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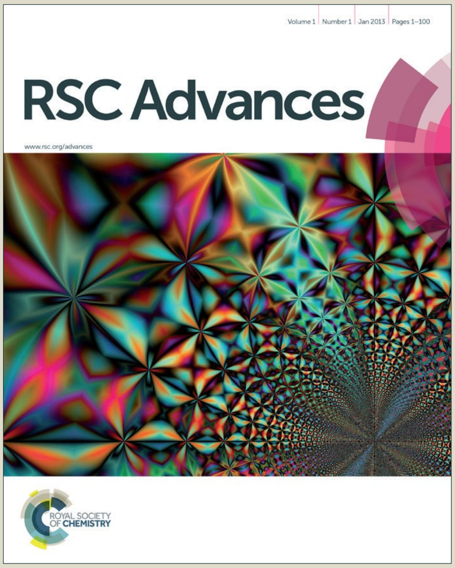

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The table of contents entry

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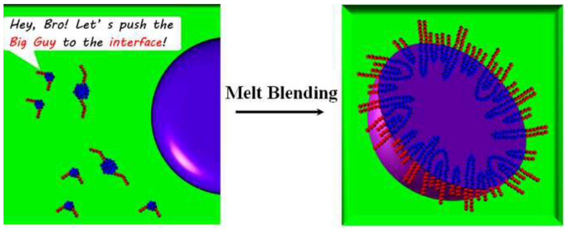

Systematical study on synergistic effects of different molecular weight PLA-PBAT-PLA tri-block copolymers on mechanical and rheological properties of PLA/PBAT blends.

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Synergistic effect of PLA-PBAT-PLA tri-block copolymers with two molecular weights as compatibilizers on mechanical and rheological properties of PLA/PBAT blends

Zhiqiang Sun, Bao Zhang, Xinchao Bian, Lidong Feng, Han Zhang, Ranlong Duan, Jingru Sun, Xuan Pang*, Wenqi Chen and Xuesi Chen

Two kinds of polylactide-poly(butylene adipate-co-terephthalate)-polylactide (PLA-PBAT-PLA) tri-block copolymers with different molecular weights (**CP1**, **CP2**) were synthesized as compatibilizers for PLA/PBAT blends. Synergistic effects of **CP1**&**CP2** on the mechanical and rheological properties of the blends have been studied in detail. The addition of small amounts of **CP1**&**CP2** increased the elongation at break remarkably and 0.5&0.5 wt% of **CP1**&**CP2** led to increase of elongation by over 8 folds. Thermal, morphological and rheological analysis showed that addition of **CP1**&**CP2** increased miscibility and interfacial bonding strength between PLA and PBAT, and decreased the melt viscosity. It was supposed that the low molecular weight compatibilizer of **CP1** with high mobility would have positive effect during the transportation of the high molecular weight **CP2** from matrix to the interface. And **CP2** played a key role in improving the interaction at the interface.

Introduction

As one of the most important bio-based and biodegradable aliphatic polyesters, polylactide (PLA) has been drawing intensive attraction in the past few decades.[1-3] PLA, especially poly(L-lactide) shows several favorable properties such as high modulus and strength comparable to that of many petroleum-based plastics. This makes it promising as a substitute for conventional polymers, e.g. in the fields of food packaging, table wares, nonwoven fibers, biomedical use, agricultural films and single-use disposable items.[4] However, the inherent brittleness or stiffness, slow crystallization, low elongation at break and physical aging of PLA resins have imposed constraints for their further applications.[5,6]

Therefore, intensive studies on improving the toughness of PLA have been carried out by means of copolymerization, plasticization and blending methods.[7,8] Among all these approaches, blending is one of the most practically and economically feasible methods for industrial applications.[9] Extensive efforts have been devoted to the study of blending PLA with other flexible and biodegradable polymers.[10] In view of its high toughness and biodegradability, poly(butylene adipate-co-terephthalate) (PBAT) was considered as a good candidate for the toughening of PLA.[11-13] The oil-based aliphatic-aromatic copolyester of PBAT is fully biodegradable, and it has been demonstrated that there is no indication of an environmental risk when PBAT was introduced into composting processes.[14] Although the dynamic mechanical analysis suggests that the presence of carbonyl groups in PBAT makes it potentially miscible with PLA, experimental results show that after blending equal to or more than 5 wt% of PBAT in PLA resin, the PBAT molecules are phase-separated with the PLA molecules.[15-17] As the macrophase separation and low adhesion between the two components would lead to poor mechanical properties of the blending materials, so that the compatibilization is essential for the application of PLA/PBAT blends.

It has been demonstrated that addition of bi-, tri- and multi-block copolymers into the blends could enhance the compatibility of most miscible and partially miscible blending systems.[18-21] The segments of these copolymers could be chemically identical with those in the respective phases, or miscible with or adhered to one of the phases. A sharp decrease in interfacial tension might be observed with the addition of small amounts of block copolymer.[22-25] Once the concentration reached the critical micelle concentration (CMC), the continue addition of more copolymer was useless. The redundant copolymer did not affect the interfacial situation but rather produced the micelles of the copolymer which would disperse in the homopolymer phases.[26] It has been proved that the CMC fell rapidly with the increasing molecular weight of the block

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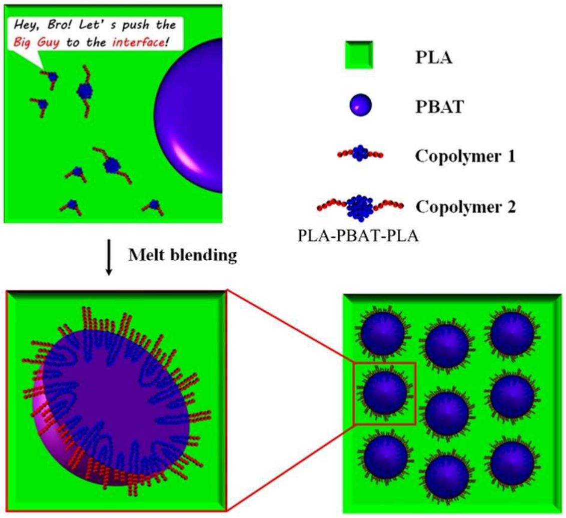
Electronic Supplementary Information (ESI) available: The synthetic process illustration, ^{1}H NMR spectra, GPC analysis of PBAT macro-initiators and PLA-PBAT-PLA tri-block copolymers; compositions of all the melt-blended specimens; tensile properties, SEM images and thermal properties of some samples. See DOI: 10.1039/x0xx00000x copolymer, as a micellar structure was preferred in the bulk of the homopolymer for long copolymer chains.[27,28]

Recently, a number of studies [29-33] have focused on the mechanical and rheological properties, as well as the morphology and miscibility of PLA/PBAT blends. Dil et al.[29] carried out a detailed examination of the miscibility, interfacial tension and morphology of PLA/PBAT blends by a variety of microscopic and rheological techniques. Arruda and coworkers [31] investigated the effects of chain extender and blend composition on the morphology and mechanical properties of the PLA/PBAT blown films. In the present work, two kinds of PLA-PBAT-PLA tri-block copolymers with different molecular weights were synthesized by ring-opening polymerization (ROP) of L-lactide (L-LA) using dihydroxy PBAT (HO-PBAT-OH) as macro-initiator. Different amounts of each triblock copolymer, as well as their mixture were intentionally added into the melt-blending system of PLA/PBAT (80/20, w/w) as compatibilizers. It was supposed that the tri-block copolymers with low molecular weight (CP1) and high mobility could act as carriers for delivering their coworkers with high molecular weight (CP2) to the interface (as illustrated by Scheme 1). The synergistic effects of the two copolymers on the mechanical and rheological properties of the blends were discussed. The two-component copolymer compatibilizers increased the elongation at break of the blends more efficiently than each of the single copolymer, at the same time maintaining other mechanical properties including Young's modulus and tensile strength. The improved mechanical properties should be attributed to the synergistic effects: low viscosity of the melts caused by the low molecular weight compatibilizer CP1, as well as the strong interaction between PLA and PBAT phases owing to the high molecular weight CP2.



Scheme 1. Schematic illustration of the synergistic compatibilization effect of two-component tri-block copolymer compatibilizers.

Experimental section

Materials

PLA (M_w =152,000 with a polydispersity of 1.3, T_g = 59.7 °C, T_m = 153.4 °C) used in this study was obtained from Zhejiang Hisun Biomaterials Co., Ltd (China). PBAT (M_w=70,000 with a polydispersity of 2.3, T_g = -31.2 °C, T_m = 119.9 °C) was purchased from BASF Corporation. HO-PBAT-OH macro-initiators and PLA-PBAT-PLA tri-block copolymers were prepared in our laboratory. The characterization data of the macro-initiators and copolymers were listed in Table 1. $Sn(Oct)_2$ and L-lactide (L-LA) were purchased from Aldrich, and L-LA was repeatedly recrystallized from dry ethyl acetate 3 times before use. Adipic acid (A.R.), 1,4-butanediol (A.R.), dimethyl terephthalate (A.R.) and tetrabutyl titanate (A.R.) were purchased from Sinopharm Chemical Reagent Co., Ltd (China) and used directly without further purification.

Representative Synthesis of HO-PBAT-OH Macro-initiator

HO-PBAT-OH macro-initiators were prepared by polycondensation reaction using tetrabutyl titanate as catalyst (Figure S1, step 1). Dimethyl terephthalate (19.4 g, 0.10 mol) , adipic acid (14.6g, 0.10 mol), 1,4-butanediol (19.8 g, 0.22 mol, overdose to ensure that the resulting polymers are terminated by -OH on both ends) and 0.1 wt% catalyst were charged into a 500 mL three-necked flask equipped with a stir bar, a nitrogen inlet and a condensation column. First, the monomer mixture was melted at 160 °C for 0.5 h. Then the temperature was raised to 180 °C and maintained for 2 h in N_2 gas atmosphere. Afterwards, the pressure of the reaction system was gradually decreased and the polycondensation reaction was continued under a final reduced pressure lower than 200 Pa for 6 h. And the temperature was increased from 180 to 225 °C during this period. At last, the flask was cooled down to room temperature, and the atmospheric pressure was restored under the protection of a nitrogen flow. After the reaction was completed, the mixture was dissolved in chloroform, and precipitated in 10-fold ice-cold ethanol. The product was subsequently separated by centrifuging, and dried under vacuum to obtain HO-PBAT-OH macro-initiators in the form of a white powder. Two kinds of HO-PBAT-OH with different components and molecular weights were prepared and used as macro-initiators (Initiator-1&2 in Table 1). Initiator-1: ^1H NMR ($CDCl_3$ with 0.05% v/v TMS, 300 MHz): δ 1.26 (s, 2H), 1.72-1.61(m, 64H),1.93-1.78(m, 40H), 2.04-1.94(s, 20H) ,2.35(s, 40H), 3.75(d of t, 4H, $J_{H,H}$ = 12 Hz, $J_{H,H}$ = 12 Hz), 4.21-4.06(m, 40H), 4.48-4.35(m, 40H), 8.16-8.08(s, 40H). Initiator-2: 1H NMR (CDCl3 with 0.05% v/v TMS, 300 MHz): δ 1.73-1.62(m, 154H),1.92-1.78(m, 86H), 2.08-1.92(s, 36H) ,2.34(s, 100H), 3.76(d of t, 4H, $J_{H,H}$ = 12 Hz, $J_{H,H}$ = 12 Hz), 4.22-4.04(m, 72H), 4.50-4.35(m, 72H), 8.16-8.07(s, 72H).

Representative Synthesis of PLA-PBAT-PLA Tri-block Copolymers

The PLA-PBAT-PLA tri-block copolymers were synthesized by ROP of L-LA using HO-PBAT-OH as a macro-initiator and $Sn(Oct)_2$ as the catalyst (Figure S1, step 2). The typical procedure was as follows: HO-PBAT-OH (Initiator-2, 10.3g, 1.14×10^{-3}mol) and L-LA (12.9g, 0.0896mol) were charged into

Table 1. ^{1}H NMR and DSC Analysis of the Synthesized Macro-initiators and Tri-block Copolymers.

Sample	^{1}H NMR				DSC	
	N_{PBA}[a]	N_{PBT}[a]	N_{PLA}[a]	M_n[b]	T_g[c] (°C)	T_m[c] (°C)
Initiator-1	10	10	0	4300	-40.6	127.5
Initiator-2	25	18	0	9000	-41.3	107.7
CP1	10	10	21	7300	3.8	118.8
CP2	25	18	38		-18.8	135.6

[a] Average number of the PBA, PBT and PLA units (N_{PBA}, N_{PBT} and N_{PLA}) in the initiators and tri-block copolymers, estimated by ^{1}H NMR. [b] M_n evaluated from ^{1}H NMR spectra. [c] Glass transition (T_g) and melting temperature(T_m) are calculated from reversing heat flow traces of DSC in the second heating run.

a 250 mL round bottom flask. After adding in a stir bar and sealing with a rubber septum, the reaction system was deoxygenated by evacuation and backfilled with N_2 for three times. Then the reaction mixture was sealed followed by immersing the flask into an oil bath preheated at 130 °C. When the monomer and initiator melted, $Sn(Oct)_2$ (4mg, 9.88×10^{-6}mol) was introduced into the flask to start the polymerization under the protection of N_2 gas. After reacting for 24 h, the mixture was cooled to room temperature and exposed to air, then dissolved in chloroform, and precipitated in 10-fold ice-cold ethanol. The product was separated by centrifuging, and dried under vacuum at 40 °C for 24 h to obtain PLA-PBAT-PLA tri-block copolymers (**CP1** & **CP2** in Table 1).

Blends preparation

Before melt-blending, PLA and PBAT were dried in a vacuum oven at 60 °C and 40 °C for 24 h, respectively, in order to prevent the polymer materials from hydrolysis during the melt blending process. The blending process was performed by a Torque Rheometer (XSS-300) with a rotor speed of 32 rpm at 180 °C for 5 min. PLA/PBAT blends at a fixed ratio (80/20, w/w) were prepared by melt blending in the presence of different amounts (i.e. from 0 to 2 wt%) of tri-blockcopolymer **CP1** or/and **CP2**. Sample codes (MB**x**-**y**) and compositions of blends are given in Table S1. Where **x** and **y** are the approximate percentage of **CP1** and **CP2** in the blends, respectively. The obtained blends were compressed into flat sheets about 1.0 mm in thickness by a compression molding machine at 180 °C under 10 MPa pressure for 5 min. Then the samples were cooled to room temperature in another compression-molding machine for further characterizations.

Characterizations

^{1}H NMR spectra were recorded on Bruker AV 300M in $CDCl_3$ (δ 7.27) at 25 °C. Chemical shifts were given in parts per million from tetramethylsilane. Gel permeation chromatograph (GPC, Waters 410) with chloroform as the eluent (flow rate: 1 mL/min, at 25 °C). Conventional calibrations were performed using polystyrene standards. Elongation at break, tensile strength, and Young's modulus of the samples were measured on a universal testing machine (Instron1211) at 25 ± 2 °C. The crosshead speed was 10.0 mm/min and the Young's modulus was measured between 0.05% and 0.25% strain. The hot molded specimens were shaped with a dumbbell-shaped cutter, and their effective length, width, and thickness were 20, 4, and 1 mm, respectively. An average value of 5 replicated measurements was taken for each sample. Differential scanning calorimeter (DSC) analysis was conducted on a TA Instrument DSC-Q100 under a N_2 atmosphere. Samples were heated to 200 °C at 10 °C/min and kept isothermal for 3 min to erase the thermal history, and then cooled to -60 °C at 10 °C/min, and finally reheated to 200 °C at the same rate. Each specimen was 4-5 mg and sealed in a 40 μl aluminum crucible. The rheological properties of blends in molten state were assessed using a parallel-plate (d = 25 mm) rheometer (Anton-Paar, Physica MCR301). The specimens were loaded between the parallel plates and melted at 190 °C for 3 min. The parallel plates subsequently compressed the molten specimens to 1.0 mm in thickness prior to each test. The viscoelastic properties of blends were determined by a dynamic frequency sweep test. The strain (5%) and frequency range (500–0.05 rad/s) were used during the testing. Complex viscosity (**η∗**), storage modulus (**G′**), as well as loss modulus (**G″**) in the molten state were obtained. The microstructure morphology of blends was observed by using scanning electron microscopy (ESEM, XL30). All samples were immersed into liquid nitrogen for 10 min, and then picked out and fractured immediately. The cryo-fracture surface was sputter coated with gold prior to examination. The acceleration voltage at the cathode was 5.0 kV.

Results and discussion

Synthesis of PLA-PBAT-PLA Tri-block Copolymer Compatibilizers

The tri-block copolymers compatibilizers (**CP1** and **CP2)** were synthesized by a two-step process (as illustrated in Figure S1). In the first step, two kinds of HO-PBAT-OH macro-initiators with two molecular weights were prepared by polycondensation reaction. During this step, 1, 4-butanediol was added overdose to ensure that both ends of the macro-initiators were terminated by –OH groups. And second, ROP of L-LA was initiated by these dihydroxy macro-initiators. The molecular structure and thermal properties of the macro-initiators and their offspring tri-block copolymers were listed in Table 1. The molecular components and the absolute molecular weight were determined by ^{1}H NMR spectra analysis. For example, the doublet of triplets (Figure S2A) at around 3.75 ppm was assigned to the methylene protons adjacent to –OH at the end of initiator-1. After the ROP of LLA (Figure S2B), the above mentioned doublet of triplets disappeared. And a multiplet appeared at about 5.18 ppm, which was assigned to the methine protons in the repeat units of PLA. Moreover, the doublet of triplets was used as an internal standard to determine the molecular structure of macro-initiators and tri-block copolymers. The singlet at 8.11 ppm was assigned to the aromatic protons of polybutylene terephthalate (PBT) repeat units. And the singlet at 2.32 ppm was assigned to the methylene protons of –CH_2COO- group in polybutylene adipate (PBA) repeat units. Thus the average number of the PBA, PBT and PLA units (N_{PBA}, N_{PBT} and N_{PLA}) in the macro-initiators and tri-block copolymer could be achieved. And the absolute molecular weight could be calculated inherently by the ^{1}H NMR results. The relative molecular weights and PDI were evaluated by GPC (Table S2). Because of the higher percentage of PBT units in initiator-1, it showed T_g and T_m higher than initiator-2 (Table 1). **CP2** showed T_m (135.6 °C) obviously higher than that of **CP1** (118.8 °C) due to its longer block chains of PLA units. And the T_m value of **CP2** was between T_m value of PBAT (119.9 °C) and PLA (153.4°C).

Mechanical Properties of Blends

In order to study the influence of copolymer compatibilizers on properties of melting blends, the melt-blended specimens with different amounts of CP1 or/and CP2 (listed in Table S1) were prepared. And the PLA/PBAT ratio was fixed to 80/20 (w/w). The typical tensile stress-extension curves of the melt-blended specimens with different compositions (Figure 1A and Figure S3) showed that the tensile property of PLLA/PBAT melt blending system could be alternated obviously by adding small amount of tri-block copolymer compatibilizers (less than 2.0 wt%). As shown in Figure S3A&S3B, the addition of 0.5 or 1.0 percent of **CP1** or **CP2** led to moderate improvements in elongation at break. However, when the amounts of the block copolymer compatibilizers were over 2%, no visible improvement were found any longer. This phenomenon is similar with the theoretical and experimental results reported for other melt blending systems in the presence of block copolymers.[21,27] It was noteworthy that adding 0.5 or 1.0 percent of **CP1&CP2** at the same time led to significantly improvement of elongation at break values (Figure 1A). The bar chart of Figure 1B visually demonstrated that MB0.5-0.5 showed elongation at break (~226%) over 8 times of MB0-0 (~27%). And this improvement in elongation was also distinctive compared to MB0.5-0 (~38%), MB0-0.5 (~66%), MB1.0-0 (~34%) and MB0-1.0 (~77%). Meanwhile, MB1.0-1.0 showed elongation at break value (204%) higher than that of MB1.0-0 (~34%), MB0-1.0 (~77%), MB2.0-0 (~13%) and MB0-2.0 (~29%). The noticeable improvements drop a hint that these two kinds of copolymers with different molecular weights might have synergistic effect on influencing the toughening properties of PLA/PBAT blends. Figure S4A&S4B showed that the tensile modulus and strength of different melt blending samples changed for blends with different amounts of compatibilizers. But the change values were statistically very little, which indicated that the addition of tri-block compatibilizers at this level (less than 2 wt%) could increase the elongation at break, while retaining the tensile modulus and strength of the blends.

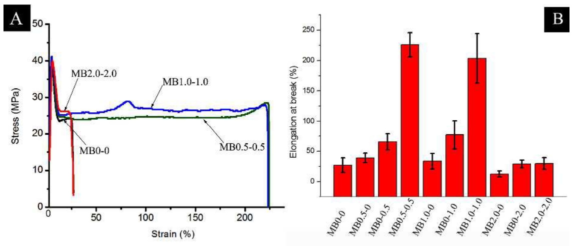


Figure 1. A) Typical stress–strain curves of MB0-0, MB0.5-0.5, MB1.0-1.0 and MB2.0-2.0. B) Average values of elongation at break of different melt-blended specimens, each sample was tested with a sample size (n) = 5.0.

Thermal Analysis of Blends

Typical DSC thermograms of PLA/PBAT specimens with different amounts of copolymer compatibilizers were shown in Figure 2. It is well known that T_g is an important indicator for the miscibility of blend components. [14] If two components are partially miscible, their T_g would shift towards each other.[34,35] The T_g of PLA and PBAT in the blends shifted towards each other after the addition of compatibilizers, suggesting improvement of miscibility between PLA and PBAT components. Sample MB0.5-0.5 with highest value of elongation at break, showed the smallest ΔT_g (gap between T_g of PLA and PBAT in the blends) among the blends listed in Table S3, which indicated better miscibility.

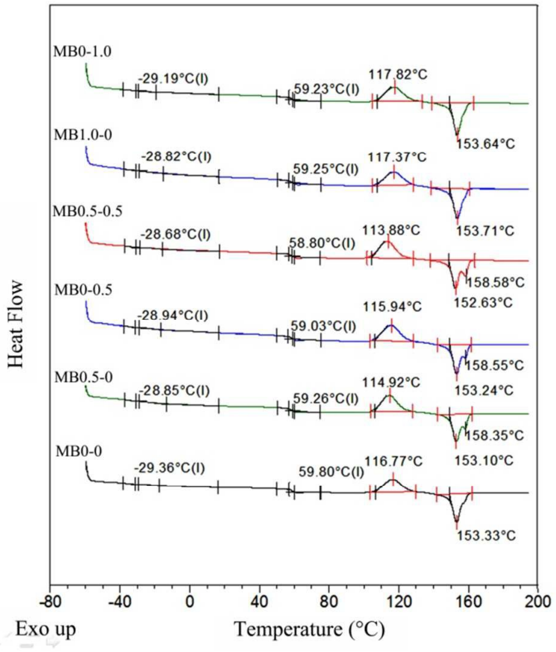


Figure 2. DSC curves of PLA/PBAT (80/20) blends with different amounts of copolymer compatibilizers. Heating rate 10 °C/ min and data from the second heat.

On the other hand, the melt blending samples of MBx-y showed in Figure 2 displayed the cold crystallization exotherms with onset temperature (T_{onset}) near 106 °C, and the cold crystallization temperature (T_c) near 115 °C. As seen from Table S3, MB0.5-0, MB0-0.5 and MB0.5-0.5 showed T_{onset}, T_c and T_m lower than that of MB0-0. Meanwhile, the enthalpy of crystallization (ΔH_c) and enthalpy of fusion (ΔH_m) of these three samples were higher than that of MB0-0. On the contrary, MB1.0-0 and MB0-1.0 showed T_{onset}, T_c, T_m and ΔH_m higher than MB0-0. Sample M1.0-0 showed $\Delta H_{c,}$ lower than MB0-0, and sample MB0-1.0 showed ΔH_c higher than MB0-0. All these results showed that by adding 0.5 wt% of **CP1** or/and **CP2** compatibilizers into the PLA/PBAT (80/20, w/w) blends could lower the crystallization temperature and increase the degree of crystallinity of the blends. This suggested that small amounts of copolymer compatibilizers could act as nucleating agent for PLA in the blends. According to our experiments, when the amounts of compatibilizers increased to over ~1 wt%, this regularity became not obvious. And the sample MB0.5-0.5 showed most obvious improvement in crystallinity, which also implied the synergistic effect of the two compatibilizers.

It was interesting that the DSC thermogram of MB0-0 showed a melting peak at 153.3 °C with a shoulder near 158 °C. The addition of 0.5 wt% of **CP1** or/and **CP2** compatibilizers clearly separated the melting peak and shoulder of MB0-0 into two individual peaks as shown in curves of MB0.5-0, MB0-0.5 and MB0.5-0.5. The peaks at higher temperatures corresponded to the shoulder of MB0-0. It has been reported that these bimodal melting peaks were induced during the DSC scans, when the less perfect crystals had enough time to melt and re-organized into crystals with higher structural perfection, and then re-melted at higher temperature.[17,36] As for MB0-0 and MB0-1.0, the melting shoulder that appeared on MB0-0 disappeared. This phenomenon also proved that small amounts of compatibilizers could increase the crystallization rate of PLA in the blends. And this improvement might be attributed to the increase of PLA chain segments mobility caused by adding low molecular weight compatibilizers.

Morphology Analysis of Blends

Typical SEM images of the cryo-fracture surfaces of MBx-y specimens were shown in Figure 3. All these blending samples had many demarcated phase-separated PBAT particles dispersing on their fracture surfaces. Figure 3A&3B showed that sample MB0-0 without copolymer compatibilizer had obvious interface between the PBAT particles and PLA matrix. And only a few of fibril structure could be seen in Figure 3A. As for sample MB0.5-0 with 0.5 wt% of **CP1**, a lot of short fibril structures appeared on the fractured surface (Figure 3C). The enlarge image of Figure 3D showed that these fibril structure mainly dispersed at the interface between PBAT particles and PLA matrix, which indicated that the **CP1** molecules were mainly located at the interface. However, obvious interface still could be seen in Figure 3D, which should be attributed to the low interfacial bonding strength between the two phases. When 0.5 wt% of **CP2** was added into the blends (seen from Figure 3E), more fibril structures could be seen compared to that in Figure 3A. And the fibril structures were obviously longer than that in Figure 3C. It was interesting that these fibril structures not only appeared at the interface, but also could be found rooting in the PLA matrix. This implied that it was more difficult for **CP2** to move from the matrix to the interface than **CP1**. Moreover, the interfacial debonding phenomenon showed in Figure 3F was more obvious than that in Figure 3B&3D, which suggested even lower interfacial bonding strength in MB0-0.5. From Figure 3C-3F, no obvious compatibilization effect could be seen at the interface by adding **CP1** or **CP2**.

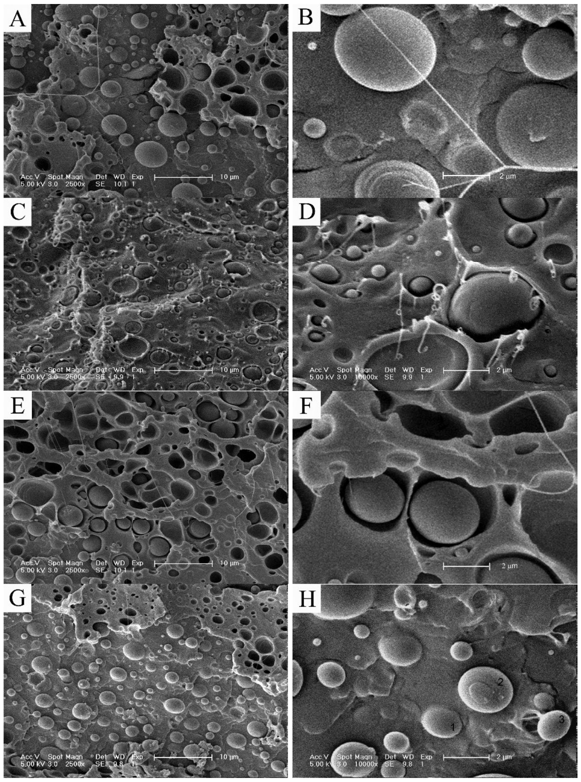


Figure 3. SEM micrographs of cryogenically fractured surfaces of PLA/PBAT (80/20, w/w) blends with different amounts of copolymer compatibilizers. A)&B), MB0-0, C)&D), MB0.5-0, E)&F), MB0-0.5, G)&H), MB0.5-0.5, respectively.

By contrast, the sample MB0.5-0.5 using 0.5&0.5wt% of **CP1&CP2** as two-component compatibilizers showed notable difference in microscopic morphology from other specimens. As shown by Figure 3G, more PBAT particles were adhered on the surface comparing with other samples, which implied stronger bonding strength at the interface. There are three PBAT particles marked in the enlarged image of Figure 3H. Particle **No.1** was mostly buried in the PLA matrix, showing no obvious interface between the two phases. A little cap-like structure could be seen on the surface of particle **No.2**, which was assumed to be a small piece of PLA torn off from the matrix. A few octopus-tentacle-like structures could be seen attached on the particle being dragged off from the PLA matrix (particle **No.3**). These three cases proved that the addition of 0.5&0.5wt% of **CP1&CP2** significantly improved the miscibility and obviously increased the interfacial bonding strength at the interface.

Furthermore, the addition of 1.0 wt% of **CP1** or **CP2** (sample MB1.0-0 and MB0-1.0) could hardly improve the miscibility of the blends (seen from Figure S5A-S5D), which showed distinctive interface and debonding between PBAT and PLA phases. As for MB1.0-1.0, the adhesion strength between the particles and matrix was higher than that of MB1.0-0 and MB0-1.0 (Figure S5E), and some cap-like structures could be found on the surface of PBAT particles. From the SEM characterizations, the synergistic effect of **CP1** and **CP2** on the interfacial miscibility of PLA/PBAT blends was intuitively observed. Apparently, it was easier for **CP1** with lower molecular weight to move to the interface during the melt blending process than **CP2** (Figure 3D&3F). But **CP1** showed poor ability in improving the interfacial miscibility and bonding strength between the two phases, which might be attributed to its short PLA and PBAT block chains. It was supposed that **CP1** could act as a carrier for **CP2,** and push **CP2** to the interface when these two compatibilizers were added at the same time. And **CP2** with longer block chains might be mainly responsible for the improvement the interfacial interaction.

Rheological Properties

The **η***, **G′** and **G″** with different amounts of **CP1** or/and **CP2** were compared in Figures 4. In Figure **4A,** M0.5-0 showed **η*** lower than MB0.5-0, and MB1.0-0 showed **η*** lower than MB0-1.0. This indicated that adding **CP1** resulted in lower viscosity than its high molecular weight counterpart of **CP2.** Among all these melt blending specimens, MB0.5-0.5 showed the lowest **η***, **G′** and **G″** at low frequencies, and only a little higher than that of MB0.5-0 at the high frequencies. The rotor speed (32 rpm) for melt blending was about 3.35 rad/s in angular frequency, which was just in the low frequency area. This means that during the blending process, MB0.5-0.5 showed melt viscosity similar with MB0.5-0, and lower than all the other blends. Moreover, MB1.0-1.0 showed **η***, **G′** and **G″** lower than MB1.0-0 and MB0-1.0. Thus these rheological curves proved that **CP1** and **CP2** had synergistic effect on decreasing the viscosity of the blends. In melting state, the

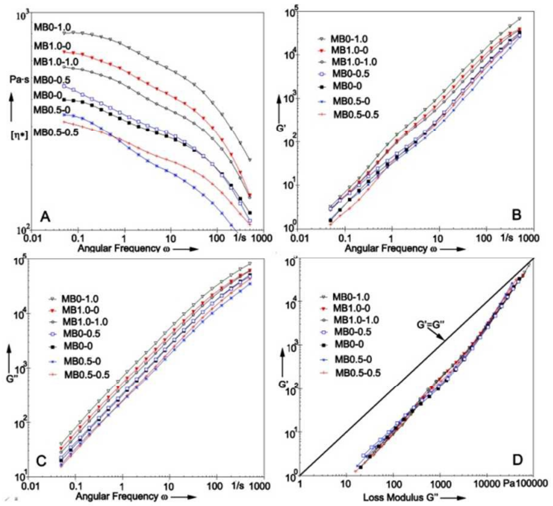


Figure 4. Rheological properties of the PBAT/PLA (80/20, w/w) blends with different amounts of compatibilizers (MBx-y) at 190 °C. A) Complex viscosity (**η***); B) Storage modulus (**G′**); C) Loss modulus (**G″**); D) Cole – Cole plots.

Cole-Cole plot is an important characterization of viscoelastic properties of polymer materials.[37-39] The straight line (**G′** = **G″**) divides the coordinate into two parts. Blow the straight line (**G′**<**G″**), the polymer materials presents major property of viscosity; on the contrary, it shows elasticity. As shown in Figure 4D, Cole-Cole plots of the PLLA/PBAT (80/20, w/w) blends were almost located below the straight line of **G′** = **G″**, which proved that these blends with different amounts of compatibilizers were more viscous than elastic component at the melting state.

Conclusions

Two kinds of PLA-PBAT-PLA triblock copolymers with different molecular weights were synthesized by ROP of L-lactide (L-LA) using HO-PBAT-OH as macro-initiators**.** Different amounts of the triblock copolymers were added into the melt-blending system of PLLA/PBAT as compatibilizers. Interestingly, these two kinds of copolymers showed synergistic effects on the mechanical and rheological properties of the blends. The addition of 0.5&0.5wt% of **CP1&CP2** led to increase of elongation at break value by over 8 folds. It was supposed that the compatibilizer with low molecular weight and high mobility had reduced the viscosity of the blends, and acted as carriers for their coworkers with high molecular weight. On the other hand, the compatibilizer with high molecular weight could increase the interaction between the PLA matrix and PBAT particles. It was expected that this paper could provide a new strategy for improving the mechanical and rheological properties of melt blending materials, which might be able to decrease the use level of copolymer compatibilizers as well as the total costs of the blends.

Acknowledgements

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Notes and references

Supporting Information

The synthetic process illustration, ^{1}H NMR spectra, GPC analysis of PBAT macro-initiators and PLA-PBAT-PLA tri-block copolymers; compositions of all the melt-blended specimens; tensile properties, SEM images and thermal properties of some samples. See DOI: 10.1039/x0xx00000x.

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Synergistic effect of PLA-PBAT-PLA tri-block copolymers with two molecular weights as compatibilizers on mechanical and rheological properties of PLA/PBAT blends

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Supporting information

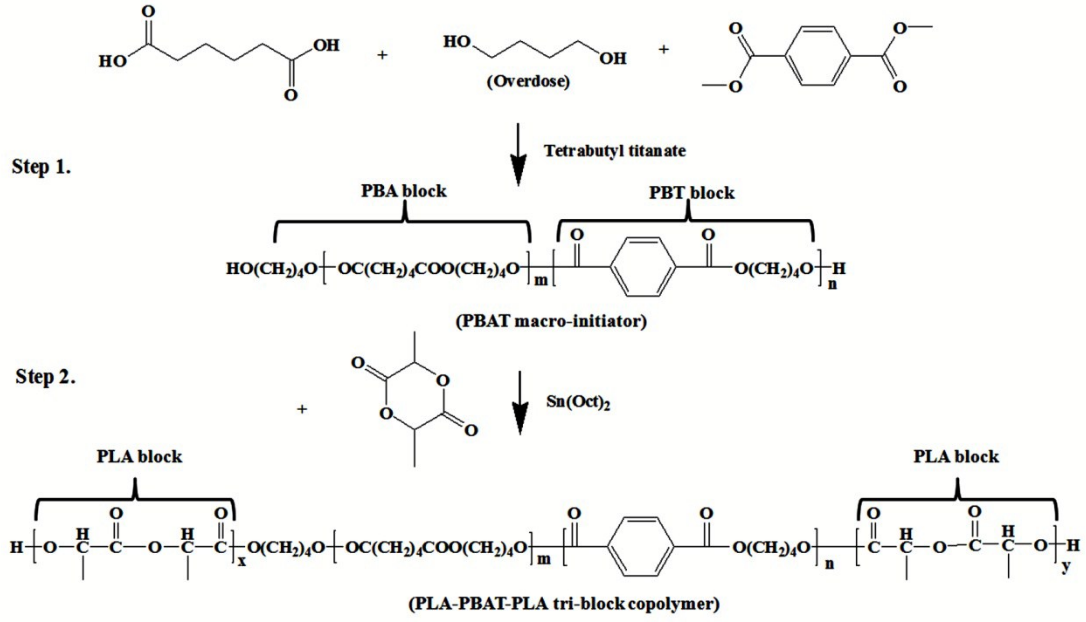

Figure S1. Synthetic process of PBAT macro-initiators and PLA-PBAT-PLA tri-block copolymers.

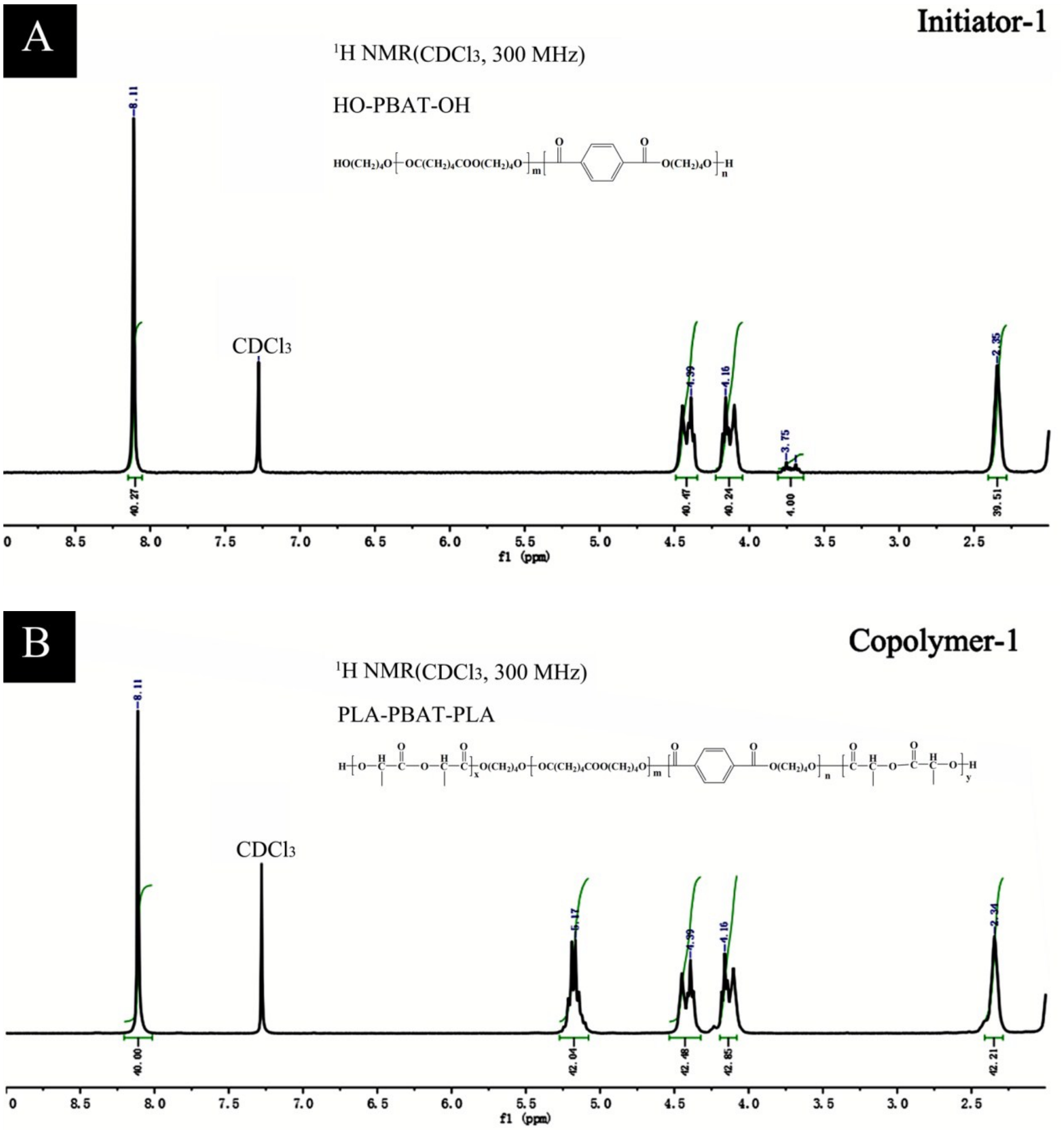

Figure S2. ^{1}H NMR Spectra of initiator-1 and tri-block **CP1**.

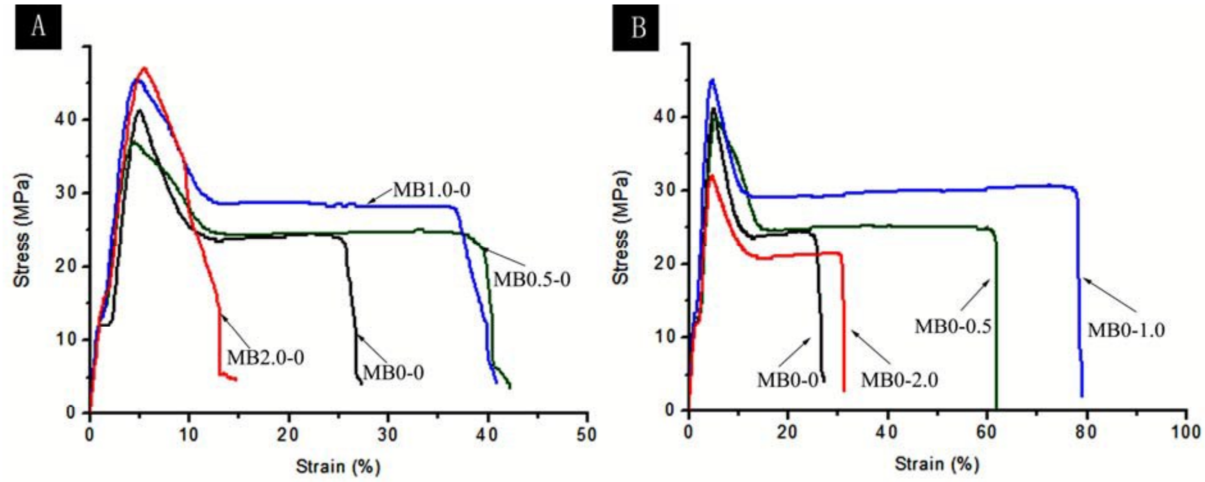

Figure S3. Typical stress–strain curves of melt-blended specimens with different amounts of **CP1** A) and **CP2** B)

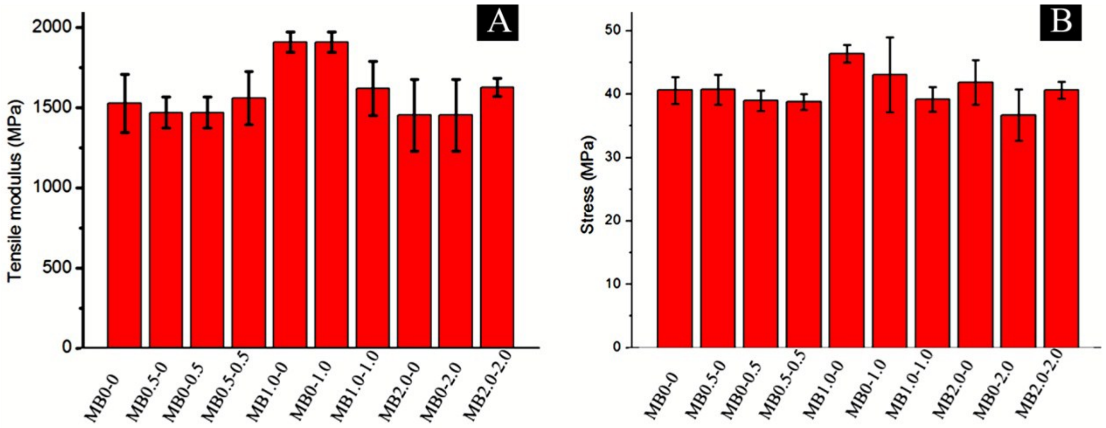

Figure S4. Average values of tensile modulus A) and strength B) of different melt-blended specimens, each sample was tested with a sample size (n) = 5.

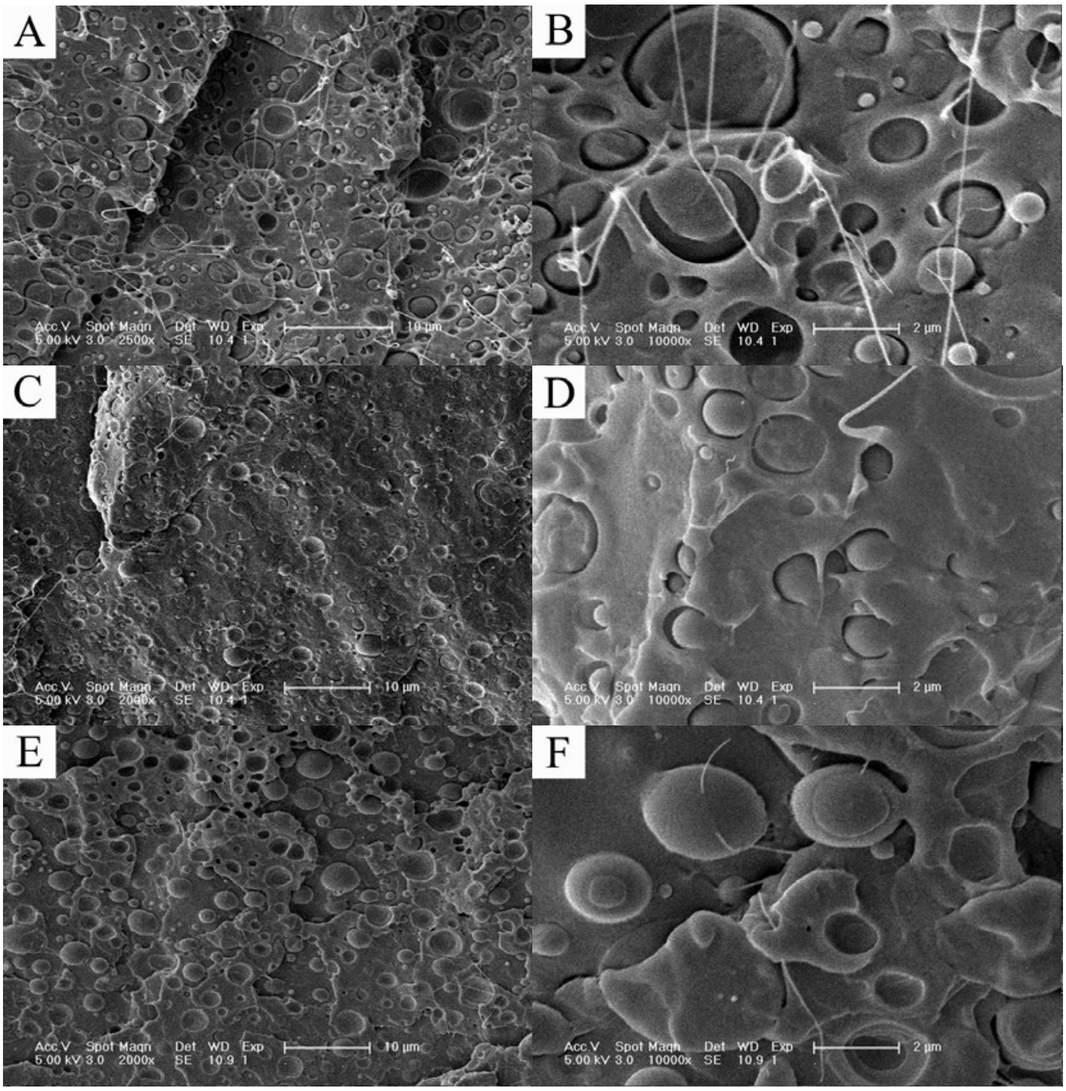

Figure S5. SEM micrographs of cryogenically fractured surfaces of PLA/PBAT (80/20, w/w) blends with different amounts of copolymer compatibilizers. A)&B), MB1.0-0, C)&D), MB0-1.0, E)&F), MB1.0-1.0, respectively

Table S1. The compositions of the melt-blended specimens. * Sample codes (MB**x-y**), where **x** and **y** are the approximate percentage of **CP1** and **CP2** in the blends, respectively.

Sample code *	**PLA (g)**	**PBAT (g)**	**CP1 (g)**	**CP2 (g)**
MB0-0	48	12	0	0
MB0.5-0	48	12	0.3	0
MB1.0-0	48	12	0.6	0
MB2.0-0	48	12	1.2	0
MB0-0.5	48	12	0	0.3
MB0-1.0	48	12	0	0.6
MB0-2.0	48	12	0	1.2
MB0.5-0.5	48	12	0.3	0.3
MB1.0-1.0	48	12	0.6	0.6
MB2.0-2.0	48	12	1.2	1.2

Table S2. GPC analysis of the synthesized macro-initiators and tri-block copolymers.

Sample Code	**GPC**		
	M_n[c] (kg/mol)	**M_w[c] (kg/mol)**	PDI[c]
Initiator-1	8.2	13.6	1.66
Initiator-2	11.9	21.2	1.79
Copolymer-1(**CP1**)	12.1	17.0	1.40
Copolymer-2(**CP2**)	18.1	29.0	1.60

Table S3. Thermal properties of different melt-blended specimens.

Sample code	ΔT_g (°C)	T_{onset} (°C)	T_c (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m (J/g)
MB0-0	90.2	106.4	116.7	17.7	153.3	20.0
MB0.5-0	88.2	106.0	114.9	19.2	153.1	21.7
MB0-0.5	87.9	106.0	115.9	20.54	153.2	22.1
MB0.5-0.5	87.5	104.4	113.9	21.3	152.6	23.3
MB1.0-0	88.1	107.4	117.4	17.3	153.7	22.0
MB0-1.0	88.4	107.5	117.8	19.9	153.6	22.8