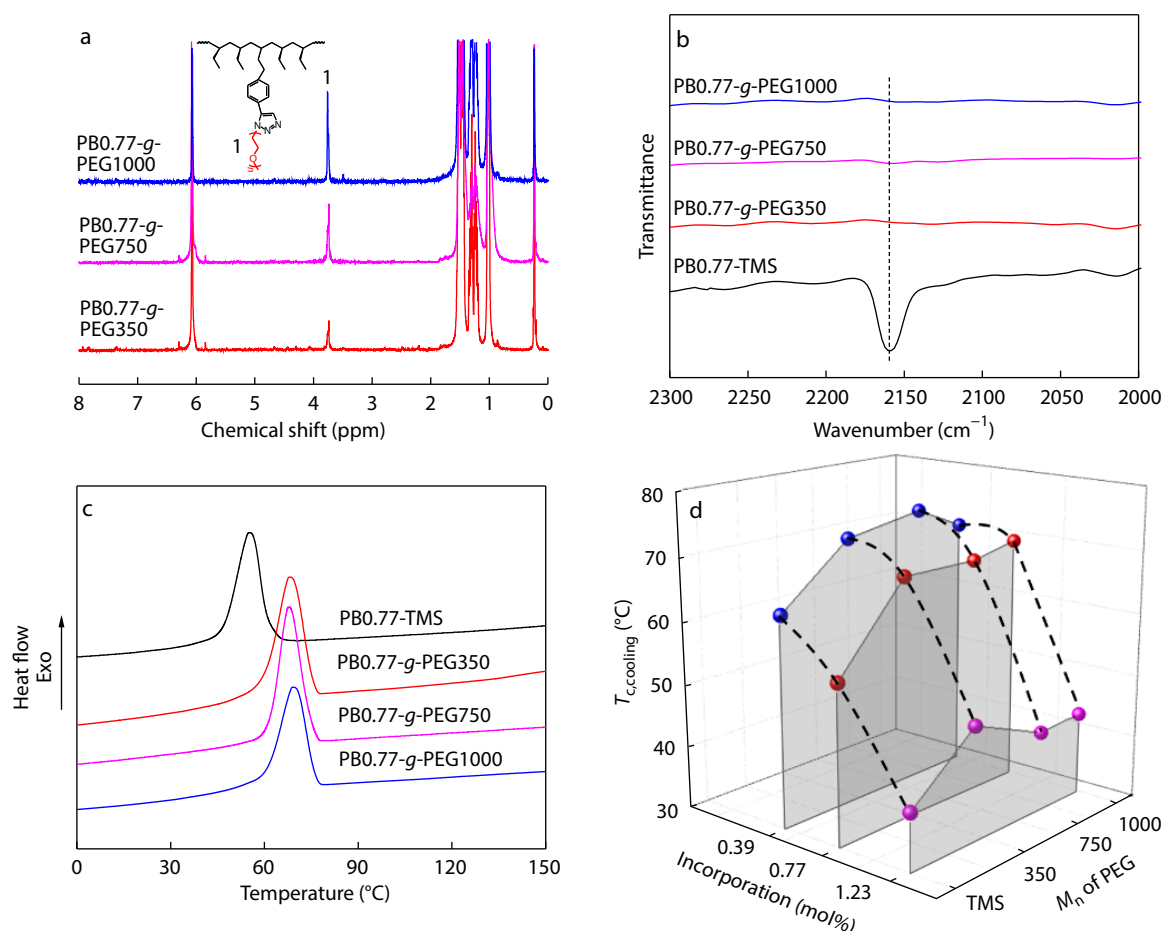


Fig. 4 (a) ^1H -NMR spectra, (b) FTIR spectra and (c) DSC cooling curves of PB-TMS and PB-*g*-PEG copolymers with 0.77 mol% co-units; (d) The $T_{\text{c,cooling}}$ values of all PB-*g*-PEG copolymers with graft densities of 0.39 mol%–1.23 mol% and graft lengths of $M_n(\text{PEG})=350$ –1000 Da.

Influences of PEG Branch Length and Density on Solid Phase Transition

Similar with above PB-TMS copolymers, all PB-*g*-PEG copolymers crystallize into the tetragonal form II with cooling. Taking the copolymers with graft density of 0.77 mol% as the representative, Fig. 5(a) shows the correlation between the branch structure and II-I phase transition kinetics. These results demonstrate that for the same incorporation of 0.77 mol%, PB-*g*-PEG copolymers have much faster phase transition than PB-TMS, irrespective of PEG length within 350–1000 Da. The f_t values at an aging time of 100 h were taken to represent the phase transition kinetics and its dependence on the length of PEG grafts was explored. From Fig. 5(b), it can be seen that although PEG branches of 350–1000 Da length were all able to make phase transition faster than TMS groups, there was a non-monotonic PEG length dependence of transition rate and the intermediate PEG length of 750 Da showed the maximum accelerating effect in transition kinetics.

It is known that for butene-1 copolymers, the linear alkyl branches containing more than 3 carbon atoms (corresponding to the linear α -olefin comonomers with >5 carbon atoms), which was introduced by copolymerizing α -olefin larger than 1-pentene as the secondary co-monomers, suppress the phase transition of form II into form I.^[22,32,36] This is consistent with our observation that PB0.77-TMS exhibits a much slower

II-I phase transition than PB-1 homopolymer. What is more interestingly is that after PEG350 branches were introduced, II-I phase transition was significantly accelerated in copolymer PB0.77-*g*-PEG350, which becomes even faster than that of PB-1. Note that this phase transition can be further accelerated with increasing graft length into $M_n(\text{PEG})=750$ Da in PB0.77-*g*-PEG750, which however decreases in PB0.77-*g*-PEG1000. It was suggested that the optimal PEG length of intermediate 750 Da leads to the maximum transition rate. Such optimal PEG length of 750 Da, corresponding to the maximum transition, was also observed in the other two PB-*g*-PEG copolymers with branch densities of 0.39 and 1.23 mol%, as shown in Fig. 6.

Furthermore, the results of Fig. 6 also present the quantitative dependence of transition on the branch densities. With the fixed branch length of $M_n(\text{PEG})=750$ Da, another maximum rate of copolymers was found with the intermediate incorporation of 0.77 mol%, although PB-TMS copolymers exhibit the monotonically slowed II-I transition kinetics with increasing the incorporation degree from 0.39 mol% to 1.23 mol%. It was implied that within the branch density range from 0.39 mol% to 1.23 mol%, there was the optimal branch density of 0.77 mol% for the fastest II-I phase transition.

It is known that the phase transition is strongly dependent on the internal stress caused by the various different thermal

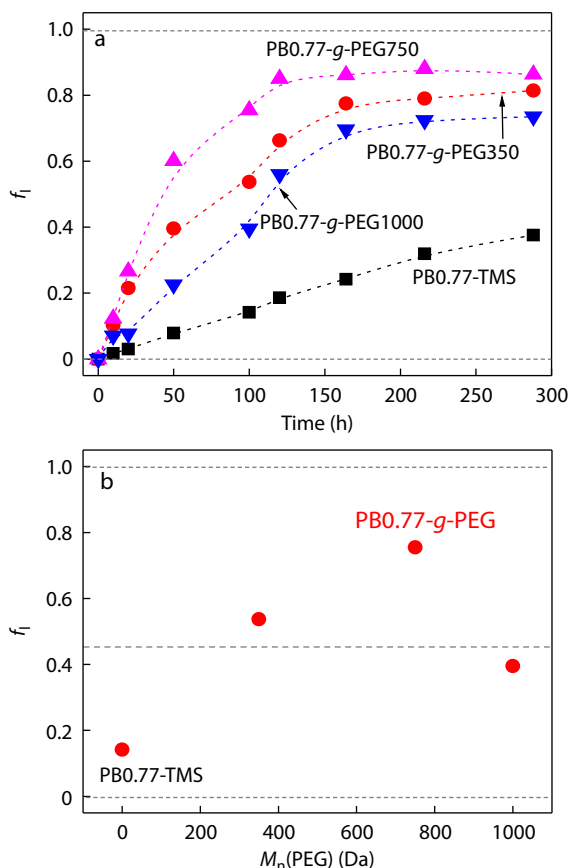


Fig. 5 (a) The II-I phase transition kinetics of PB-TMS and PB-g-PEG with different PEG lengths at the room temperature. The incorporation was 0.77 mol%. (b) The form I fraction of copolymers with 0.77 mol% co-units after aging at room temperature for 100 h. (The gray dotted line indicates the form I fraction of PB-1)

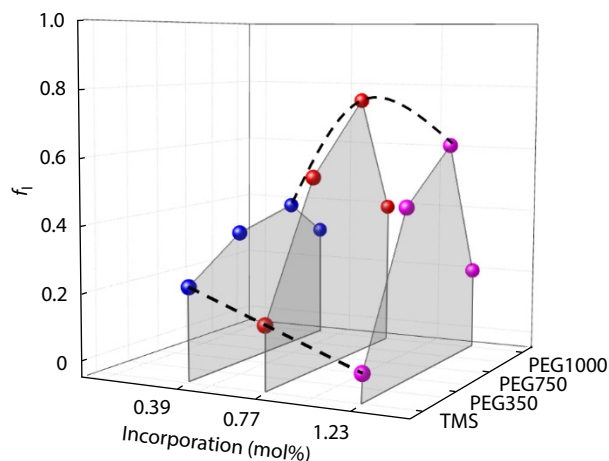


Fig. 6 The fraction of transformed form I in total crystallites in copolymers grafted with different densities and lengths of PEG grafts, after aging at the room temperature for 100 h.

expansion coefficients between crystalline and amorphous PB-1, which are 1.2×10^{-4} – 1.4×10^{-4} and 2.2×10^{-4} – 2.6×10^{-4} $^{\circ}\text{C}^{-1}$, respectively.^[39] This means that in PB-1 homopolymer, the internal stress is associated with different thermal expan-

sions between crystallite and amorphous regions, and internal stress cannot be generated until the start of cooling crystallization, where the onset temperature of non-isothermal crystallization was 84 $^{\circ}\text{C}$ in PB-1. Differently, PEG branches have a large thermal expansion coefficient over 7×10^{-4} $^{\circ}\text{C}^{-1}$.^[53,54] On one hand, irrespective of whether PB-1 is crystalline or amorphous, the thermal expansion coefficient difference between phases of PEG and PB-1 is much larger than that between the crystalline and amorphous regions of PB-1. On the other hand, the internal stress may start to be generated since the high temperature, at which phase separation happens, i.e., 180 $^{\circ}\text{C}$ in PB-g-PEG copolymers, much higher than the aforementioned 84 $^{\circ}\text{C}$ in PB-1. Thus, the internal stress in PB-g-PEG copolymers seems much larger than that of PB-1.

The PB-1 main chains and polar PEG branches tend to separate into different phases, because of their immiscibility. Considering the fact that PEG branches are covalently connected with PB-1 main chain, these branch points are mainly located on the interface between PB-1 and PEG phases, and they are likely to act as the interphase links to facilitate the transport of internal stress. The small angle X-ray scattering experiments were performed to characterize the potential phase separation in PB-g-PEG copolymers. Only some PB-g-PEG copolymers with graft densities of 0.77 mol% and 1.23 mol% could show the distinct SAXS signals of phase separation. Note that these copolymers with distinct phase separation correspond to the significantly accelerated phase transition. Combining the SAXS and TEM characterizations, the periodicity of the separated phases was determined and plotted as the variant for the phase transition kinetics, see Fig. 7. These results suggested a direct correlation between the II-I transition kinetics and the periodicity of separated phases, where the smaller phase periodicity is more beneficial to ac-

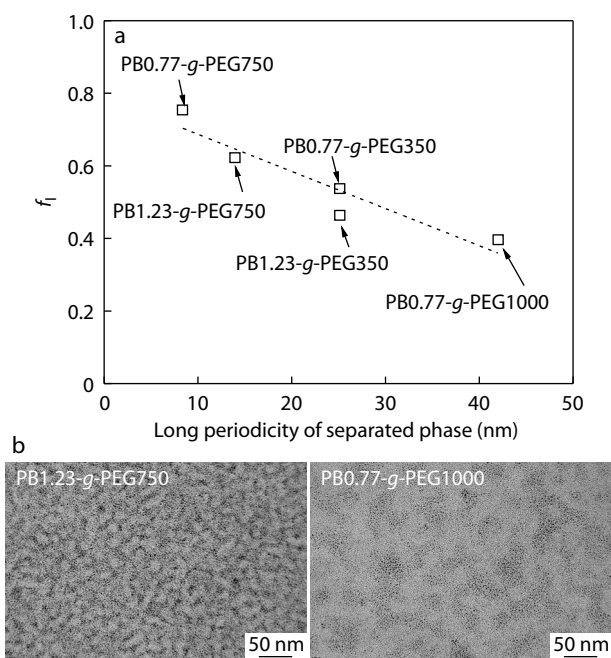


Fig. 7 (a) The correlation plot of transformed form I, f_I , with the periodicity of separated phases; (b) Typical TEM images of PB-g-PEG copolymers.

celerating II-I transition. This probably associated with the reason that the separated phases with the small periodicity have the relatively large interface, where those branching points connected two phases could facilitate the transport of internal stress to trigger the form I nucleation.

CONCLUSIONS

The post-metallocene catalytic system was employed to copolymerize butene-1 with 4-[4-(trimethylsilylalkynyl)-phenyl]-1-butene (Ph-TMS) to introduce the steric TMS groups into the isotactic polybutene-1 main chain. Subsequently, by reaction intermediate method, the polyethylene glycol branches were introduced by replacing trimethylsilyl with the azido-terminated polyethylene glycol. In this way, a series of poly(ethylene glycol) grafted polybutene-1 copolymers (PB-*g*-PEG) were prepared as the model materials to investigate the relation between the phase transition and the macromolecular architecture. For these PB-*g*-PEG copolymers studied in this work, branch density was controlled by varying the incorporation from 0.39 mol% to 1.23 mol%, while the branch length was tuned by changing PEG molecular weight within 350–1000 Da. The DSC results show that the introduction of poly(ethylene glycol) can cause the crystallization much faster than the steric TMS groups, although their incorporations were the same. More interestingly, the II-I phase transition of copolymers PB-*g*-PEG with PEG branches, have the much faster phase transition from tetragonal phase into trigonal phase than PB-TMS. Quantitatively, the kinetics of II-I phase transition is strongly dependent on both of branch density and length. As branch density was increased from 0.39 mol% to 1.23 mol%, the fastest transition kinetics was found with the intermediate 0.77 mol% branches. On the other hand, when PEG branch length was increased from $M_n=350$ Da to $M_n=1000$ Da, the optimal PEG branch of $M_n=750$ Da showed the maximum fraction of transformed form I for the fixed aging durations. These results clearly established the quantitative correlation between II-I phase transition with the PEG branch density and length.

NOTES

The authors declare no competing financial interest.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-022-2850-x>.

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