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Tuning the Properties of Biodegradable Poly(Butylene Succinate) Via Random and Block Copolymerization

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Abstract: In this mini-review, the effect of random and block copolymerization on crystallization and properties of biodegradable poly(butylene succinate) is outlined. For random copolymerization, the effect of minor co-monomers can be divided into two categories: In most of the cases, the minor co-monomer units will be excluded from the crystal lattice of the major monomer units, which leads to the decreased melting point, lower crystallinity and slower crystallization kinetics. Consequently, the copolymers will be more flexible. Copolymerization with other aliphatic units results in enhanced biodegradation rate, while copolymerization with aromatic units may depress the biodegradation rate. There is an exceptional case, e.g. in poly(butylene succinate-co-butylene fumarate), where the co-monomer units can cocrystallize with the major monomer units in the whole range of copolymer composition, resulting in almost invariant degree of crystallinity. Whether some content of co-monomer units is included in the crystal lattice of the major monomer units or not is still an open question and deserves further study. Furthermore, block copolymerization is an alternative option to tune the properties, which may open a new window for designing biodegradable polymers, especially thermoplastic elastomers. Block and multiblock copolymers combine the properties of the different blocks and the crystallization behavior depends on the block length and miscibility of the blocks. When the block length is large enough, the melting point of such block will not vary much with its content, which is distinctly different from the random copolymers. Incorporation of more hydrophilic blocks, such as aliphatic polyethers will considerably enhance the hydrolytic degradation rate.

Keywords: Poly(butylene succinate), Random copolymerization, Block copolymerization, Crystallization, Biodegradability.

INTRODUCTION

Due to arising concerns about sustainable development, biodegradable polymers have attracted more and more attention during the past decades. Among them, poly(butylene succinate) (PBS) and its copolymers are a family of polymers with tunable physical properties and biodegradation rate, balanced mechanical properties and a wide processing window [1-4]. PBS homopolymer shows a melting point at around 114°C and has the similar mechanical properties to polyethylene. PBS can be thermally processed via extrusion, injection molding, film blowing and thermoforming, leading to wide applications in the field of packaging, commodity articles, supermarket bags and agricultural mulch films, etc. However, PBS articles and films are not so transparent and ductile due to the high degree of crystallinity. Copolymerization, including random and block copolymerization, is a feasible way to tune the condensed state structures so as to tailor design the degree of crystallinity, thus tune the mechanical properties and the biodegradation rate [5-20]. Synthesis, the crystalline structures, biodegradation and its industrial applications have been reported in the previous reviews [3]. In this mini-review, the effect of random and block copolymerization on crystallization, mechanical properties and biodegradation rate will be outlined.

RANDOM COPOLYMERS OF POLY(BUTYLENE SUCCINATE)

Random copolymers are a type of polymers with co-monomer units randomly appearing in the polymer backbone, which leads to the decrease of the sequence length of the major monomer units. For semicrystalline PBS copolymers, the effect of copolymerization on the properties depends on whether the co-monomer units can be included in the crystalline lamellar core of PBS or not. Usually, the co-monomer units are excluded from the crystalline lamellar core, thus the random copolymerization with small amount of co-monomers will lead to decrease of the lamellar thickness, thus lowering of the melting point, the degree of crystallinity, tensile strength and elastic modulus. On the other hand, increase of elongation at break, impact strength and biodegradation rate is expected to improve with the decreased crystallinity [5-10]. However, we do observe the cases that the co-monomer units are included in PBS crystalline region [21, 22]. Thus the degree of

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crystallinity will hardly change with copolymerization. In the following text, we will briefly summarize some research results by the two categories separately.

POLY(BUTYLENE SUCCINATE) RANDOM COPOLYMERS WITH THE MINOR CO-MONOMER UNITS EXCLUDED FROM THE CRYSTALLINE REGION

Various dicarboxylic acids [5-12] and glycols [13-20] have been randomly copolymerized with succinic acid and butanediol to produce PBS random copolymers. When the content of the minor co-monomer units is less than 40 mol%, copolymerization leads to steadily decreased melting point (Tm) and degree of crystallinity (Xc) whatever type of co-monomers are incorporated if these co-monomer units are excluded from the crystalline lamellar core, as shown in Figure **1** and Table **1**. It is revealed that the monomers with bulky substituent groups, *e.g.* phenyl, demonstrate more rapid decrease of the melting point and crystallinity with copolymerization,

In the whole composition range, PBS copolymers usually demonstrate the lowest melting point and the lowest crystallinity at a mediate content of co-monomer units [23]. For poly(butylene succinate-co-butylene adipate) (PBSA) [24-26] and poly(butylene succinate-co-ethylene succinate) (PBSES) [27], the minimum Tm and Xc appears at around 50 mol%. The result for PBSES is shown in Figure **2**.

Whether the co-monomer units are totally excluded into the amorphous region is still an open question. There are some evidences that these co-monomer units are excluded from the PBS crystalline core. For instance, the solid-state ^{13}C NMR characterization of poly(butylene succinate-co-20 mol% butylene adipate)

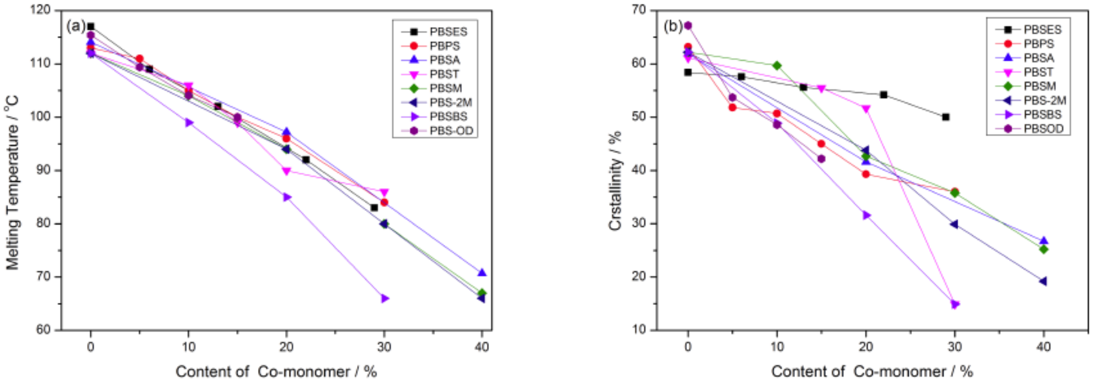


Figure 1: Effect of copolymerization on the melting point (**a**) and degree of crystallinity (**b**) of various random copolymers when the co-monomer units are excluded from the crystalline region. The abbreviates of the samples and the references of the data are listed as follows. PBSES: poly(butylene succinate-co-ethylene succinate) [27]; PBPS: poly(butylene succinate-co-propylene succinate) [13]; PBSA: poly(butylene succinate-co-butylene adipate) [36]; PBST: poly(butylene succinate-co-butylene terephthalate) [5]; PBSM: poly(butylene succinate-co-butylene methylsuccinate) [3]; PBS-2M: poly(butylene succinate-co-butylene dimethylsuccinate) [3]; PBSBS: poly(butylene succinate-co-butylene phenylsuccinate) [6]; PBSOD: poly(butylene succinate-co-1,2-octylene succinate) [14]. The figure is drawn by the authors using the data from the cited references.

Table 1: Thermal Properties and Degree of Crystallinity of PBSA Random Polyesters [4]. Copyright (2010) Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Polymer	ΔH_m (J/g)	ΔH^o_m (J/g)	T_m (°C)	T_g(°C) ^{a}	Crystallinity^b (%)	Crystallinity^c (%)
PBS	67.4	110.3	112	-18	61.1	39.66
PBSA-5^d	96.0	110.3	108	-21	87.0	54.47
PBSA-10	72.5	110.3	103	-23	65.7	45.83
PBSA-15	79.8	110.3	99	-27	72.3	45.27
PBSA-20	59.5	110.3	92	-34	53.9	46.83

[a] The glass transition temperature (Tg) was adopted from the tanδ peak measured by dynamic thermal analysis.
[b] The degree of crystallinity was the ratio of melting enthalpy determined by DSC to the melting enthalpy of complete crystalline PBS (110 J/g).
[c] The degree of crystallinity was calculated from WAXD results.
[d] The number indicates the molar percentage of adipic acid in the total feeded acids for synthesis of PBSA copolyester.

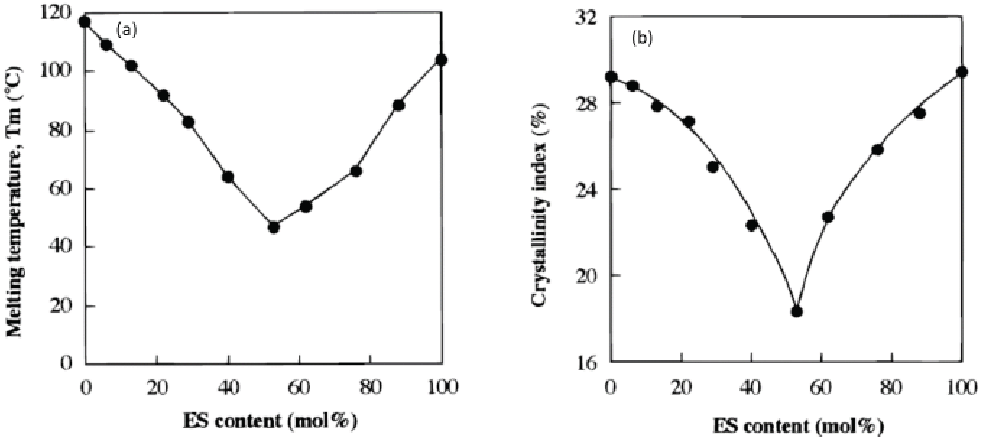


Figure 2: Effect of ethylene succinate (ES) content on the melting point (**a**) and degree of crystallinity (**b**) of poly(butylene succinate-co-ethylene succinate) random copolymers. Reprinted (adapted) with permission from ref 24. Copyright (1997) American Chemical Society.

has revealed that the butylene adipate units are not included in the PBS crystalline region since the butylene adipate units demonstrate only one relaxation time [28]. There are also reports showing that the co-monomer units of smaller size may be included in the crystalline lamellar core to some extent. For example, the minimum melting point and degree of crystallinity of poly(butylene succinate-co-propylene succinate) (PBPS) appears at the propylene diol content of 75 mol%, as presented in Figure **3a**. It is more easier for the propylene succinate to be accommodated in the PBS crystal lattice than it is for the butylene succinate units to be included in the poly(propylene succinate) crystal lattice [29]. Furthermore, the slight increase (less than 2 %) of the spacing of X-ray diffraction plane with increasing propylene succinate units from 0 to 43 mol% indicates some degree of inclusion of propylene succinate units into the unit cell of PBS. In contrast, poly(butylene succinate-co-butylene terephthalate) (PBST) copolymer with 30 mol% butylene terephthalate units possesses the lowest melting point, [5, 30] as shown in Figure **3b**. PBST with 60 mol% butylene succinate still shows the crystal lattice of poly(butylene terephthalate) type, while PBST with 30 mol% of butylene terephthalate demonstrates different crystal lattice from PBS, as shown in Figure **4**. Namely, the butylene terephthalate units are more easily to be excluded from PBS crystal lattice, while more butylene succinate units can be tolerated in poly(butylene terephthalate) crystal lattice.

When the minor co-monomer units are excluded from the crystal lattice of the major monomer units, the total crystallization rate (reciprocal of the half-time of crystallization) and the radial growth rate of spherulites will decrease with copolymerization, as revealed in Figure **5a** and **5b**.

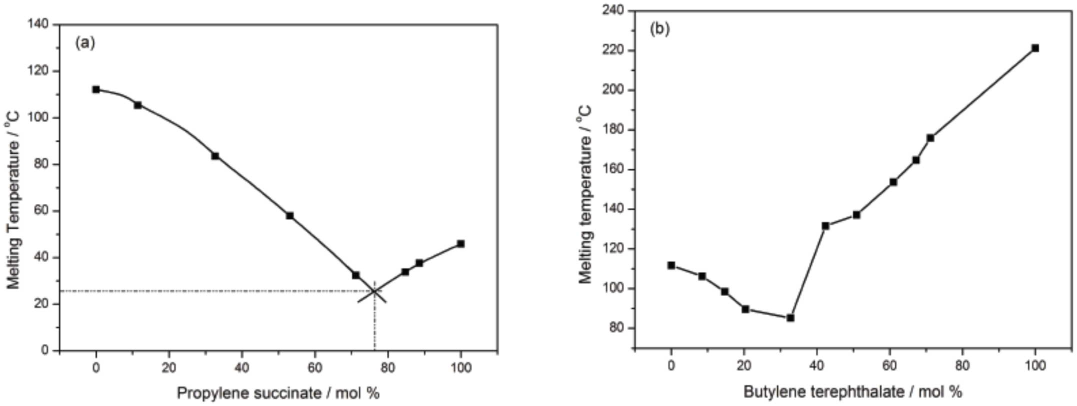


Figure 3: Effect of copolymerization on the melting point of poly(butylene succinate-co-propylene succinate) (**a**) and poly(butylene succinate-co-butylene terephthalate) (**b**). Figure 3a is adapted with permission from ref 26. Copyright (2007) American Chemical Society.

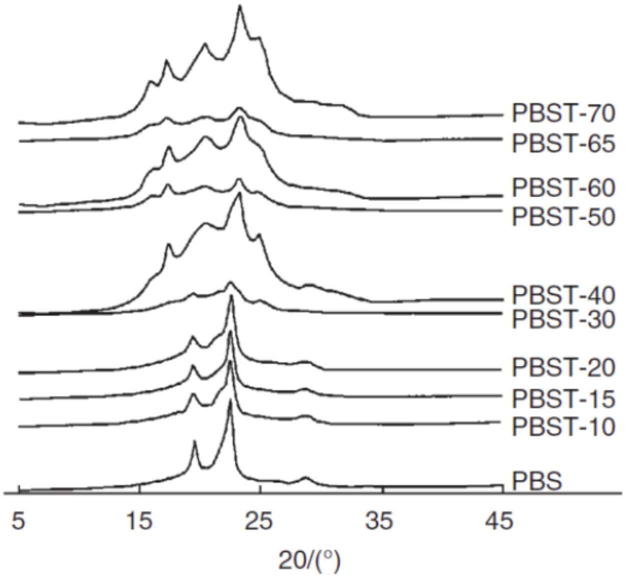


Figure 4: Wide-angle X-ray diffractogram of PBS and poly(butylene succinate-co-butylene terephthalate) (PBST). The number after PBST indicates the molar percentage of butylene terephthalate. The figure is adopted from reference 3. Copyright (2009) Springer-Verlag Berlin Heidelberg.

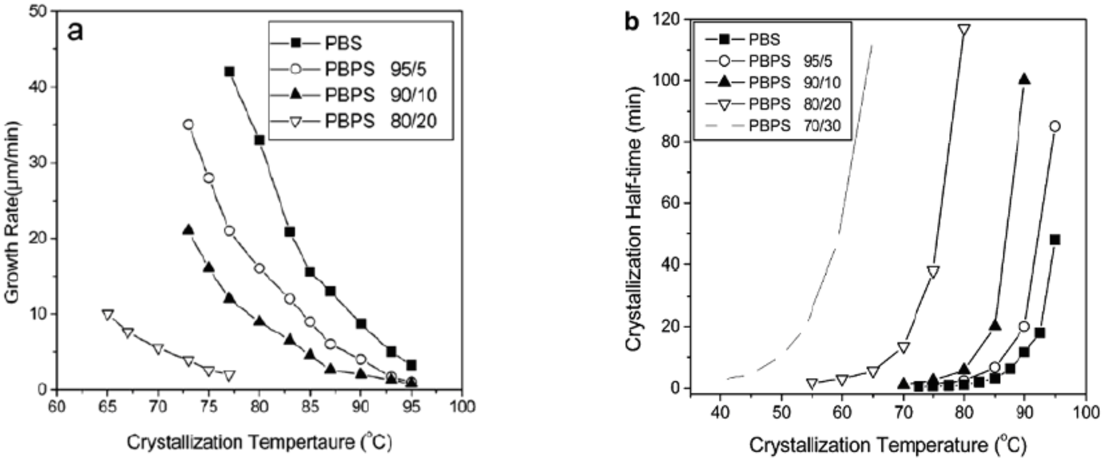


Figure 5: Radial growth rate of the spherulites (**a**) and the crystallization half-time (**b**) of poly(butylene succinate-propylene succinate) (PBPS). The number after PBPS indicates the molar ratio of butylene succinate to propylene succinate. The figures are adapted with permission from ref 29. Copyright (2007) American Chemical Society.

The mechanical properties of PBS copolymers mainly depend on the condensed state structures, including the degree of crystallinity providing that the molecular weights are similar. When the content of the co-monomer units is less than 40 mol%, the tensile strength tends to decrease and the elongation at break will increase due to the decreased crystallinity.

Unsaturated polyesters can be synthesized via incorporation of monomers with C=C bonds, such as muconic acid [31], malic acid [32, 33] and butene diol [34]. These unsaturated polyesters can be further chemically modified [32, 33].

The biodegradability of PBS copolymers varies with the chemical composition and the degree of crystallinity. Copolymerization with other aliphatic units results in enhanced biodegradation rate, while copolymerization with aromatic units may depress the biodegradation rate, as shown in Figure **6**. Generally, PBS copolymerized with aromatic co-monomers degrades slower than that with aliphatic co-monomers. For example, at the same content of co-monomer units, 20 mol%, poly(butylene succinate-co-butylene phenylsuccinate) degrades much slower in the activated sludge than poly(butylene succinate-co-

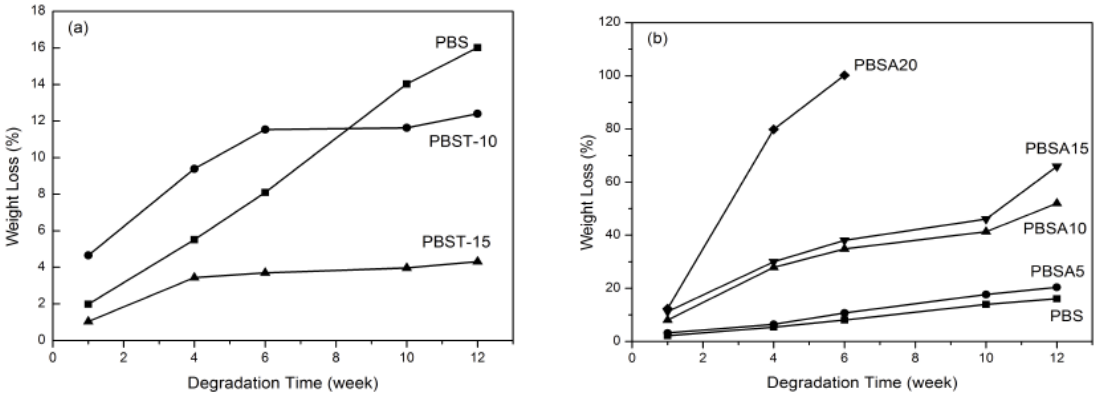


Figure 6: Biodegradation of films of poly(butylene succinate-co-butylene terephthalate) (PBST) (**a**) and poly(butylene succinate-co-butylene adipate) (PBSA) (**b**). The number after PBST and PBSA indicates the molar content of butylene terephthalate and that of butylene adipate, respectively. The figures are adopted from reference 4. Copyright (2010) Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

butylene methylsuccinate) and poly(butylene succinate-co-butylene dimethylsuccinate) [3, 4]. For PBS copolymerized with aliphatic co-monomers, the copolymers with the lowest crystallinity demonstrate the highest biodegradation rate. For example, PBSA shows the highest biodegradation rate when the butylene adipate content is near 50 mol% [24, 35, 36]. The enzymatic hydrolysis of poly(butylene succinate-co-ethylene succinate) show the similar trend [27]. Besides the degree of crystallinity, the chemical structure of co-monomers also has a considerable effect on the enzymatic degradation rate [37].

POLY(BUTYLENE SUCCINATE) COPOLYMERS WITH THE MINOR CO-MONOMER UNITS INCLUDED IN THE CRYSTALLINE REGION OF THE MAJOR MONOMER UNITS

In the above cases, the minor co-monomer units in the PBS copolymers are excluded from the crystalline region of the major monomer units, leading to decreased melting point and lowered degree of crystallinity. Is there any exception that the minor co-monomer units can cocrystallize with the major monomer units? Yes, there is. It had been reported that poly(butylene succinate-co-butylene fumarate) copolymers (PBSF) with the co-monomer units up to 20 mol% showed almost an unchanged crystallinity [21]. We speculated that the two types of monomer units can co-crystallize in the same crystal lattice. To confirm the proposition, we synthesized a series of PBSF copolymers with a wide range of butylene fumarate content [22]. It is found that in the whole composition range, the melting point of PBSF increases linearly with the copolymerization composition and the melting enthalpy hardly changes, as shown in Figure **7**.

Wide angle X-ray diffraction results demonstrate that PBSF shows a very similar crystal lattice to PBS, except that the unit cell parameters vary a little with copolymerization, as revealed in Figure **8**. The unit cell parameter *a* and *b* of poly(butylene fumarate) (PBF) increases by 4% and decreases by 2% compared to PBS, respectively. The area of the unit cell in the *ab* plane decreases only 2% from PBF to PBS [22].

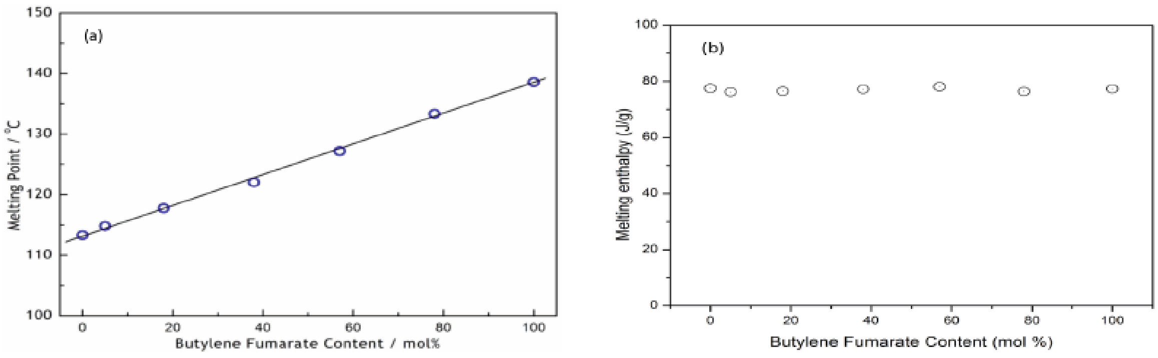


Figure 7: Melting point (**a**) and melting enthalpy (**b**) of poly(butylene succinate-co-butylene fumarate) random copolymers. Figure 7a is adapted with permission from ref 22. Copyright (2012) American Chemical Society.

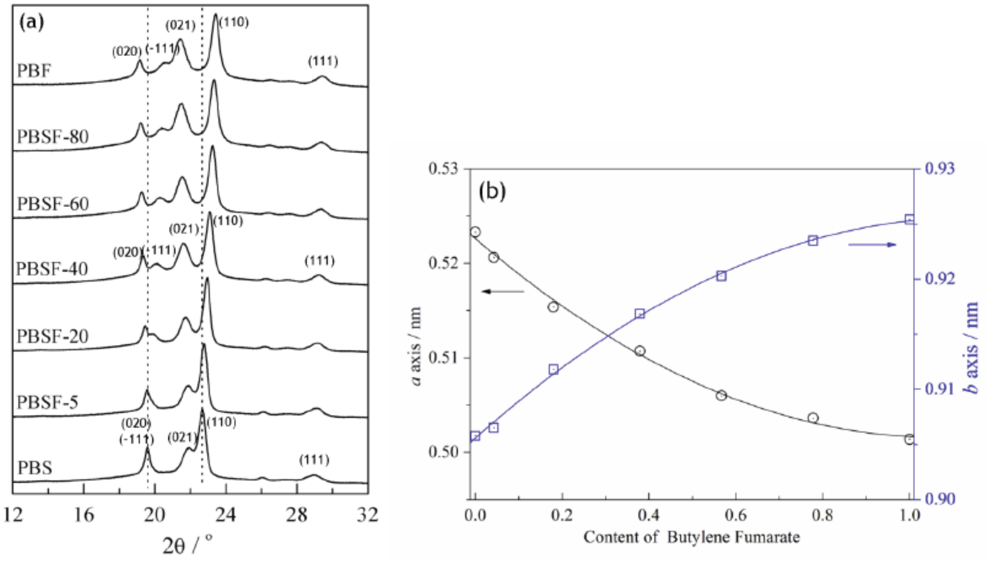


Figure 8: (**a**) WAXD diffractograms of poly(butylene succinate) (PBS), poly(butylene fumarate) (PBF) and their random copolymers poly(butylene succinate-co-butylene fumarate) (PBSF) isothermally crystallized at 70 ºC. The number after PBSF indicates the molar ratio of butylene fumarate; (**b**) Variation of the unit cell parameters of crystal lattice with composition. Reprinted with permission from ref 22. Copyright (2012) American Chemical Society.

This reveals that butylene succinate and butylene fumarate units in PBSF copolymers can cocrystallize in the same crystal lattice, namely, this is a strict isomorphism in the whole composition range. The reason is attributed to the fact that the two monomer units have almost the same size and the *trans* configuration of the fumarate units in the PBSF copolymers is very similar to the conformation of the succinate units in the PBS crystal lattice. It was reported that the succinate units adopt *trans* conformation in the crystalline lattice of the usual α form crystals. The only difference between the fumarate and succinate units is that the former possesses a double bond. When we copolymerized PBS with malic acid, the malate units with gauche configuration were excluded from PBS crystal lattice.

Since the C=C double bond in the fumarate units hinders the free rotation of the backbone, the decreased entropy barrier during crystallization of PBSF copolymers leads to increase of the total crystallization rate and the radial growth rate of the spherulites, as shown in Figure **9**.

The minor variance of the crystal lattice of PBSF copolymers is of particular interest. The biggest difference of crystal lattice between PBS and PBF is 2.1%. The little mismatch between PBS and PBF allows for epitaxial crystallization of PBS on PBSF perfectly [38]. The experimental results reveal that PBSF, especially PBF can work as a highly efficient nucleating agent for PBS [39]. After addition of 2 wt % PBF, the crystallization temperature of PBS during

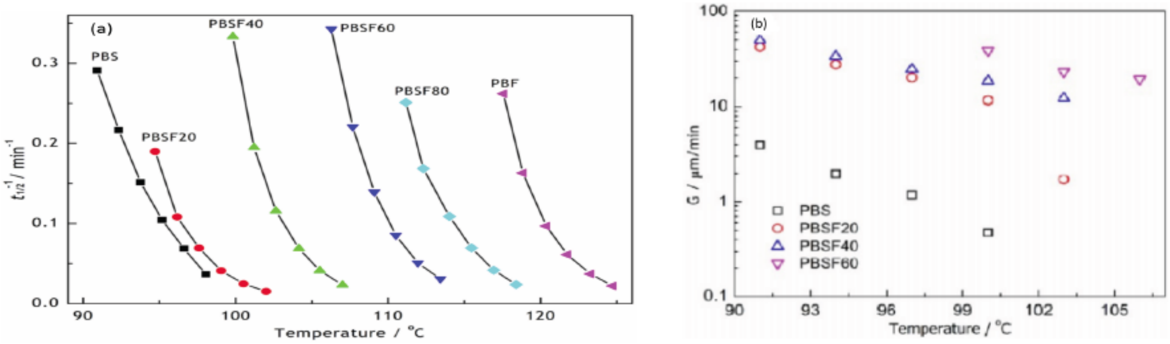


Figure 9: Crystallization half-time (**a**) and the radial growth rate of spherulites of poly(butylene succinate) (PBS), poly(butylene fumarate) (PBF) and their random copolymers poly(butylene succinate-co-butylene fumarate) (PBSF) isothermally crystallized at various temperatures. The number after PBSF indicates the molar ratio of butylene fumarate. Reprinted with permission from ref 22. Copyright (2012) American Chemical Society.

cooling from melt increases by 19 ºC, from 74 to 93 ºC. The total crystallization rate at 100 ºC increases by 15 folds compared to pristine PBS. Compared to the usual small molecular nucleating agents, the polymeric nucleating agent is more efficient, cheaper and can be finely dispersed in the polymer matrix.

The enzymatic degradation experiment of PBSF copolymer system with low content of butylene fumarate has been investigated by Nikolic *et al* in 2003 [21]. The degradation rate decreases with the increasing content of unsaturated units in the copolymer of PBSF. The reason for the decreasing degradation rate is supposed due to the decrease of spherulite diameter. We speculate that the stronger interaction between the unsaturated units in the crystal lattice may be another reason.

BLOCK COPOLYMERS CONTAINING POLY(BUTYLENE SUCCINATE)

Block copolymers have two or more homopolymer units linked by covalent bonds and they have the advantage of defined structure in each block compared to random copolymers. If the poly(butylene succinate) block has a defined and high enough block length, its melting point will not vary much with the weight percentage of the block, which is distinctly different from the random copolymers with melting point varying considerably with copolymerization. In this section, block copolymers refer to AB type diblock copolymer or ABA type triblock copolymer. Multi-block copolymers will be discussed in the following section. Biodegradable block copolymers are prepared mostly by sequential addition of monomers using living polymerization, in which the unit ratio, the length of each block and the block arrangement can be tuned in a desired and precise way. Extensive work has been carried out on biodegradable block copolymers, such as poly(L-lactide)-*b*-poly(butylene succinate)-*b*- poly(L-lactide) (PLLA-*b*-PBS-*b*-PLLA) [40-43], poly(D-lactide)-*b*-poly(butylene succinate)-b- poly(D-lactide) (PDLA-*b*-PBS-*b*-PDLA) [43, 44], poly(ethylene glycol)-*b*-poly(butylene succinate) (PEG-*b*-PBS) and poly(butylene succinate)-*b*-poly(ethylene glycol)-*b*-poly(butylene succinate) (PBS-*b*-PEG-*b*-PBS) [45].

The crystallization process of diblock or triblock copolymers is rather complex and affected by many factors including interactions between two blocks, the length and ratio of two blocks, the ability of crystallization of the blocks and so on. For instance, the crystallization behaviors of PDLA and PBS blocks in PDLA-*b*-PBS-*b*-PDLA strongly depend on the composition [44]. For the PDLA block, its crystallization rate is lower than that of PDLA homopolymer. For the PBS block, its crystallization rate varies with the block length of PDLA, and the crystallization rate is the highest in the B-D 2-2 specimen, which is a result of nucleation and confinement by PDLA block. The stress-strain curves of the PLLA-*b*-PBS-*b*-PLLA block copolymers with different compositions are shown in Figure **10**. Neat PLLA exhibits an elongation at break of only 4.2% without yielding during the course of stretching, while all the block copolymers yield before break [41]. The strain at the break of the triblock copolymer containing 25 wt% of PBS increases up to 380%, much higher than that of neat PLLA.

MULTI-BLOCK COPOLYMERS OR SEGMENTED COPOLYMERS CONTAINING POLY(BUTYLENE SUCCINATE)

Multi-block copolymers, or segmented copolymers, often consist of multiple covalently bonded oligomeric segments with different structure and properties.

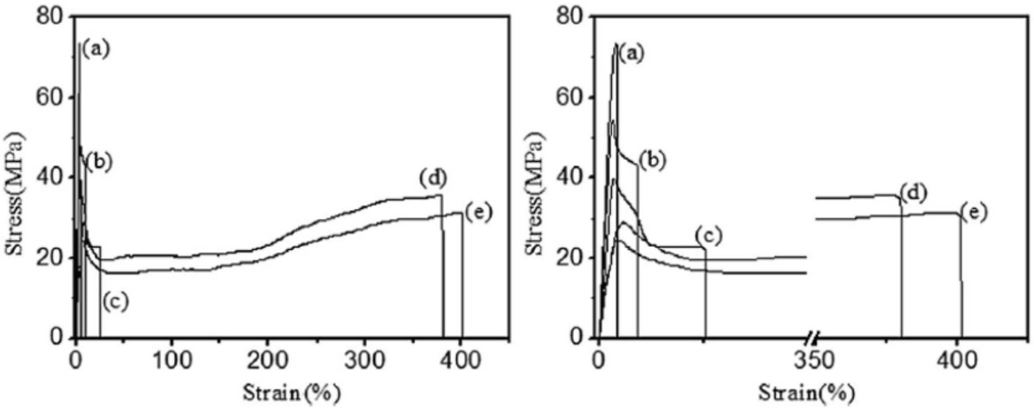


Figure 10: Stress-strain curves of the PLLA-*b*-PBS-*b*-PLLA block copolymers with different PBS contents: (**a**) neat PLLA; (**b**) 5%; (**d**) 15%; (**d**) 25%; (**e**) 35%. The right curves show details of the stress-strain curves around the yield points. Adopted from Ref 41. Copyright (2005) Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

Compared to diblock or triblock copolymers which have well-defined block length and narrow polydispersity, the block length, overall molecular weight and polydispersity of segmented copolymers cannot be controlled that precisely. But much more choices of polymer structures are offered by segmented copolymers. It is known that a random microstructure often leads to a sharp decrease of melting temperature and crystallinity, which limits the application of end-use materials. This problem can be avoided by preparing segmented copolymers. Conventionally, the biodegradable segmented copolyesters can be synthesized by step-growth polymerization, which involves two steps: in the first step, low molecular weight oligomeric polyester segments with terminal hydroxyl groups are prepared. In the second step, chain extenders are used to link different segments, yielding high molecular weight segmented polyester. A variety of aliphatic segmented copolyesters has been prepared, including poly(ethylene succinate)-*b*-poly(butylene succinate) [46, 47], poly(butylene succinate)-*b*-poly(L-lactide) [48-50] , poly(butylene terephthalate)-*b*-poly(butylene succinate) [51], poly(butylene succinate)-*b*-poly(ε-caprolactone) [52, 53], Poly(L-lactide)-*b*-poly(butylene succinate-co-butylene adipate) [54], poly(butylene succinate)-*b*-poly(propylene carbonate) [55], etc.

The properties of segmented copolyesters are influenced by many factors, such as the miscibility, crystallizability, the relative content and the length of each segment and so on. Zeng *et al*. [56] prepared biodegradable segmented copolymer poly(butylene succinate)-*b*-poly(l-lactic acid) (PBS-*b*-PLLA) and found that PBS segments are well compatible with PLLA segments. The crystallization process is predominantly caused by PBS segments and the mechanical test shows that the toughness of PLLA could largely be improved after introducing PBS segments. In addition, Zeng *et al*. [46] prepared a series of biodegradable double crystalline poly(ethylene succinate)-*b*-poly(butylene succinate) (PES-*b*-PBS) segmented copolyesters with various PES and PBS block lengths. The number average molecular weight of PES segment ranges from 3380 to 6500 g/mol and that of PBS segment ranges from 2940 to 6740 g/mol. When the segment length of PBS and PES are less than 4710 g/mol, the amorphous phase of the two blocks are miscible. When the block length increases to more than 5430 g/mol, the amorphous phases of the two blocks change to be partially miscible and the miscibility decreases with increasing block length. Furthermore, the crystallizability of PES block increases, which is explained by the nucleating effect of the existed PBS crystal.

In poly(butylene succinate)-*b*-poly(propylene succinate) (PBS-*b*-PPS) [57] segmented copolymers with one crystalline block and one amorphous block, the microstructure and deformation process during drawing were studied. The noncrystalline PPS chains predominantly locate in the amorphous phase of PBS. The transition from α crystal to β crystal is observed for all PBS-*b*-PPS samples. The critical stress for α-β crystal transition is about 70 MPa, which is independent of PPS blocks. The universal critical stress for crystal transition is explained by a single microfibril stretching mechanism, as shown in Figure **11**.

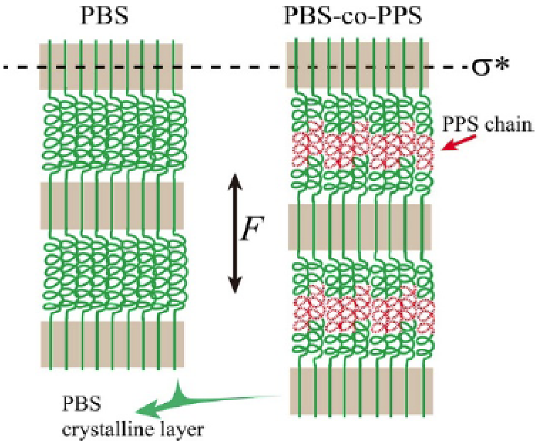


Figure 11: Schematic illustrating the origin of universal critical stress for poly(butylene succinate)-*b*-poly(propylene succinate) (PBS-*b*-PPS) based on single microfibril-stretching-mechanism. The straight green lines in gray region represent PBS chains in amorphous layer. The PPS chains are drawn as red dashed curves. Adopted from Ref [57] (Copyright 2014. Reproduced with permission from American Chemical Society).

Another method to obtain poly(butylene succinate-*b*-ether) segmented copolymers is via polycondensation of succinic acid, butane diol with hydroxyl-terminated polyether, such as poly(ethylene glycol) (PEG) [58-60], poly(propylene glycol) (PPG) [61], poly(tetramethylene glycol) (PTMG) [62-64]. In fact, it is another example of random copolymerization. Though the length of polyether segment is defined, the length of polyester segment is random. As a result, the melting point of the polyester segment and the tensile stress of the materials will decrease, while the elongation at break and impact strength will increase with increasing content of the polyether when the content of polyether is not too high [61, 63, 64].

Besides their biodegradability, the multiblock polymers can be applied as functional materials. For example, Huang *et al.* [60] synthesized thermally-induced shape memory segmented copolymer poly(butylene succinate)-poly(ethylene glycol) (PBSEG) by polycondensation from succinic acid, 1,4-butanediol and PEG diol. In PBSEG molecular chains, the PBS segments act as crystallizable hard segments that could supply strong physical net points for permanent shape and the soft PEG segments act as switching segments at 27.5-51.4 ºC. The shape memory test shows that PBSEG has excellent shape memory effect with recovery ratio up to 90%, as demonstrated in Figure **12**, indicating that this copolymer may find potential application in intelligent medical devices. In addition, Huang *et al.* [65]. investigated the fractional crystallization, homogeneous nucleation of the PEG segment and self-nucleation behavior of the PEG segment within miscible double crystalline PBSEG.

Most of the aliphatic polyesters have poor hydrophilicity while polyethers have good hydrophilicity. Several studies [59, 61, 64, 66] investigated the biodegradation and hydrolytic degradation of aliphatic block polyesters containing polyether segments. The results showed that with the introduction of polyether segments, the hydrolytic degradation is accelerated while the biodegradation rate remains almost constant. Figure **13** shows the accelerated enzyme catalyzed hydrolysis in the segmented polymer.

Another method to obtain segmented or multi-block polyesters is via polycondensation of two hydroxyl-terminated homopolyesters, e. g., poly(butylene succinate) with another polyester, such as poly(butylene terephthalate) [67], poly(ethylene

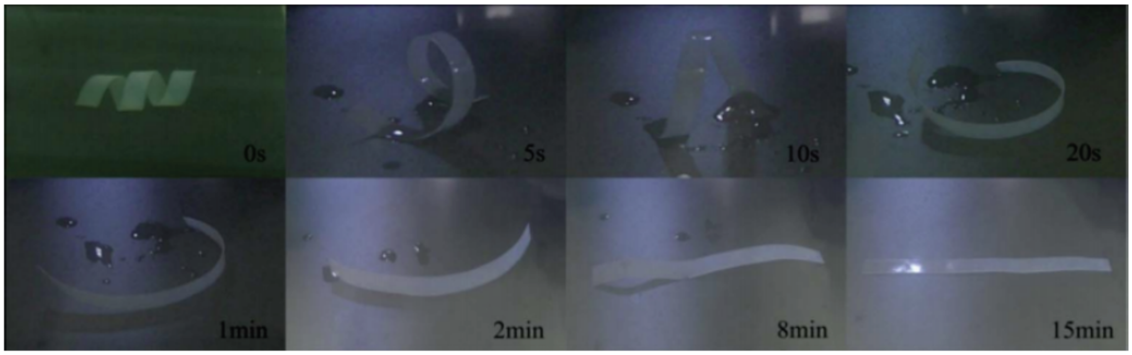


Figure 12: A series of photographs showing the shape-memory effect of PBSEG from temporary shape (spiral) to permanent shape (straight) at 37ºC [60] (Copyright 2012. Reproduced with permission from Royal Society of Chemistry).

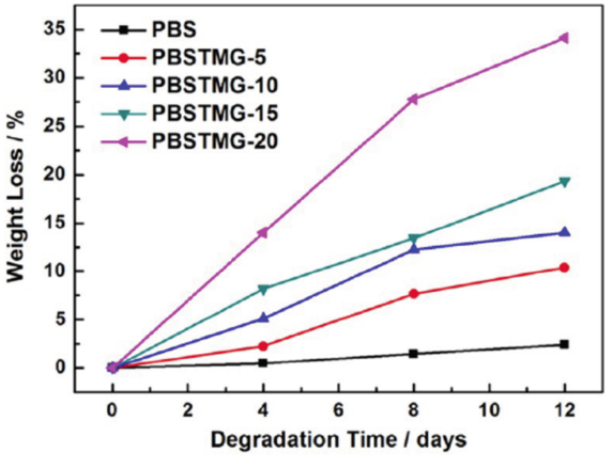


Figure 13: Weight losses of PBS homopolymer and poly(butylene succinate)-co-poly(tetramethylene glycol) (PBSTMG) segmented polymer films in enzymatic degradation tests in a 1 mg/mL enzyme solution for different days at 35 °C. The amano lipase from *Pseudomonas fluorescens* was used as the enzyme. The Arabic number in the sample name indicates the weight percentage of the polyether blocks. Adopted from Ref 64 (Copyright 2017. Reproduced with permission from American Chemical Society).

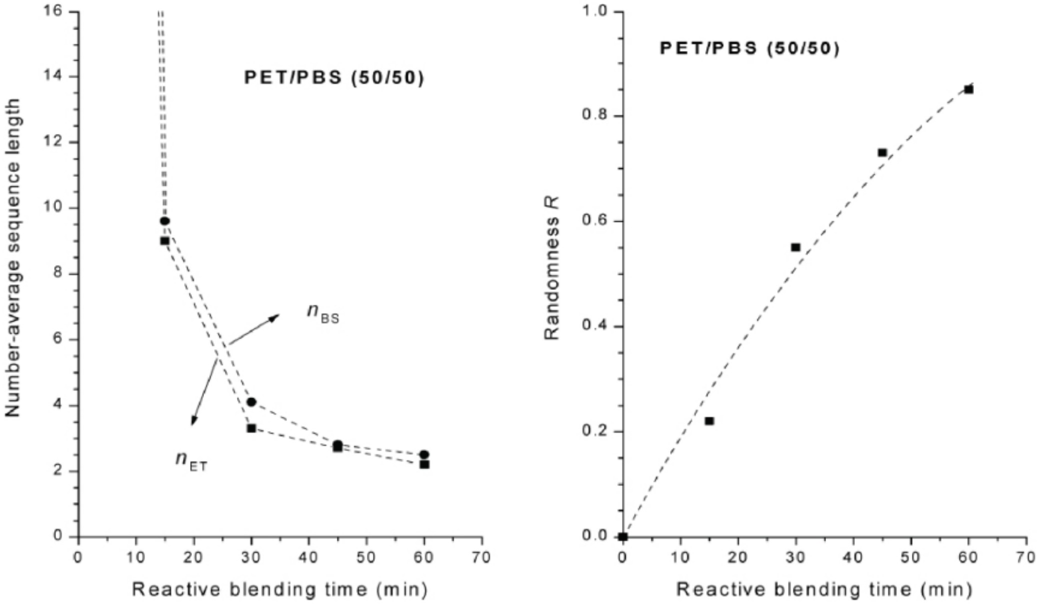


Figure 14: Variation of the number-average sequence lengths (left) and the degree of randomness (right) upon reactive blending (catalyzed transesterification) of the PET/PBS (50/50) blend. Adopted from Ref 68 (Copyright 2003. Reproduced with permission from Elsevier Science Ltd.).

terephthalate) [68], poly(butylene fumarate) [69] , polylactide [70]. In this method, the number average sequence length decreases and the randomness increases with reaction time, as revealed in Figure **14**. [68]. The multiblock copolymers can be utilized as compatibilizers for the corresponding homopolymers [70].

The molecular formulae of the random and block copolymers containing butylene succinate units in this review are summarized in Table **2**.

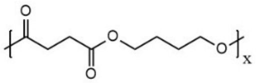
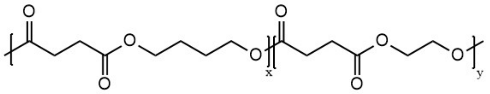
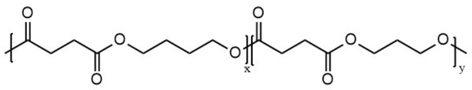
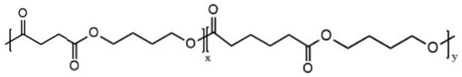
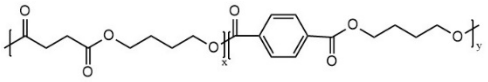
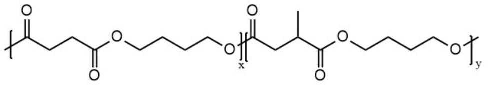
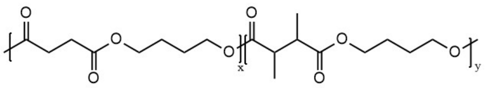
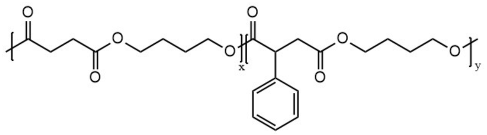
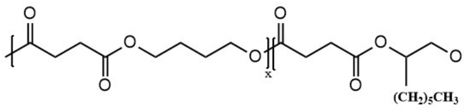
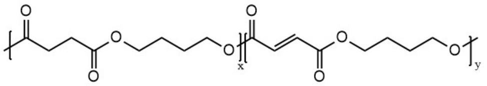
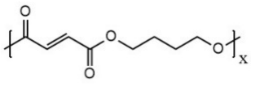
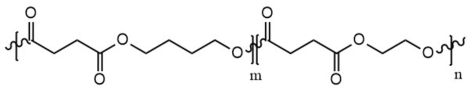
CONCLUSIONS AND PERSPECTIVE

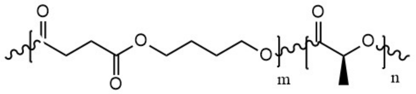
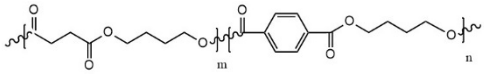
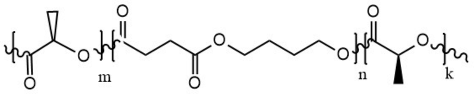
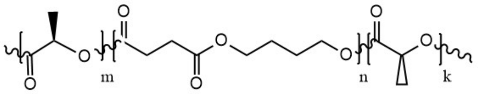
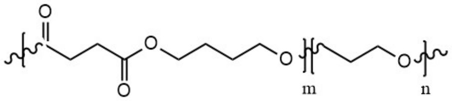
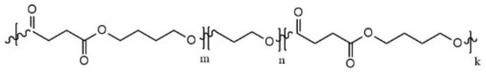
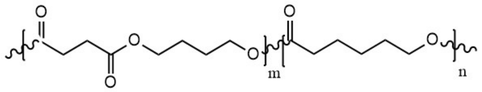
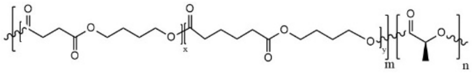
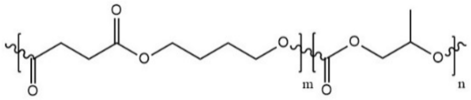
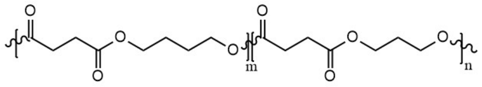
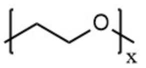
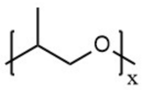
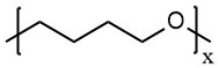
Random and block copolymerization are effective methods to tailor design the thermal, mechanical properties and the biodegradation rate of poly(butylene succinate). For random copolymers, depending on the size and configuration of the co-monomer units, the co-monomer units will be excluded or included in the crystalline lamellar core of the major monomer units, respectively. In the former case, copolymerization with a small amount of co-monomer units leads to decreased melting point and crystallinity, thus resulting in weaker tensile strength and larger elongation at break. Biodegradation rate depends on not only the degree of crystallinity but also the chemical composition of the copolymer. Lower crystallinity enhances biodegradation rate and the aromatic co-monomer units may hinder biodegradation. In the case of poly(butylene succinate-co-butylene fumarate) (PBSF), the two types of monomer units can both be included in the crystal lattice due to the almost same size and conformation of butylene succinate and butylene fumarate units in the crystal lattice. Consequently, the degree of crystallinity of PBSF hardly changes with copolymerization. Both the total crystallization rate and radial growth rate of PBSF spherulites during isothermal crystallization increase with the content of butylene fumarate.

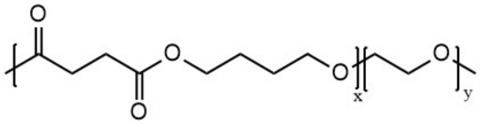
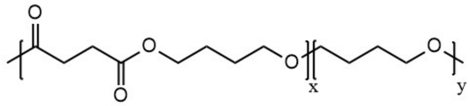
For block copolymers, the introduction of hydrophilic block to AB type diblock and ABA type triblock aliphatic copolyesters have been used in biomedical fields, such as drug release. Segmented block copolyesters have been studied intensively because of the feasible synthetic procedures and balanced properties. The segmented copolyesters show no obvious reduction of melting temperature if the segment length is large enough, while maintaining high elongation at break and excellent ductility. The advantages are important for applications of the block copolymers. Recently, biobased chemicals have been adopted as comonomers of PBS. Representative examples include the 2,5-furandicarboxylic acid [11, 71, 72], isosorbide [72, 73] and ricinoleic acid [74]. However, the biodegradation rate might slow down due to the introduction of cyclic structure.

There are still some open questions and challenges in the field. For instance, whether or not some co-monomer units are included in the crystalline lattice of

Table 2: Abbreviation, Full Name and the Molecular Formula of the Polymers Mentioned in the Review

Abbreviation	Full Name	Molecular Formula	Ref. No.
PBS	poly(butylene succinate)		5-20
PBSES	poly(butylene succinate-*co*-ethylene succinate)		27
PBPS	poly(butylene succinate-*co*-propylene succinate)		13
PBSA	poly(butylene succinate-*co*-butylene adipate)		36
PBST	poly(butylene succinate-*co*-butylene terephthalate)		5
PBSM	poly(butylene succinate-*co*-butylene methylsuccinate)		3
PBS-2M	poly(butylene succinate-*co*-butylene dimethylsuccinate)		3
PBSBS	poly(butylene succinate-*co*-butylene phenylsuccinate)		6
PBSOD	poly(butylene succinate-*co*-1,2-octylene succinate)		14
PBSF	poly(butylene succinate-*co*-butylene fumarate)		21,22
PBF	poly(butylene fumarate)		22
PES-*b*-PBS	poly(ethylene succinate)-*b*-poly(butylene succinate)		46

PBS-b-PLLA	poly(butylene succinate)-*b*-poly(l-lactic acid)		56
PBT-*b*-PBS	poly(butylene terephthalate)- *b*-poly(butylene succinate)		51
PLLA-*b*-PBS-*b*-PLLA	poly(L-lactide)-*b*-poly(butylene succinate)-*b*- poly(L-lactide)		40-43
PDLA-*b*-PBS-*b*-PDLA	poly(D-lactide)-*b*-poly(butylene succinate)-*b*- poly(D-lactide)		43,44
PEG-*b*-PBS	poly(ethylene glycol)-*b*-poly(butylene succinate)		45
PBS-*b*-PEG-*b*-PBS	poly(butylene succinate)-*b*-poly(ethylene glycol)-*b*-poly(butylene succinate)		45
PBS-*b*-PCL	poly(butylene succinate)-*b*-poly(ε-caprolactone)		52,53
PLLA-*b*-PBSA	Poly(L-lactide)-*b*-poly(butylene succinate-co-butylene adipate)		54
PBS-*b*-PPC	poly(butylene succinate)-*b*-poly(propylene carbonate)		55
PBS-*b*-PPS	poly(butylene succinate)-*b*-poly(propylene succinate)		57
PEG	poly(ethylene glycol)		58-60
PPG	poly(propylene glycol)		61
PTMG	poly(tetramethylene glycol)		62-64

PBSEG	poly(butylene succinate)-*co*-poly(ethylene glycol)		63
PBSTMG	poly(butylene succinate)-*co*-poly(tetramethylene glycol)		62-64

the major monomers are not yet clear. Meanwhile, block copolymerization has been utilized to improve the ductility of PBS without much loss of the melting point, which deserves further study and may lead to new type of biodegradable thermoplastic elastomers. For the block copolymers, there may be microphase separation in melt. If both the two blocks can crystallize, the final crystalline morphology will be more complicated and the final properties will strongly depend on the processing and crystallization conditions. In addition, industrialization of PBS random copolymers is much easier and the commercial products are available. On the contrary, the large-scale production of PBS based block copolymers are still in progress.

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