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Polybutylene succinate, a potential bio-degradable polymer: synthesis, copolymerization and bio-degradation

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Poly(butylene succinate) is one of the emerging bio-degradable polymers, which has huge potential to be employed in a wide range of applications. Furthermore, it is also recognized as one of the biopolymers of choice due to its environmentally benign nature and biodegradability. Even though PBS has various advantages, brittleness, thermal stability and a lack of the high molecular weight required for industrial applications restricts its commercial implementation. Various catalyst systems have been employed to produce high molecular weight PBS. In addition, various strategies like copolymerization and the preparation of composites and blends have been attempted to improve the physical and mechanical properties of PBS. However, the synthesis of high molecular weight PBS with enhanced properties still remains a challenging task. Herein, catalyst systems that have been employed towards the synthesis of PBS and its copolymers as well as its property enhancements (including bio-degradation) through copolymerization are covered in detail. This will provide readers with a detailed and systematic understanding of the catalysis, copolymerization and biodegradation of PBS.

Introduction

Hermann Staudinger (father of polymer science) was honored with the Nobel Prize for Chemistry for his pioneering research on macromolecules. His extensive research led to a basic understanding as well as designing the applications for polymers in

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Miss. K. S. Savitha graduated with her M.Sc. (Polymer Science) from the University of Mysore, Karnataka, India. After receiving her M.Sc. she started her research career as a project assistant at the Siddaganga Institute of Technology, Tumkuru. After a year's experience in developing polymer electrolyte membranes for fuel cell applications, she moved to the CSIR-CFTRI to continue her research career in understanding the migration of additives from polymers, especially for food packaging applications. Currently, she is pursuing her PhD at the University of Mysore and her current research is focused on developing efficient methods for polybutylene succinate synthesis.

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Bharatkumar Paghadar graduated with his M.Sc. (Organic Chemistry) from Sardar Patel University, Gujarat, India. After his master's degree, he started his professional research career in the agrochemicals industry, where he was involved in R&D and subsequent technology transfer from lab to plant. After spending six years of his research career in agrochemicals, he moved to the pharmaceutical industry and was involved for three years in lab/plant validation of a few APIs. Then he changed his research career to the development of organometallic group (IV) transition metal complexes, Z–N catalysts and chrome catalysts for polyolefin synthesis.

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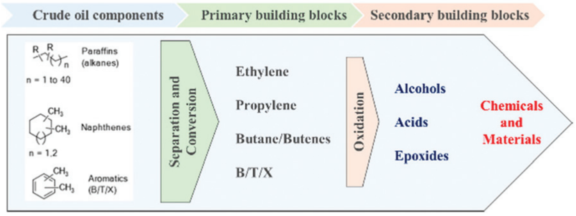

Fig. 1 Chemicals and materials from crude oil.

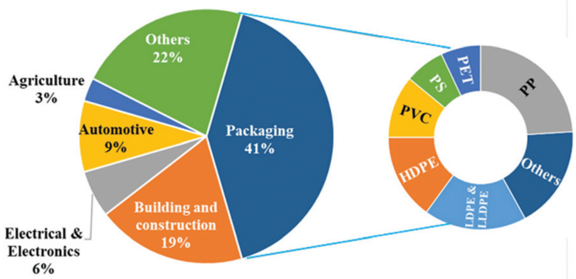

Fig. 2 General distribution and application of plastics.

every day life as commodities and specialty (special functional) polymers.[1] In addition, the petrochemical revolution of the last century led to the production of polymers such as polyethylene (HDPE, LDPE, LLDPE), polypropylene (PP), poly(vinyl chloride) (PVC), poly(ethylene terephthalate) (PET), and polystyrene (PS) in large quantities from fossil resources (Fig. 1).[2] Furthermore, they have gained significant importance as the material of choice for various applications such as food packaging, cosmetics, personal hygiene, building and construction, pharmaceuticals, automobiles, electrical devices and electronics, agriculture, *etc.*, due to their low cost combined with excellent mechanical, thermodynamic and insulation properties (Fig. 2).[3]

However, because of their durability and non-biodegradability, many synthetic petrochemical based polymers tend to accumulate in the environment rather than degrading, which has led to severe environmental plastic pollution. The presence of a considerable amount of aromatic moieties in polymers increases the durability and hence they are not biodegradable. At the beginning of the twenty first century, the accumulation of plastic waste and its negative environmental impact coupled with an increase in oil prices have led to the development of biodegradable polymers, which are generally referred to as synthetic or processed organic macromolecules derived from biological resources (Fig. 3).[4]

In recent years, the design and use of environmentally benign polymers from renewable resources are of significant interest among scientists in both academia and industry. Two different strategies can be employed for improving the ecological and sustainable aspects of polymeric materials. The first strategy mainly emphasizes the need for new bio-alternatives to petrochemical based polymers and the second one focuses on the end-of-life situation, which includes either bio-degradation, recycling, incineration, landfill or composting. Bio-based alternatives are of significant importance as they can save up to 315 million tons of CO_2 equivalents annually.[2,5]

Furthermore, bioplastic alternatives have been developed for almost every conventional petroleum based polymer as well as for their corresponding applications (Fig. 4). In this regard, biodegradable polyesters, such as poly(lactic acid) (PLA), poly

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R. L. Jagadish

Prof. Dr R. L. Jagadish obtained his PhD from the University of Mysore, Karnataka, India. He started his career at a fine chemicals manufacturing company. After eight years, he joined Vikrant Tyres Ltd, at Mysore, India, as Technical Officer. After nine years at Vikrant Tyres, he moved from industry to academia and became an Assistant Professor in the Department of Polymer Science, Sir M. Visveswaraiah, Post Graduate Centre, Mandya, India. Currently, he is continuing his academic career as Professor and he has received various awards from industry as well as from academia.

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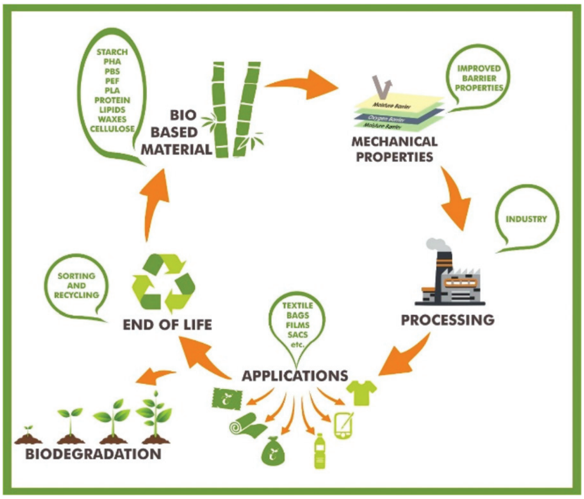

Fig. 3 Circular economy of bio-based packaging and textiles.

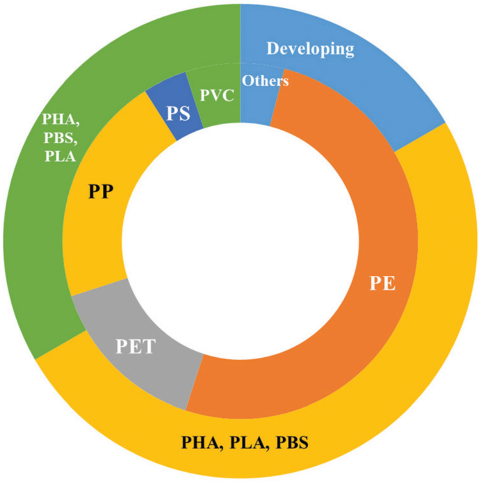

Fig. 4 Bio-alternatives for petroleum based polymers.

(butylene succinate) (PBS), polyhydroxyalkanoates (PHAs) and aliphatic–aromatic copolyesters, have gained increasing interest as bio-alternatives to traditional oil-based commodity polymers, such as polyolefins and poly(ethylene terephthalate) (PET).[6] In addition, various renewable polymers, including thermoplastics,[7] thermosets,[8] and vitrimers,[9] with good performances have also been developed to mimic traditional petroleum-based polymers.

Moreover, the global production of bio-plastics (bio-based/non-biodegradable and biodegradable (Fig. 5) is expected to increase from 2.4 million tonnes in 2021 (which is <1% of the total volume of petroleum based polymers) to 7.59 million tonnes in 2026 with an annual growth rate (CAGR) of about 21% (Fig. 6a). In particular, the global production of PBS is expected to increase from 4% in 2021 to 16% in 2026 (Fig. 6b). Moreover, the segment wise global production of biodegradable polymers in 2021 is explained in Fig. 6b.[2h]

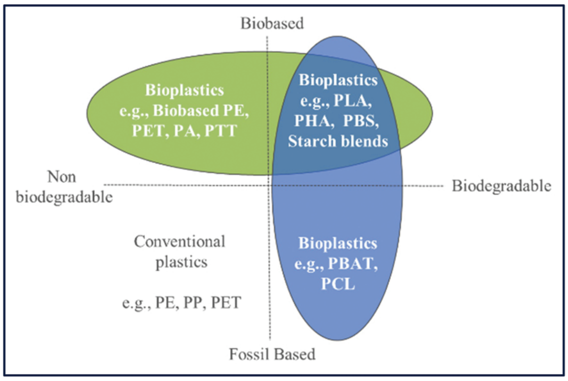

Fig. 5 Handy coordinate system of bioplastics.

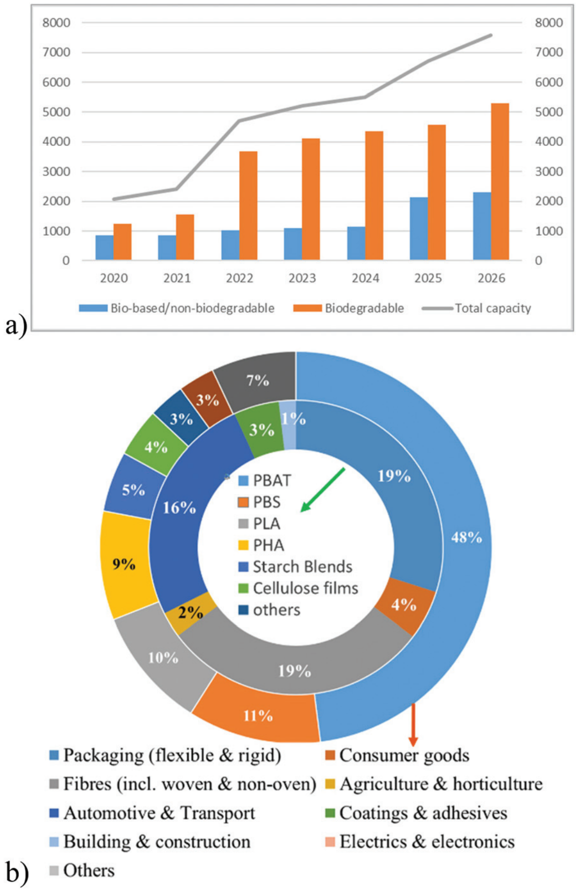

Fig. 6 Global production of bioplastics in 2021 by (a) volume (in kilo tonnes) (b) polymer type (bio-degradable) and segment (non-biodegradable and biodegradable).

These bio-based polymers are capable of providing new macromolecular frameworks with superior properties.[10] Among the bio-based polymers, poly(hydroxyalkanoate)s, poly (lactic acid), and poly(butylene succinate) (PBS) are of considerable interest and have already led to large scale production to cater to various applications such as packaging, agriculture, biomedical, automotive, electrical, pharma-

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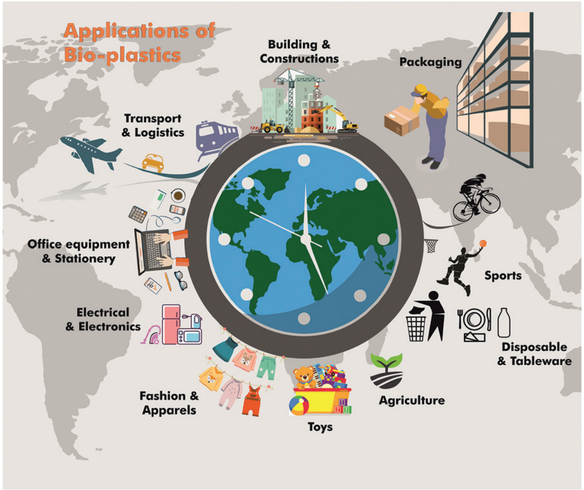


Fig. 7 Bioplastics and their applications in our day-to-day life.

ceutical, *etc.* (Fig. 7). Poly(butylene succinate) belongs to the poly(alkylene dicarboxylate) family, which can be synthesized by the reaction of 1,4-butanediol with succinic acid.[11]

Bio-based synthesis of monomers (SA and BDO) for PBS

Recent developments in fermentation technology led to the production of bio-based monomers on an industrial scale. In the fermentation process, specific bacterial strains such as *Actinobacillus succinogenes*, *Mannheimia succiniciproducens*, *Anaerobiospirillum succiniciproducens* and recombinant *Escherichia coli* converts substrates such as corn starch, whey, cane molasses, glycerol, and wood hydrolysates into succinic acid in high yields, with lower amounts of by-products.[12] This production of SA *via* a fermentation process is mainly an environmentally benign method which utilizes CO_2 to convert the substrates into the products.[13]

Moreover, succinic acid (SA) is one of the top twelve bio-based building blocks that are produced from carbohydrates, and thus has a potential market in the chemical industry.[14] A bio-synthetic method for the production of 1,4-butanediol (BDO) also involves the fermentation of sugars, glucose, starch, xylose, *etc.* (Fig. 8) to yield SA and subsequent reduction of the SA leads to BDO. Conversely, the direct synthesis of BDO through the fermentation of sugars, by using engineered *E. coli*, has also been reported in the literature.[15] The synthesis of both SA and BDO from biomass feedstocks appears to be particularly interesting, as it gives access to the production of fully bio-based PBS (Scheme 1).[16]

Synthesis of polybutylene succinate

Aliphatic polyesters are an important class of sustainable polymers under investigation due to the degradation of ester bonds under enzymatic conditions. Extensive research work has been carried out in developing biodegradable polymers, such as poly(caprolactone) (PCL), poly(butylene succinate) (PBS), poly(lactic acid) (PLA), and poly(butylene adipate-*co*-butylene terephthalate) (PBAT).[2,13,17] In particular, PBS exhibits several interesting properties, such as barrier and thermal properties, melt processability, chemical resistance and most importantly biodegradability. Thus, it has gained considerable attention as a potential biodegradable polymer to mimic petroleum based polymers in various applications.[2–6,15b]

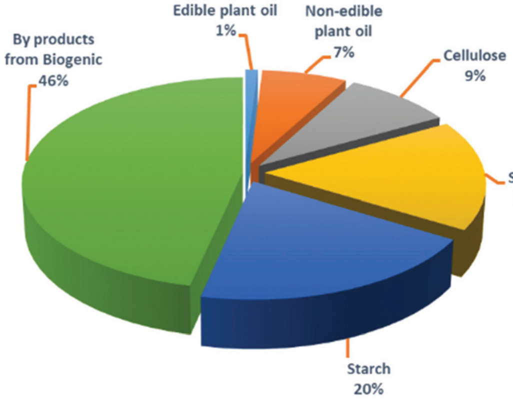
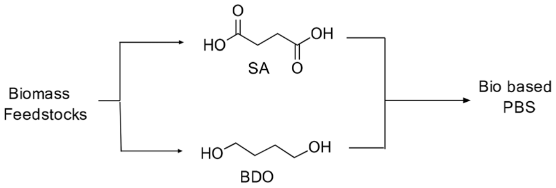
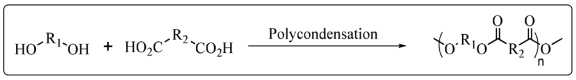


Fig. 8 Biomass feedstock for bio-based polymers.



Scheme 1 Synthesis of fully bio-based PBS.

In the early 1930s, Carothers first initiated the preparation of industrially important polymers *via* the condensation reaction, which included polyamides and other aliphatic polyesters (Scheme 2).[18] Nylon 66, of the polyamide family, was quickly identified during middle of the last century as one of the potential fiber-forming polymers. In copolyesters, the molecular weight of the obtained PBS polymer was very low and resulted in a weak and brittle polymer.[19] Extensive research work is being carried out in developing efficient synthetic methods for the production of high molecular weight PBS. However, the preparation of high molecular weight aliphatic polyesters from dicarboxylic acids and diols still remains a challenging task due to their low thermal stability.[20]



Scheme 2 Synthesis of polyesters.

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Conventional method for the synthesis of PBS

In general, the synthesis of PBS involves two steps, in which the first step is the esterification or trans-esterification (for production of oligomers) reaction at 160–180 °C followed by polycondensation (or) trans-esterification (for extension of the chain length) of the resulting oligomers at 230–250 °C under vacuum (Scheme 3).[21] Various organo-metals, metal oxides, and metal halides have been used as catalysts to improve the efficacy of the polymerization reaction.[22]

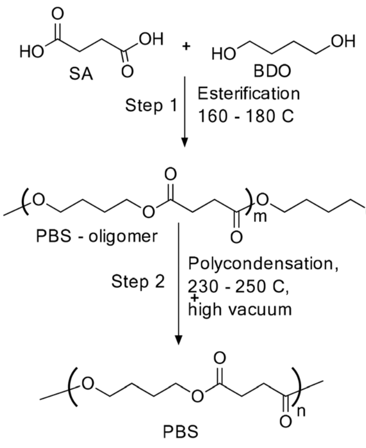
Titanium alkoxide based catalysts

Titanium tetrabutoxide (TBT) is the most widely used catalyst for the synthesis of PBS and it copolymers due to its catalytic efficiency.[23]

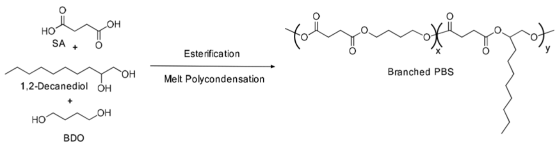
Branched polybutylene succinates were prepared by a two-stage esterification and condensation polymerization strategy using 1,4-butanediol, 1,2-decanediol, and succinic acid in the presence of TBT as a catalyst (Scheme 4).[24]

PBS copolymers with a rigid C≡C structure were also prepared by the copolymerization of BDO, SA and acetylene dicarboxylic acid using TBT catalyst. PBS and poly(butylene succinate-*co*-butylene acetylenedicarboxylate) (PBSAD) copolymers with M_n = 4.45 and 2.48 × 10^4 g mol^{-1} respectively were synthesized under the same reaction conditions (Scheme 5).[25]

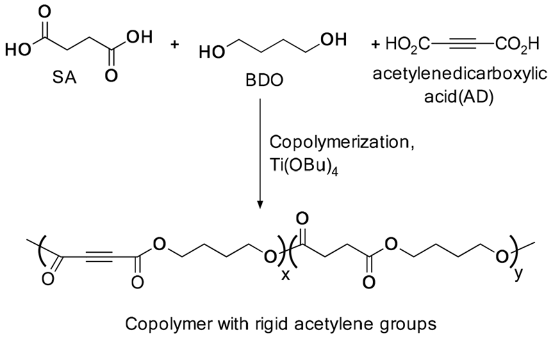
A new copolymer, poly(butylene succinate/dithiodipropionate), P(BSBDTDP), was successfully synthesized using 3,3-dithiodiproprionic acid as a comonomeric unit in the presence of the TBT catalyst (Scheme 6).[26]



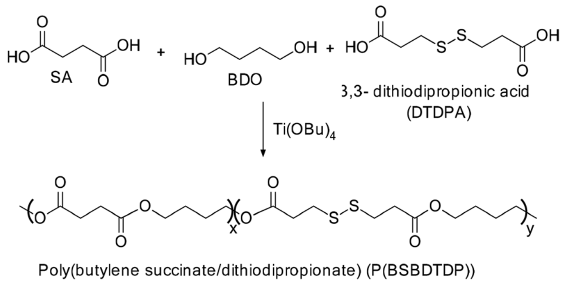
Scheme 3 Two step synthesis of PBS.



Scheme 4 Synthesis of branched PBS.



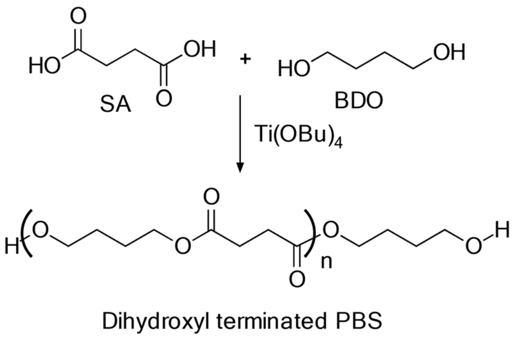
Scheme 5 Synthesis of PBS with rigid functional groups.



Scheme 6 Synthesis of p(BSBDTDP) copolymer.

Also, dihydroxyl terminated PBS prepolymers, which are mainly used for chain extension and the copolymerization reaction, were also prepared by the reaction of BD and SA in the presence of the TBT catalyst (Scheme 7).[27]

Poly(butylene succinate-*co*-propylene succinate) (PBSPS) copolymer was prepared by a bulk polymerization reaction in two steps using di-acid and diol in the presence of TBT as the catalyst (Scheme 8).[28a] Glycerol is used as a partial cross-linking agent to improve the thermal and mechanical properties of the copolymer. A polymer with M_n = 1.85 × 10^4 g mol^{-1}, M_w = 9.84 × 10^4 g mol^{-1} and PDI = 5.32 was synthesized.[28b]



Scheme 7 Synthesis of dihydroxyl terminated PBS.

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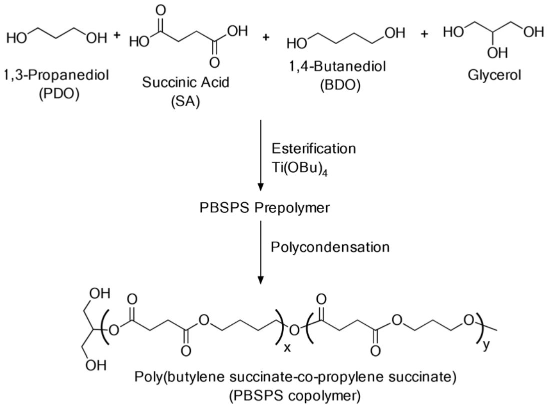
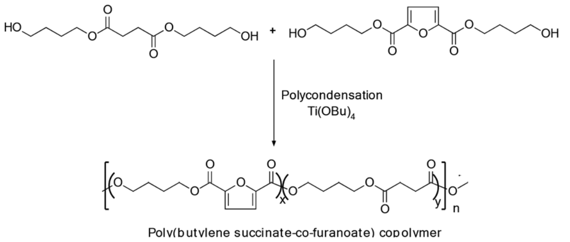


Scheme 8 Synthesis of PBSPS copolymer.



Scheme 9 Synthesis of poly(butylene succinate-*co*-furanoate) copolymer.

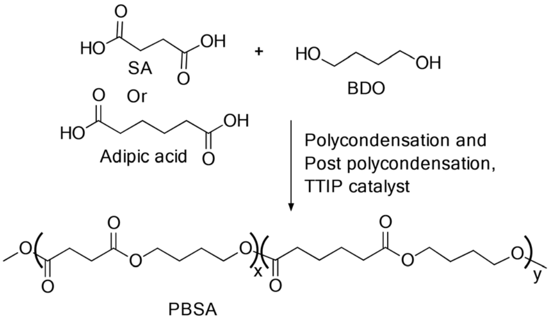
Aliphatic–aromatic bio-based poly(butylene succinate-*co*-furanoate) (PBSFc) copolymer was prepared by a melt polycondensation reaction of the corresponding esters in the presence of TBT as a catalyst. The number average molecular weights for PBS and PBSFc were 1.52 and 1.27 × 10^4 g mol^{-1} and the corresponding PDI values were 2.03 and 2.12, respectively (Scheme 9).[29]

Titanium tetrabutoxide as a modifier and compatibilizer

Interestingly, TBT was also employed as a modifier and compatibilizer in preparing polyester blends. Polymer blends prepared using poly(butylene succinate-*co*-adipate) and poly(ε-caprolactone) in the presence of the TBT catalyst demonstrated good compatibility and this might be due to the transesterification reaction between the polymers and, in addition, the viscosity of the blends tended to increase with an increase in catalyst concentration.[30]

Titanium tetraisopropoxide as a catalyst

Titanium tetraisopropoxide is the next preferred catalyst for the synthesis of PBS and its copolymers. Numerous synthetic methods reported in the literature used titanium tetraisopropoxide as a catalyst for both esterification and polycondensation reactions.



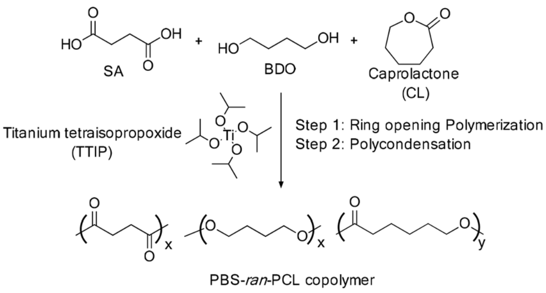
Scheme 10 Poly(butylene succinate-*ran*-butylene adipate) random copolymers (PBSA).

Poly(butylene succinate-*ran*-butylene adipate) random copolymers (PBSA)[31] (Scheme 10) and high molecular weight poly[(butylene succinate)-*ran*-(ε-caprolactone)] copolyesters (PBS-*ran*-PCL)[32] were prepared by melt polycondensation over a wide composition range using TTIP as a polycondensation catalyst. PBS with M_n = 7500, M_w = 21 470 and PDI = 2.9 was synthesized using this protocol (Scheme 11).[32]

Furfural is one of the most important bio-based compounds, which in turn can be readily produced from cellulose. Furthermore, furfural, on oxidation and subsequent reduction of the resulting fumaric acid, led to the formation of bio-based succinic acid and 1.4-butanediol. Tachibana and co-workers reported the titanium tetraisopropoxide mediated synthesis of PBS with M_n = 85 000 and M_w/M_n = 2.6. Furthermore, it was found that, both bio-based and petroleum based PBS synthesized using TTIP as a catalyst, were found to have similar properties (Scheme 12).[33]

The synthesis of PBS (M_n = 6.49 × 10^4 g mol^{-1}, M_w = 12.47 × 10^4 g mol^{-1} and PDI = 1.87) and its copolymers containing 1,4-cyclohexane dimethylene succinate (CHDMS) or butylene 1,4-cyclohexanedicarboxylate (BCHDA) units was further exploited *via* melt polycondensation using TTIP as a catalyst (Scheme 13).[34]

TTIP was further explored towards the synthesis of poly (butylene succinate-*co*-hexamethylene succinate) (P(BS-*co*-HS))



Scheme 11 Poly[(butylene succinate)-*ran*-(ε-caprolactone)] copolyesters (PBS-*ran*-PCL).

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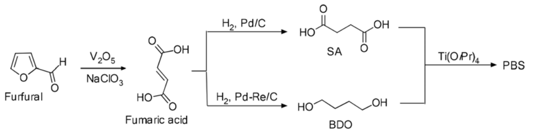
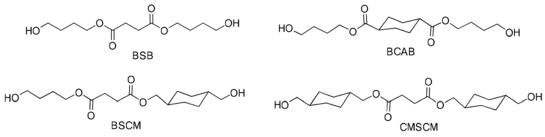
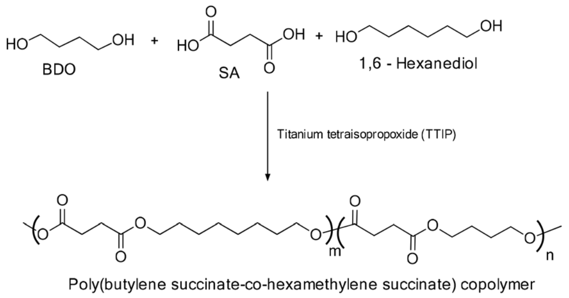


Scheme 12 Synthesis of PBS from furfural.



Scheme 13 Comonomers for PBS.



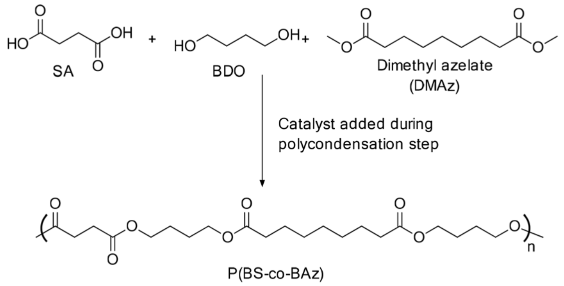
Scheme 14 Synthesis of poly(butylene succinate-*co*-hexamethylene succinate) (P(BS-*co*-HS)).

copolyesters. The intrinsic viscosity of the PBS homopolymer obtained was found to be 0.67 dl g^{-1} (Scheme 14).[35]

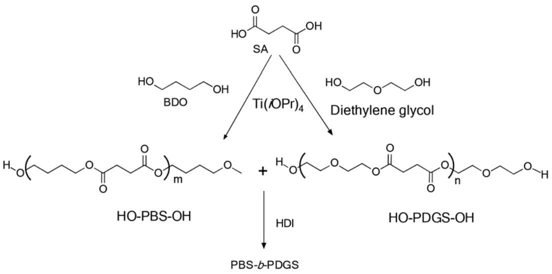
Efficiency of titanium based catalysts

However, titanium based catalysts are sensitive to moisture and water is the by-product formed during the esterification reaction. Thus, it is observed that the addition of titanium based catalysts during the esterification reaction reduces the activity of the catalyst, when compared to the addition of the catalyst during the polycondensation step. This is directly related to the stability of the catalyst in the presence of the by-product (water) formed during the esterification step.[36] Thus, to improve the catalytic efficiency, the catalyst was added during the polycondensation step (Scheme 15).[2c,31]

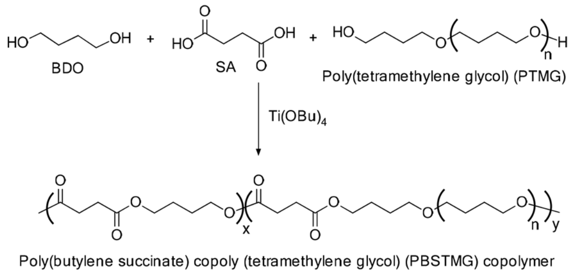
Poly(butylene succinate-*b*-poly(diethylene glycol succinate) (PBS-*b*-PDGS) multiblock copolymers were synthesized using chain extenders *via* HO-PBS-OH and HO-PDGS-OH precursors, which in turn were prepared by using TTIP as a catalyst. During polymer precursor synthesis, the catalyst was added during the polycondensation step. PBS homopolymer with $M_n = 3.5 \times 10^{-4}$ g mol^{-1}, $M_w = 15.1 \times 10^{-4}$ g mol^{-1} and PDI = 4.3 was synthesized under the same reaction conditions using chain extenders (Scheme 16).[37]



Scheme 15 Synthesis of P(BS-*co*-BAz).



Scheme 16 Synthesis of PBS-*b*-PDGS.



Scheme 17 Synthesis of poly[(butylene succinate)-*co*-poly(tetramethylene glycol)]s (PBSTMGs).

Poly[(butylene succinate)-*co*-poly(tetramethylene glycol)] (PBSTMG) copolymers were synthesized by a two step esterification and polycondensation reaction using SA, BD and poly (tetramethylene glycol) (PTMG) in the presence of the TBT catalyst (Scheme 17), in which the catalyst was added during the polycondensation step.[38]

Even in the few methods reported in the literature, the catalyst was added in parts in both the esterification and polycondensation steps to improve the conversion and achieve a high molecular weight of the polymer (Scheme 18).[39]

Titanium alkoxides in the presence of stabilizers

It is very well known that the synthesis of high molecular weight PBS still remains a challenging task due to its low thermal stability. Thus, the use of thermal stabilizers, in combination with a Lewis acid catalyst, has also been explored in producing high molecular weight copolyesters. As a result, tita-

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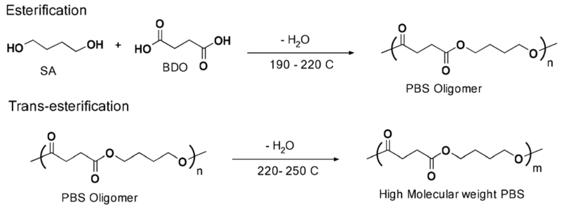


Scheme 18 Synthesis of high molecular weight PBS.

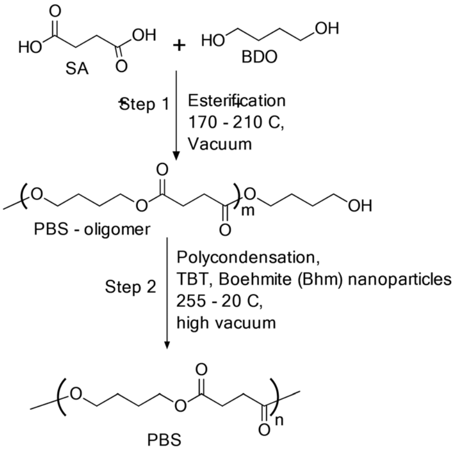
nium(IV) butoxide as a polycondensation catalyst, in combination with polyphosphoric acid as a thermal stabilizer, was utilized for the synthesis of poly(butylene succinate)/nanoboehmite composites[40] (Scheme 19).

The same catalyst combination was used to promote the polycondensation reaction towards the synthesis of poly(butylenesuccinate-*co*-fumarate) copolymer and poly-alkylene succinates with an odd and even number of methylene units.[41] The addition of polyphosphoric acid (PPA) during the polycondensation step was also reported for the synthesis of poly(butylene-*co*-propylene succinate) copolymer. It is believed that the addition of PPA will reduce unwanted side reactions like etherification and polymer degradation.[42]

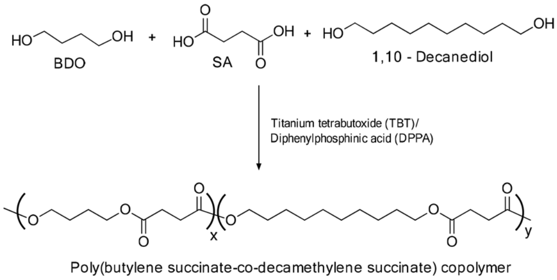
Qiu *et al.* demonstrated the use of a combination of titanium(IV) butoxide and diphenylphosphinic acid as a catalyst and co-catalyst system for the synthesis of poly(butylene succinate-*co*-decamethylene succinate) copolyesters (Scheme 20).[43]

Similarly, Zhou *et al.* used titanium tetraisopropoxide, in combination with diphenylphosphinic acid (DPPA), as a catalyst for the polycondensation reaction to synthesize poly(butylene succinate) and poly(ethylene glycol) copolymers (Scheme 21). The formation of a high molecular weight copolymer, with $M_w = 9.32 \times 10^4$ was observed when the ratio of BD : PEG2000 was around 95 : 5.[44]

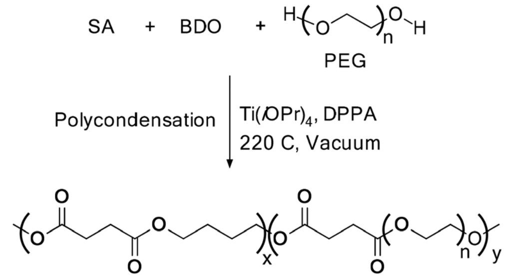
The combination of TBT as a catalyst and triphenyl phosphate as a stabilizer was also utilized for the synthesis of high molecular weight PBS with $M_n = 6.3 \times 10^4$ g mol^{-1} and an intrinsic viscosity of 1.53 dL g^{-1} (Scheme 22).[45]



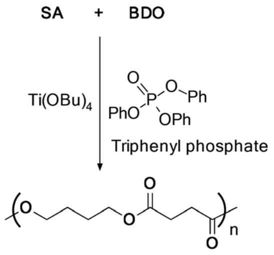
Scheme 19 Synthesis of PBSF copolymer using TBT in combination with *p*-hydroxyanisole.



Scheme 20 Synthesis of poly(butylene succinate-*co*-decamethylene succinate) copolyesters.



Scheme 21 Synthesis of poly(butylene succinate) and poly(ethylene glycol) copolymer.



Scheme 22 Synthesis of PBS using TBT in the presence of stabilizer.

Tin based catalysts

To find an efficient catalyst system, Ishii and co-workers screened various metal catalysts, like 1-chloro-3-hydroxy-1,1,3,3-tetrabutyldistannoxane, Ti(i-OPr)$_4$, Al(i-OPr)$_3$, Sn, and SnCl$_2$, for PBS synthesis (Table 1). Moreover, they explored different distannoxane catalysts, such as CHTD, HTTD, DCTD and CHTOD, for the synthesis of PBS (Fig. 9) (Table 2).

From the experimental screening, 1-chloro3-hydroxy-1,1,3,3-tetrabutyl-distannoxane (CHTD) exhibited better catalytic activity than the other catalysts and PBS thus obtained has an inherent viscosity of 0.99 dL g^{-1} and the number-average molecular weight (M_n) and weight-average molecular weight (M_w)

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Table 1 Efficiency of metal catalysts

Catalyst	□$_{\text{inh}}$ (dL g^{-1})
None	0.49
Ti(i-OPr)$_4$	0.51
Al(i-OPr)$_3$	0.69
Sn	0.59
SnCl$_2$	0.69
CHTD	0.99

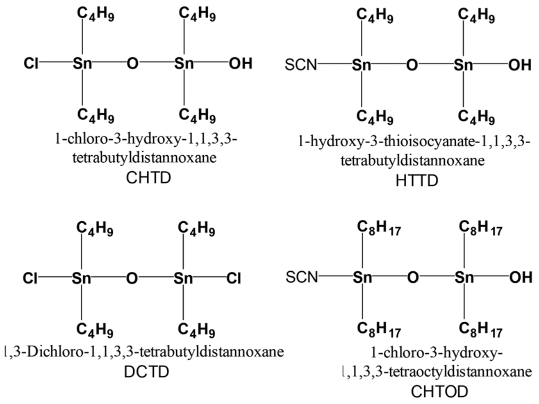
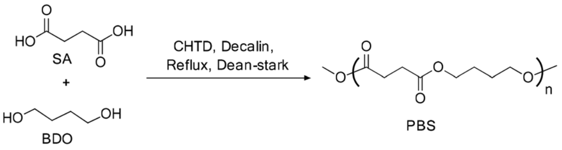


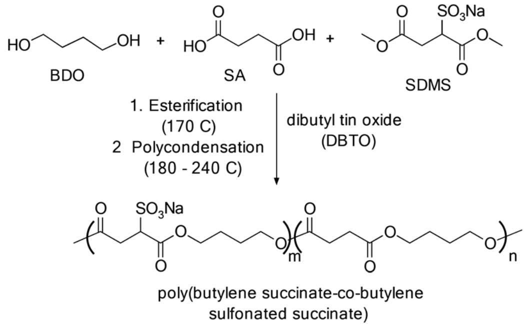
Fig. 9 Different distannoxane catalysts (CHTD, HTTD, DCTD and CHTOD).

Table 2 Efficiency of distannoxane catalysts

Catalyst	□$_{\text{inh}}$ (dL g^{-1})
DCTD	0.83
HTTD	0.76
CHTD	0.99
CHTOD	0.90



Scheme 23 Synthesis of PBS using 1-chloro3-hydroxy-1,1,3,3-tetrabutyl-distannoxane (CHTD) catalyst.



Scheme 24 Synthesis of PBS using DBTO.

values were 9.25 × 10^4 g mol^{-1} and 1.76 × 10^4 g mol^{-1} respectively (Scheme 23).[46]

The use of 1,3-dichloro-1,1,3,3-tetrabutyldistannoxane (DCTD) was explored as a catalyst for the synthesis of PBS with M_w of 1.02 × 10^4 g mol^{-1}.[47] The application of dibutyl tin oxide (DBTO) as a catalyst for both esterification and polycondensation steps was realized during the synthesis of poly(butylene succinate) (M_w = 11.2 × 10^4 g mol^{-1} and PDI = 2.2) and its ionomers (Scheme 24).[48]

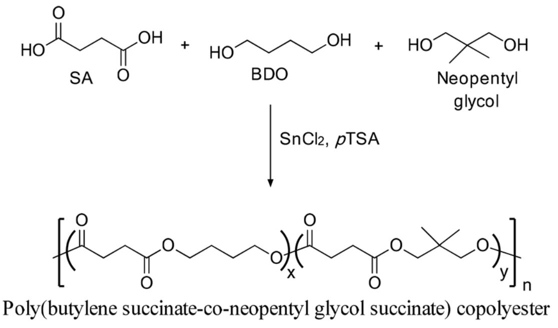
DBTO was further used for the synthesis of PBS copolymers using the carbohydrate-based diol 2,4 : 3,5-di-*O*-methylene-D-mannitol (Manx). The DBTO catalyst is found to be mild and demonstrates a higher catalytic activity compared to TBT, which aids the polymerization of thermally sensitive sugar monomers at lower temperatures and also with reduced reaction times. The M_w of the resulting PManxS homopolyester was higher than 30 000 g mol^{-1} with a PDI of 2.3.[49]

Stannous chloride and 4-methylbenzenesulfonic acid were used as a catalyst combination for the esterification reaction towards the synthesis of poly(butylene succinate-*co*-neopentyl glycol succinate) co-polyesters (Scheme 25).

Furthermore, stannous chloride has also been used as a catalyst to promote the polycondensation reaction.[50] Moreover, tin octoate was also explored as a catalyst for synthesis of dihydroxyl terminated PBS.[51] High molecular weight PBS with M_n = 9.5 × 10^4 Da and M_w = 16.5 × 10^4 Da was prepared using Sn(Oct)$_2$ catalyst *via* the ring opening polymerization of butyl succinate lactone, which in turn was prepared from PBS oligomers using zinc oxide as a catalyst (Scheme 26).[52]

Lee and co-workers employed tin octate as a catalyst in the presence of macro-initiators, such as polyethylene glycol (PEG), during the synthesis of PBS as well as its diblock (PEGPBS) and triblock (PBS-PEG-PBS) copolymers (Scheme 27).[53]

The PDLA-*b*-PBS-*b*-PDLA tri-block copolymer was synthesized by the ring opening polymerization of D-LA in the presence of hydroxyl capped PBS and tin(II) 2-ethylhexanoate (Sn(Oct)$_2$) respectively as the macro-initiator and catalyst (Scheme 28).[54]



Scheme 25 Synthesis of PBS using SnCl$_2$ in combination with pTSA.

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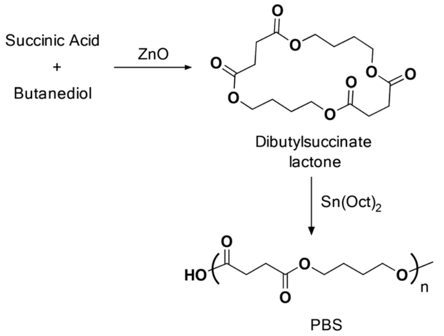
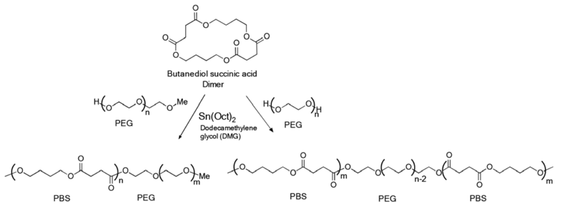
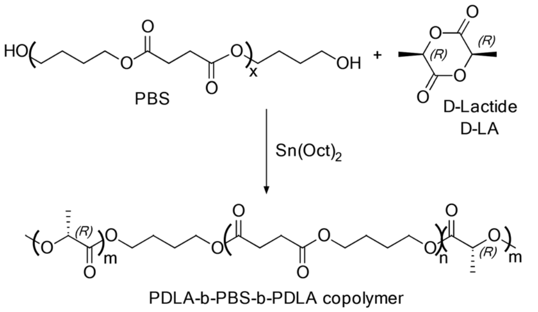


Scheme 26 Synthesis of PBS *via* ring opening reaction.



Scheme 27 Synthesis of di- and tri-block (PBS-PEG-PBS) copolymers.



Scheme 28 Synthesis of PDLA-*b*-PBS-*b*-PDLA tri-block copolymers.

Furthermore, the efficiency of a metal catalyst, such as antimony(III) oxide (Sb_2O_3), tin(II) 2-ethylhexanoate ($SnOct_2$) and titanium(IV) butoxide ($Ti(OBu)_4$), for the polycondensation reaction was evaluated by Ferreira *et al.* (Table 3), and from their experimental results, it was realized that titanium(IV) butoxide ($Ti(OBu)_4$) exhibited better catalytic activity than the tin and antimony based catalysts. Additional studies regarding the concentration of the catalyst towards the polycondensation reaction indicated that an increase in catalyst concentration and temperature would lead to unwanted side reactions *via* polymer degradation, which in turn resulted in the isolation of a polymer with a broad molecular weight distribution.[55]

Table 3 Efficiency of metal catalysts

Catalyst	M_w (KDa)	PDI
$Sn(Oct)_2$	1.35	9.6
Sb_2O_3	1.70	6.2
$Ti(OBu)_4$	1.80	7.1

Other (Zr, Sn, Hf, Sb, Bi and La) Lewis acid catalysts

Jacquel *et al.* reported the use of zirconium(IV) *n*-butoxide as a catalyst for the preparation of aromatic–aliphatic co-polyesters (poly(butylene succinate) copolymers) containing rigid bio-based comonomers like isosorbide (Fig. 10). During the synthesis, zirconium(IV) *n*-butoxide was added during the polycondensation step.[56] PBS thus synthesized possessed $M_n = 5.9 \times 10^4$ g mol^{-1} and the reduced viscosity was found to be 2.01 dL g^{-1}.

Rare earth metal triflates like $Sc(OTf)_3$, $Y(OTf)_3$, $Sm(OTf)_3$, $Yb(OTf)_3$, $La(OTf)_3$ and scandium(III) trifluoromethanesulfonimide ($Sc(NTf_2)_3$) were also explored as catalysts for poly(butylene succinate) ionomer synthesis.[57]

Poly(butylene succinate-*co*-butylene terephthalate) was prepared by the reaction of BDO, SA and PTA using a rare earth metal as a catalyst under melt polycondensation reaction conditions. The weight average molecular weight and polydispersity index of the isolated polymer were found to be 9.4×10^4 Da (M_w) and 1.64 (PDI). The corresponding homopolymers, PBS (with $M_w = 12.0 \times 10^4$ Da; PDI = 1.70) and PBT (with $M_w = 11.5 \times 10^4$ Da; PDI = 1.66) were also synthesized using the same method.[58]

The efficiency of various organo metals like titanium(IV) *n*-butoxide, hafnium(IV) *n*-butoxide, tin 2-ethylhexanoate, zirconium(IV) *n*-butoxide, antinomy(III) *n*-butoxide, and bismuth neodecanoate, and metal oxides like germanium(IV) oxide and antimony(III) oxide were analysed as catalysts for PBS synthesis (Fig. 11). It was evident from their experimental results that the efficiency of the catalyst was found to be Ti ≫ Zr ~ Sn > Hf

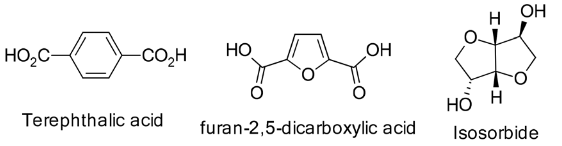


Fig. 10 Comonomers for the synthesis of aromatic–aliphatic copolyesters.

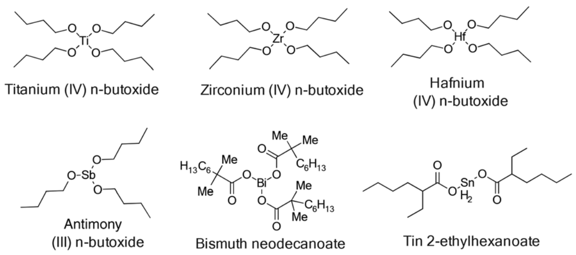


Fig. 11 Metal catalysts for PBS synthesis.

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> Sb > Bi. Conversely, metal oxides of germanium and antimony exhibited desirable catalytic activity in combination with hydroxy acids (lactic acid or glycolic acid), which could act as chelating agents.[59]

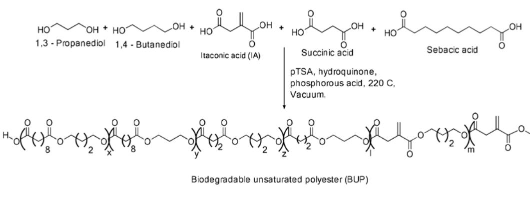
However, the overall transesterification rate decreased with respect to high concentrations of hydroxy acids. This is due to the substitution reaction of hydroxy acids with PBS during the polymerization reaction. Moreover, it was noticed that catalytic residues, especially titanium based catalysts, present in the polymer were found to promote the hydrolytic degradation of the polymer.[59] Additional catalysts, such as triazabicyclodecene and tosic acid, were found to be less effective at producing high molecular weight polyesters.[60]

The efficiency of TBT and zinc acetate at synthesizing the aromatic/aliphatic copolyester (HBA/PBS) was further systematically investigated. From the results, TBT was found to be a better catalyst than zinc acetate and hydroxyl benzoic acid would undergo the transesterification reaction with PBS to yield PBS rich segment and HBA (*p*-hydroxybenzoic acid) rich segment polyesters. Furthermore, the reaction time tended to have some influence on polymerization but not on the crystal structure.[61]

Metal (Bi, Ca, Mg and Zn) chlorides and triflates

The importance of various metal salts (bismuth, calcium, magnesium and zinc) towards the synthesis of PBS was explored in the literature. The intrinsic viscosities of the synthesized polymers were found to be 0.36 to 0.37 dL g^{-1} using zinc chloride and 0.24 to 0.25 dL g^{-1} and 0.33 to 0.61 dL g^{-1} respectively using $BiCl_3$ and $MgCl_2$ as catalysts. Furthermore, it was realized that $BiCl_3$ exhibited enhanced catalytic activity compared to other metal chlorides and triflates, such as $ZnCl_2$, Zn triflate, $MgCl_2$, Mg triflate and $CaCl_2$.[62]

Moreover, *para*-toluenesulfonic acid has also been explored as a polycondensation catalyst along with an inhibitor (hydroquinone) and stabilizer (phosphorous acid) for the synthesis of biodegradable unsaturated polyester (Scheme 29).[63]



Scheme 29 *p*TSA as a polycondensation catalyst in PBS synthesis.

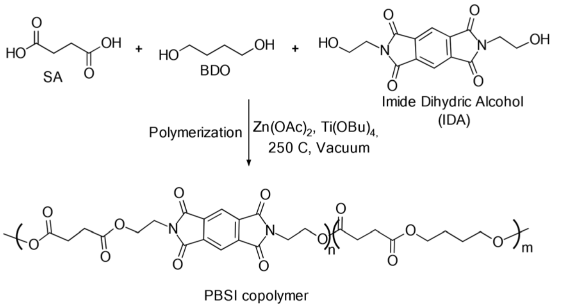
Dual metal catalyst system

To improve the efficiency of the synthesis and also to achieve high molecular weight PBS, various Lewis acid combinations as a catalyst system were explored in the literature. Zinc acetate, in combination with titanium(IV) butoxide, was utilized as a catalyst system for the polycondensation reaction to synthesize high molecular weight poly(butylene succinate) containing rigid imide units (Scheme 30).[64]

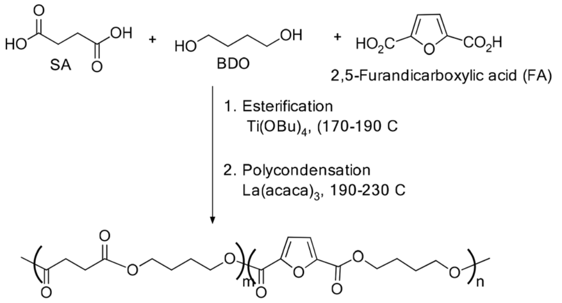
Furthermore, the use of the zinc acetate–titanium butoxide catalyst combination was exploited towards the esterification reaction to synthesize aliphatic–aromatic biodegradable copolyesters.[65] In the zinc acetate–titanium butoxide catalyst combination, the use of zinc acetate as a trans-esterification catalyst and titanium butoxide as a catalyst for the polycondensation reaction has also been investigated towards the synthesis of PBS (M_w = 7.4 × 10^4 g mol^{-1}, M_n = 1.6 × 10^4 g mol^{-1} and PDI = 2.2).[66]

The use of titanium(IV) butoxide and lanthanum(III) acetylacetonate hydrate, respectively, as catalysts for esterification and polycondensation reactions have also been exploited to synthesize poly(butylene succinate-*co*-butylene furandicarboxylate) copolyesters (Scheme 31).[67]

Zhang and co-workers synthesized functional biodegradable poly(butylene succinate) with UV stabilizers covalently linked to the polymer backbone using conventional synthetic methods. However, they used titanium tetrabutoxide as an esterification catalyst and La(acac)$_3$ as a catalyst for the polycondensation reaction towards the synthesis of functionalized PBS. The molecular weight of the PBS polymer thus obtained using La(acac)$_3$ was found to be 10.4 × 10^4 g mol^{-1}



Scheme 30 Zinc acetate and titanium(IV) butoxide catalyst combination for PBS synthesis.



Scheme 31 Synthesis of poly(butylene succinate-*co*-butylene furandicarboxylate) copolyesters.

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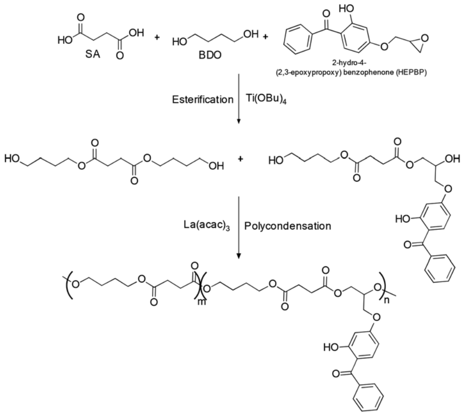


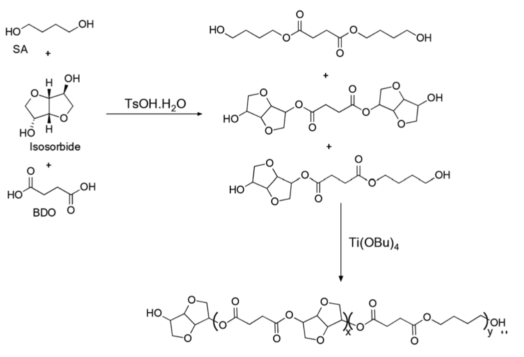
Scheme 32 Synthesis of functionalized PBS.

with M_n of about 6.4×10^4 g mol^{-1}. Furthermore, they varied the UV stabilizer ratio and found that a maximum M_w of 14.4×10^4 g mol^{-1} for the functional PBS was obtained when the molar ratio of HEPBP was about 0.5% (Scheme 32).[68]

A mixture of stannous octoate and stannous chloride as catalysts, in combination with 4-methylbenzenesulfonic acid as a co-catalyst, for the esterification reaction was reported for the synthesis of poly(butylene succinate-*co*-ε-caprolactone) copolymer.[69]

Dual catalyst system for PBS copolymer synthesis

In order to improve the efficacy of the PBS synthesis, different catalysts for the esterification and polycondensation reactions have been explored. Qu *et al.* reported the synthesis of poly(butylene-*co*-isosorbide succinate) using *p*-TSA as an esterification catalyst and titanium(IV) butoxide as a polycondensation catalyst (Scheme 33). However, TBT is found to be less effective with an increase in isosorbide content. Furthermore, they observed that steric hinderance was found to be an critical factor in deciding the efficiency of the catalyst. They explored Sb_2O_3 (antimony(III) oxide) and $Sb_2(OCH_2CH_2O)_3$ as catalysts for the synthesis of the PBIS copolymer. Due to lower steric hinderance, Sb_2O_3 is found to be more efficient than sterically crowded $Sb_2(OCH_2CH_2O)_3$.[70]



Scheme 33 Synthesis of poly(butylene-*co*-isosorbide succinate) (PBIS) copolyester.

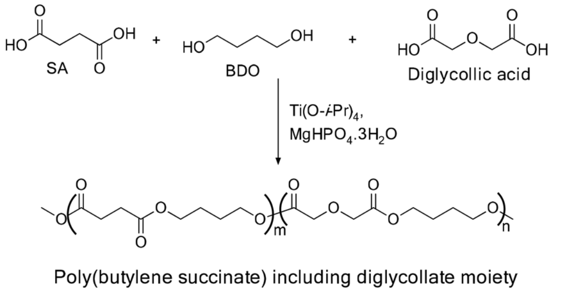
Titanium tetraisopropoxide, in combination with magnesium hydrogen phosphate trihydrate as a catalyst component, has also been explored for the synthesis of PBS copolymers.[71] It was observed that the co-catalyst magnesium hydrogen phosphate trihydrate accelerated the polycondensation reaction during PBS synthesis (Scheme 34).[71,72]

Titanium(IV) butoxide and dibutyl tin oxide respectively, in combination with the stabilizer Irganox 1010, were utilized as a catalyst system for producing PBS copolyesters using isosorbide and 2,4 : 3,5-di-*O*-methylene-D-glucitol (Glux-diol) co-monomers.[73]

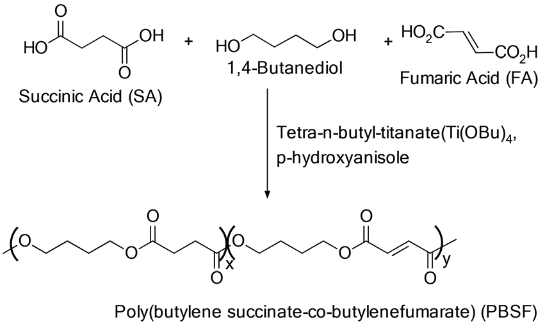
A combination of TBT and *p*-hydroxyanisole was employed as the catalyst and radical inhibitor respectively for the synthesis of poly(butylene succinate-*co*-butylene fumarate) copolyester (Scheme 35).[74]

Poly(butylene succinate-*co*-cyclohexanedimethylene succinate)s (PBCSs) with varied compositions were prepared by the polycondensation reaction between cyclohexanedimethylene succinate (CS) and butylene succinate (BS) using anhydrous tin(II) chloride in combination with *p*-toluenesulfonic acid as a catalyst (Scheme 36).

Under the same reaction conditions, the corresponding homopolymers, PBS (with $M_n = 4.1 \times 10^4$ g mol^{-1} and PDI 2.17) and PCS (with $M_n = 2.8 \times 10^4$ g mol^{-1} with PDI 2.08) were prepared.[75] The stannous chloride and 4-methylbenzenesulfonic acid catalyst combination was also used for



Scheme 34 Synthesis of PBS copolymer using TTIP and magnesium hydrogen phosphate trihydrate.



Scheme 35 Synthesis of PBSF copolyester.

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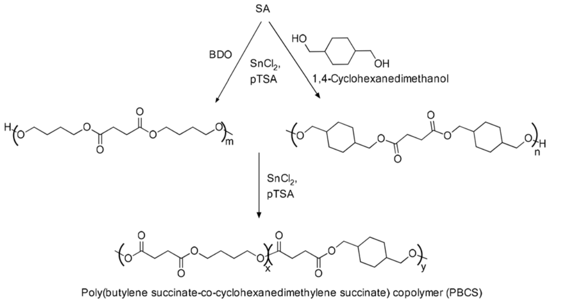
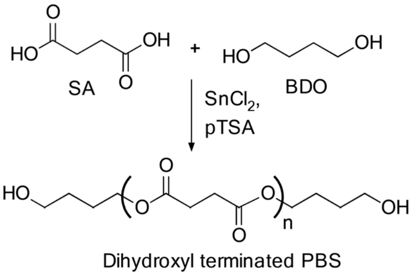


Scheme 36 Synthesis of PBCS copolyester.



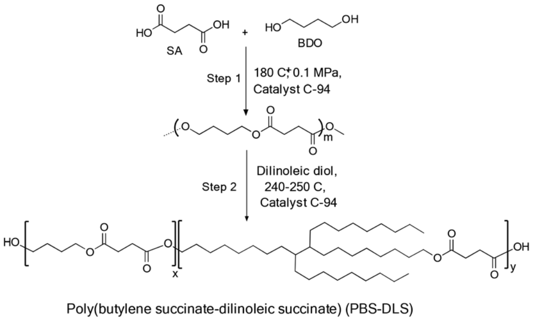
Scheme 37 Synthesis of dihydroxyl terminated PBS using $SnCl_2$ and pTSA catalyst system.

the synthesis of dihydroxyl terminated PBS *via* a two step esterification and polycondensation reaction using SA and BDO (Scheme 37). The M_n and PDI values of the synthesized PBS under the reaction conditions are found to be 4.1 × 10^4 g mol^{-1} and 1.43 respectively.[76]

Heterogeneous catalysts

Most of the catalysts used for PBS synthesis are homogeneous in nature. The recovery and recycling of homogeneous catalysts is yet another challenging task and may lead to additional environmental pollution. Furthermore, the presence of the catalyst at ppm levels leads to degradation of the polymer during processing at high temperatures. Hence, removal of the catalyst from the final polymer will provide additional thermal stability to the polymer during processing.[59] In general, heterogeneous catalysts are preferred over homogeneous catalysts due to the ease of recovery and recycling of the active catalyst.

Recently, Sn-attapulgite was used as a heterogeneous catalyst for the synthesis of PBS with high intrinsic viscosity, high molecular weight and enhanced thermal properties. In addition, the Sn-attapulgite catalyst was found to exhibit better catalytic activity than that of $SnCl_2$.[77] Furthermore, Stępien *et al.* used a hydrolytically stable titanium dioxide/silicon dioxide co-precipitated C-94 catalyst for the synthesis of poly(butylene succinate–dilinoleic succinate) (PBS-DLS) copolymer under heterogeneous conditions. In addition, the use of thermal stabilizers was avoided during copolymer synthesis even at high temperatures (240 °C) (Scheme 38).[78]



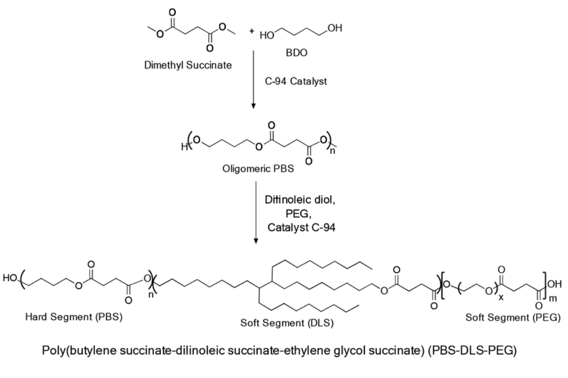
Scheme 38 Synthesis of PBS-DLS copolymer.

Using the same C-94 catalyst system, new poly(butylene succinate–dilinoleic succinate–ethylene glycol succinate) (PBS-DLS-PEG) copolymers containing PBS as the hard segment and DLS and PEG as the soft segments were successfully synthesized through a two-step polycondensation reaction (Scheme 39).[79]

Suspension polymerization

Polymerization in the bulk or solution phase has some inherent disadvantages, which include a long reaction time, high temperature and high viscosity of the reaction media. In general, due to low thermal stability, the polymers resulting from most of the melt-state polycondensations will have low molecular weights. Solution polymerization, in certain cases, can be considered as a potential alternative to overcome the disadvantages associated with bulk or solution phase polymerizations.

In 1961, Lesek and Khromeček reported the first suspension polycondensation reactions for the preparation of ion exchange resins.[80] Later, this methodology was extended to the synthesis of condensation polymers like poly(phenylene terephthalamide),[81] polybenzimidazoles,[82] polyimides,[83] *etc.* Recently, PBS microparticles, with M_w ranging from 0.32 to 8 × 10^4 g mol^{-1} and M_n = 0.12–7.2 × 10^4 g mol^{-1}, were produced *via* suspension polycondensation, and the properties of the resulting polymer were suitable for personal care and cosmetics applications (Fig. 12).[84]



Scheme 39 Synthesis of PBS-DLS-PEG copolymers.

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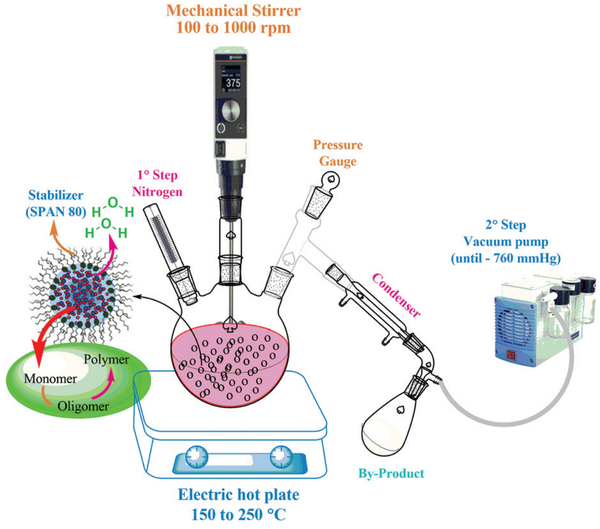


Fig. 12 Synthesis of PBS *via* suspension polymerization.

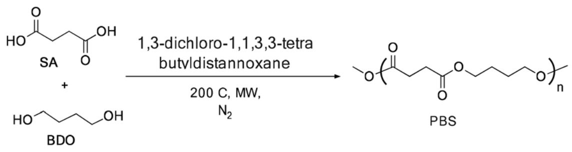
Solid state polymerization (SSP)

It is believed that limitations associated with melt polymerization, such as high reaction temperatures, color (from titanium based catalysts), low reactivity and possible side reactions can be overcome by the application of solid state polymerization. PBS with M_w = 7.2 × 10^4 g mol^{-1} and M_n = 4.4 × 10^4 g mol^{-1} was produced *via* the solid state polymerization technique. Moreover, it was found that there was an effective increase in M_w and thermal properties of PBS produced *via* SSP.[85]

Microwave assisted synthesis

Velmathi and co-workers demonstrated the rapid synthesis of poly(butylene succinate) (PBS) with a weight-average molecular weight (M_w) of 2.35 × 10^4 g mol^{-1} using microwaves in the presence of 1,3-dichloro-l,1,3,3-tetrabutyldistannoxane as a catalyst (Scheme 40).[47] Furthermore, they screened various catalysts such as $Ti(OiPr)_4$, $ZrCl_4$, $SnCl_2$, *p*-TSA.H_2O, $HfCl_4{\cdot}2THF$, $Sc(OTf)_3$, and dibutyldichlorotin(IV) for PBS synthesis. From the experimental results, it was evident that $SnCl_2$ was an efficient catalyst for the synthesis of PBS under microwave conditions. The generality of the methodology was further extended to synthesize other polyesters derived from various diols and diacids.[86]

Similarly, Nagahata *et al.* also explored the synthetic utility of the microwave assisted synthesis of PBS and proposed that the increased reaction rate under microwave conditions was due to the efficient removal of by-products formed during the reaction.[87] Furthermore, the synthesis of PBS using microwave irradiation was found to be more efficient than the corresponding conventional heating procedures.[47,87]



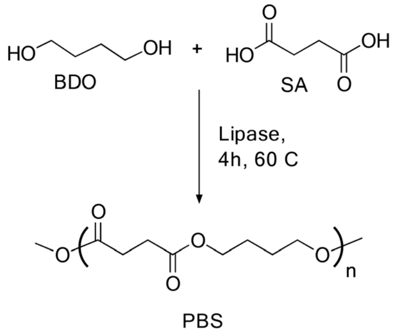
Scheme 40 Microwave mediated synthesis of PBS.

Enzyme mediated synthesis of PBS

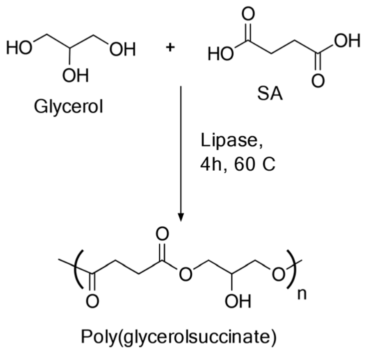
In addition to chemical synthesis, enzymatic methods for the production of PBS have also been explored. Lipase Novozym 435 (*Candida antarctica*) is used for the synthesis of polyesters under mild reaction conditions (Scheme 41).[88]

The enzymatic method was further extended to the synthesis of poly(glycerol succinate) (Scheme 42). The molecular weight (M_w) and PDI of poly(butylene succinate) synthesized under enzymatic conditions were found to be 5.90 × 10^4 g mol^{-1} and 2.23 respectively.[88]

High molecular weight copolyesters, poly(butylene succinate-*co*-dilinoleic succinate), with both hard and soft segments were also prepared by the reaction of diethyl succinate, 1,4-butanediol, and dimer linoleic diol in the presence of *Candida Antarctica* lipase B (CAL-B) as a bio-catalyst in diphenyl ether as a solvent (Scheme 43). Copolymers with M_n ranging from 1.14 × 10^4 g mol^{-1} to 3.64 × 10^4 g mol^{-1} and M_w ranging from 2.85 × 10^4 g mol^{-1} to 7.33 × 10^4 g mol^{-1} were synthesized using enzyme mediated copolymerization.[89,90]



Scheme 41 Enzyme mediated synthesis of PBS.



Scheme 42 Enzyme mediated synthesis of poly(glycerol succinate).

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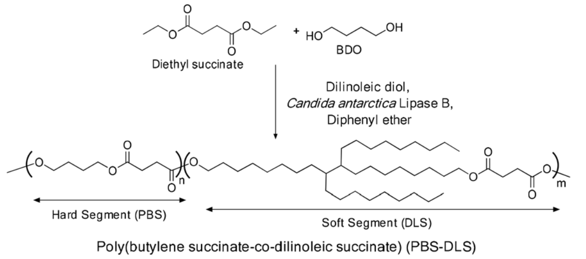
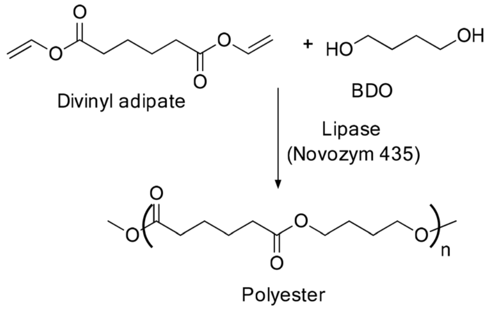


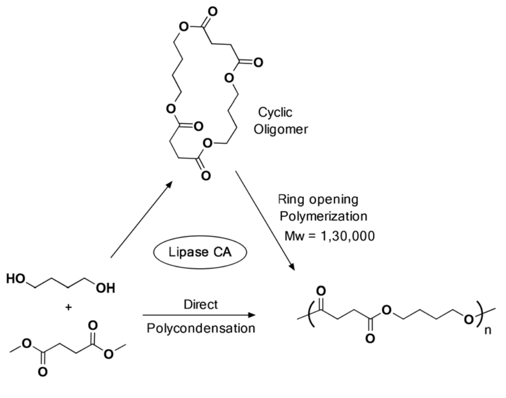
Scheme 43 Synthesis of PBS:DLS copolymer using lipase B catalyst.

Enzyme mediated polymerization of divinyl adipate with 1,4-butanediol resulted in isolation of the corresponding polymer with a weight average molecular weight (M_w) of about 2.32×10^4 g mol^{-1} (Scheme 44).[91] Interestingly, the use of divinyl adipate shifts the equilibrium of the polycondensation reaction towards the forward direction and this is due to the rapid tautomerization of the by-product vinyl alcohol into acetaldehyde.

Sugihara *et al.* recently developed a lipase Novozym 435 mediated green approach for the synthesis of high molecular weight PBS (M_w of 13×10^4 g mol^{-1}) through ring opening polymerization of the cyclic oligomers (Scheme 45).[92] Ren *et al.* introduced a two step protocol for polymerizing 1,4-butanediol and dimethyl succinate to give the corresponding PBS with molecular weights as high as $M_w = 7.3 \times 10^4$ gmol^{-1}, for which the catalyst Novozym 435 was added during the second polycondensation step.[93]



Scheme 44 Enzyme mediated polymerization of divinyl adipate with 1,4-butanediol.



Scheme 45 Synthesis of PBS *via* ring opening polymerization.

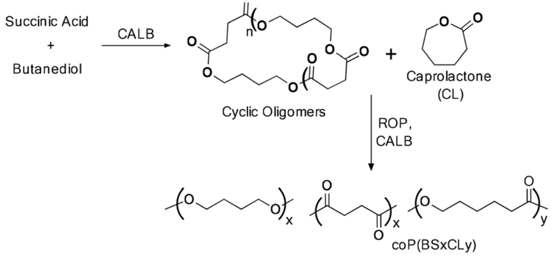
The generality of this method was further explored in synthesizing various PBS copolymers, such as poly(butylene succinate-*co*-butylene malate) (PBSM), poly(butylene succinate-*co*-butylene fumarate) (PBSFu), and poly(butylene succinate-*co*-butylene terephthalate) (PBST). The differences in the activities of the enzymes towards different di-acid monomers led to the formation of PBS copolymers with different molecular weights. Furthermore, from the literature it is evident that significant progress has been made in lipase-catalysed polymerization at temperatures below 90 °C.[94]

Poly(butylene succinate-*ran*-caprolactone) copolyesters (PBS-*ran*-PCL) with different compositions were synthesized by the ring opening polymerization of the corresponding cyclic oligomers of PBS and caprolactone using lipase CALB as a catalyst (Scheme 46). The M_n, M_w and PDI values of the PBS homopolymer produced under these enzymatic conditions were 4.7×10^4 g mol^{-1}, 6.1×10^4 g mol^{-1} and 1.3 respectively.

Furthermore, the influence of the ring size on copolymerization was systemically investigated and, from the results, it is evident that, irrespective of the size of the oligomers, the rate of enzyme mediated ROP is almost the same and results in polymers without significant changes in their molecular weights. However, the molecular weights of polyesters generated by enzymatic ROP are greatly influenced by the polymerization conditions, concentration of the catalyst, monomer and reaction temperature.[95]

Copolymerization of 1,4-butanediol (1,4-BDO)/2,3-butanediol (2,3-BDO) and succinic acid in the presence of an enzyme, Novozym®435 (N435) (about 10 wt% of immobilized *Candida antarctica* lipase B resulted in the formation of the corresponding poly(1,4-butylene succinate-*ran*-2,3-butylene succinate) (PBBS) copolymer (Scheme 47).

Solvent, temperature and concentration of the enzyme play a significant role in deciding the molecular weight of the polymer. Copolymerization using diphenyl ether as the solvent at 90 °C with the enzyme (10 wt%) afforded the corresponding co-polymer with high molecular weight ($M_n = 4.3$ g mol^{-1}) and high 2,3-BDO contents. A decrease in M_w with an increase in 2,3-BDO content indicates the differences in enzymatic reactiv-



Scheme 46 Synthesis of PBS-*ran*-PCL copolymers.

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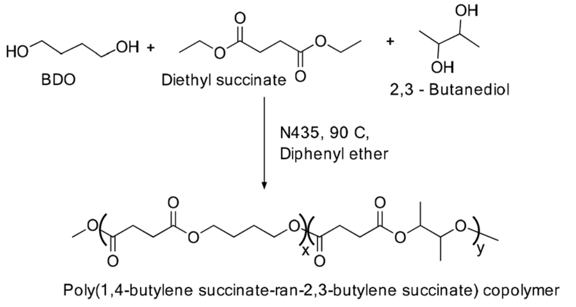
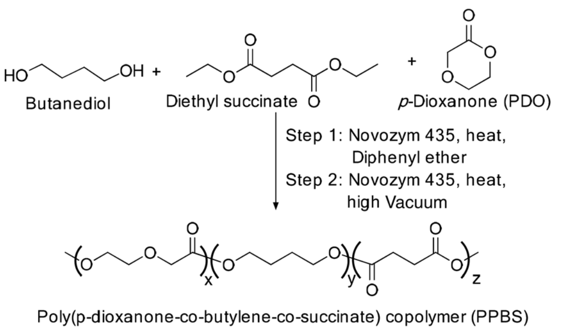


Scheme 47 Enzyme mediated polymerization of 1,4-butanediol (1,4-BDO)/2,3-butanediol (2,3-BDO) and succinic acid.



Scheme 48 Enzymatic synthesis of poly(*p*-dioxanone-*co*-butylene-*co*-succinate) (PPBS) copolyester.

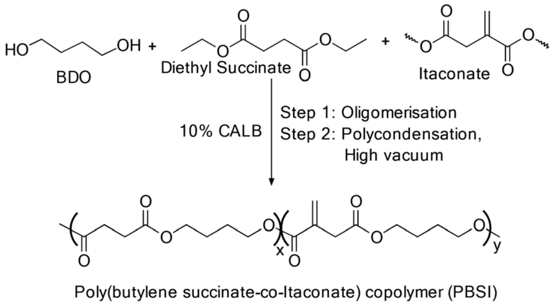
ity towards primary (1,4-DBO) and secondary (2,3-BDO) butane diols.[96]

Poly(*p*-dioxanone-*co*-butylene-*co*-succinate) (PPBS) copolyester was synthesized by the reaction of DES, BD and PDO under enzymatic conditions using 5 wt% of Novozym-435 as a catalyst in diphenyl ether as the solvent. M_n values of the synthesized homopolymer (PBS) and copolymer (PPBS) under the same reaction conditions were 1.31×10^4 g mol^{-1} and 1.9×10^4 g mol^{-1} respectively (Scheme 48).[97]

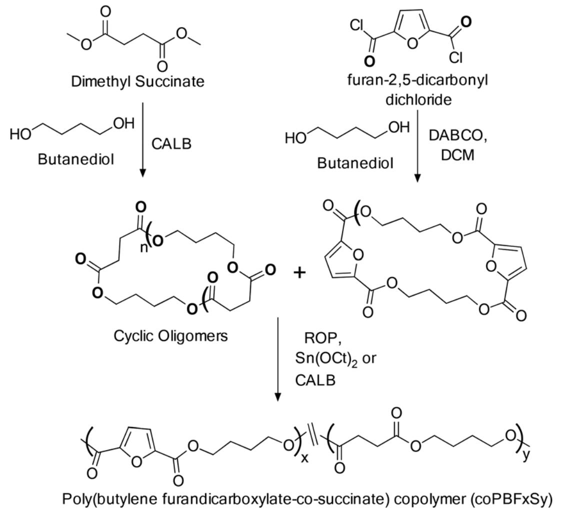
A truly green synthesis approach was employed for the synthesis of poly(butylene succinate-*co*-itaconate) (PBSI) copolymers using bio-based commercially available succinate, itaconate and 1,4-butanediol under enzymatic copolymerization conditions in the presence of *Candida antarctica* lipase B (CALB, in immobilized form as Novozym® 435) catalyst (Scheme 49). Moreover, diphenyl ether proved to be an efficient solvent system for this enzyme mediated copolymerization.[98]

Enzymatic *vs.* Lewis acid mediated synthesis of PBS

Aromatic–aliphatic poly(butylene furandicarboxylate-*co*-succinate) copolyester was prepared by a ring opening polymerization reaction under both enzymatic and Lewis acid catalyzed conditions using CALB or Sn(Oct)$_2$ respectively as the catalyst (Scheme 50). Copolyesters with M_w in the range of ~5–6.5 × 10^4 g mol^{-1} and 1.5×10^4 and 4.5×10^4 g mol^{-1} were produced respectively under chemically and enzymatically catalyzed ROP.



Scheme 49 Green method for the synthesis of poly(butylene succinate-*co*-itaconate) (PBSI) copolymers.



Scheme 50 Enzyme and Lewis acid catalyzed synthesis of aromatic–aliphatic copolyester.

The ROP method is found to be a milder and more efficient method for producing poly(butylene 2,5-furandicarboxylate-*co*-succinate) copolyesters with high molecular weights when compared to the corresponding melt polycondensation method. The rate of enzyme mediated ROP is found to be high but produces copolyesters with low molecular weights. The copolymer composition can be easily controlled through ROP by controlling the feed ratio.[99]

PBS and its copolymers

In recent years, bio-based plastics and biopolymers have gained considerable interest and account for approximately 1% of global polymer production. Similarities in the physical and mechanical properties of bioplastics with respect to poly-

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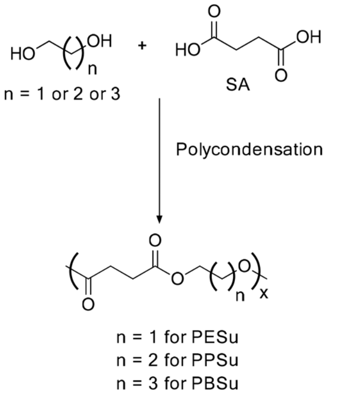
olefins, combined with the ease of processability using existing conventional equipment for polyolefins, has broadened their scope as potential alternatives to petroleum based non-biodegradable polymers.[2a] PBS is considered to be a potential alternative to fossil based polymers especially in packaging (films and boxes) and agriculture (mulch films) applications, where biodegradability is an added advantage. In addition, PBS has found increasing interest in biomedical applications. However, the relatively high cost and relatively lower physical and mechanical properties, with respect to conventional fossil fuel based polymers, largely restrict their applications in thermoplastic processing, foaming, filming, rigid packaging, and cosmetic and beverage bottles, where stiffness and thermal stability are critical requirements.[15b,100]

To widen the application window of PBS towards performance materials, extensive research is being carried out to improve the thermal, mechanical and biodegradability properties of aliphatic polyesters. As a result, various chemical and physical methodologies, such as chain extension, copolymerization, forming cross-linking networks, and the use of polymer blends and composites, have been reported in the literature to improve the physical and chemical properties of PBS.[6,75–81,101]

Homo-polymers

Polyalkylene succinates

The crystallization and melting behaviour of poly(ethylene succinate) (PESu), poly(propylene succinate) (PPSu) and poly(butylene succinate) (PBS) were examined (Scheme 51). The formation of large spherulites and a linear increase in the spherulite radius with time was observed for PESu and PBS copolyesters. Conversely, small spherulites were observed for PPSu copolyesters; moreover, enzymatic hydrolysis is faster in the amorphous phase, especially between spherulites, than inside them. The crystallization half-times for PPSu are much longer than those of corresponding PBS. However, lower crystallinity, melting temperature and heat of fusion were observed for PPSu compared to those of PBS, which possesses a high crystallinity and melting temperature.[102]



Scheme 51 Synthesis of poly-alkylene succinates.

PBS is a semi-crystalline polymer, which exhibits a melting point around 115 °C and a heat distortion temperature (HDT) of about 97 °C. PBS exhibits two crystal forms, α- and β-forms, of which the α-form is more common, while the β-form exists only under strain, which, in turn, converts into the α-form after the removal of strain. Moreover, the physical properties of PBS can be varied by the incorporation of comonomers.[15b]

Co-polymers

In general, copolymerization is a widely known chemical method for tuning the physical, mechanical and thermal properties of the desired homopolymers. In recent years, extensive research was carried out to develop PBS based copolymers for various applications. As a result, numerous PBS based copolyesters with enhanced physical and mechanical properties have been reported in the literature.[103] In this review, we tried our best to capture recent advancements in PBS copolymers.

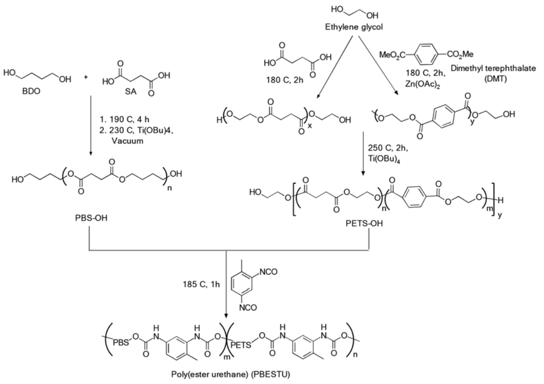
Copolymers *via* the chain extension reaction

Chain extension is a constructive approach to improve/increase the molecular weights of the polymer, which, in turn, will improve the mechanical and physical properties of the corresponding polymer.

Multiblock poly(ester urethane) (PBESTU)

A novel PBESTU was synthesized *via* the chain extension reaction of hydroxyl terminated poly(butylene succinate) (PBS-OH) and poly(ethylene succinate-*co*-ethylene terephthalate) (PETS-OH) using toluene-2,4-diisocyanate (TDI) as the chain extender (Scheme 52).

Interestingly, the two polymer segments in the copolymers are found to be compatible and exhibit a single glass transition temperature. Furthermore, it was observed that the PBS segment could enhance the crystallization capacity and thereby increase the mechanical properties of the polymers.



Scheme 52 Synthesis of multiblock poly(ester urethane) (PBESTU) *via* chain extension reaction.

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Moreover, it is evident that the composition of the samples has no influence on the tensile strength and elongation at the break. However, an increase of the number of PBS segments tends to increase the Young's modulus and this is due to the better crystallization of PBESTUs.[104]

The PBESTU20 (PBS (20):PETS (80)) copolymer is found to be nearly amorphous, and its T_g is below its testing temperature (16.6 °C). Furthermore, its stress–strain curve is in agreement with that of a typical elastomer. In contrast, the stress–strain curves of PBEST40 (PBS (40):PETS (60)) and PBEST100 (PBS (100):PETS (0)) are found to be similar and in accordance with those of crystalline polymers. The thermal stability of the polymer slightly decreases with an increase in PBS content.

PBT-PBS copolymers

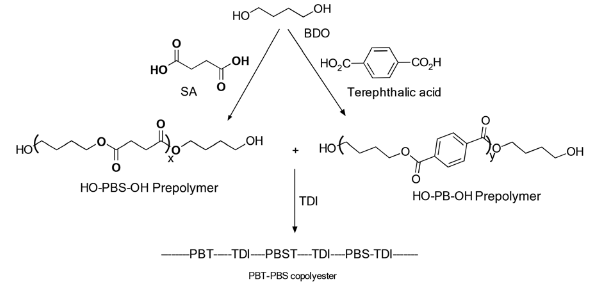
The chain extension reaction methodology under melt conditions was employed to synthesize a series of PBT-PBS copolyesters using dihydroxyl terminated PBT (HO-PBT-OH) and PBS (HO-PBS-OH) prepolymers in the presence of a chain extender (toluene-2,4-diisoyanate (TDI))(Scheme 53).

A clear single glass transition was observed for all the PBT-PBS copolyesters between the T_g values of PBT (44.0 °C) and PBS (−28.7 °C), which clearly indicated the miscibility of non-crystallized phases of PBT and PBS. Furthermore, a single crystallization peak was observed for all the copolyesters. Moreover, an increase in PBS content in the copolymer resulted in a lowering of the crystallization temperature and induced broadness in the crystallization peak. This clearly indicates that an increase in the PBS content of the copolymer decreases the crystallization rate, which is believed to be due to increased flexibility of the molecular chains and restricted crystal formation of the PBS component. Additionally, an increase in the degree of randomness decreases the melting and crystallization temperatures and increases the T_g of the copolymer.

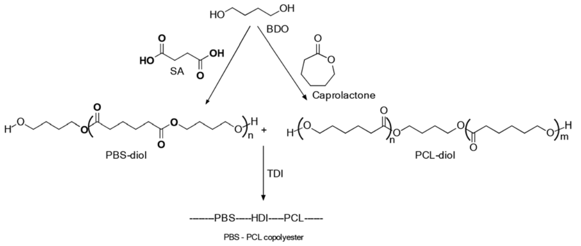
The molecular weights of HO-PBT-OH or HO-PBS-OH play a significant role in deciding the randomness of the synthesized copolyester. An increase in the molecular weight of either HO-PBT-OH or HO-PBS-OH increases the thermal stability and prevents the trans-esterification reaction.[105]

PBS-PCL copolymers

Copolyesters using PBS and PCL diols were synthesized *via* a chain extension reaction (Scheme 54). The resulting copolyesters exhibited a two-stage degradation behaviour (PCL followed by PBS segments), and copolymerization improved the thermal stability of PCL. Incompatibility between the PBS and PCL segments in the amorphous region resulted in separate melt and crystallizing properties. Thus, the PBS segment tended to crystallize first followed by the PCL segment. The incorporation of the PCL segment significantly enhanced the impact strength of the multiblock copolymers, and the copolymers became unbreakable with PCL contents higher than 10 wt%. Tensile strength, flexural strength, and the flexural modulus decrease with an increase in the PCL content and copolymers with PCL contents of 10–30 wt% display desirable tensile strength and excellent impact resistance properties.[106]



Scheme 53 Synthesis of PBT-PBS copolyester.

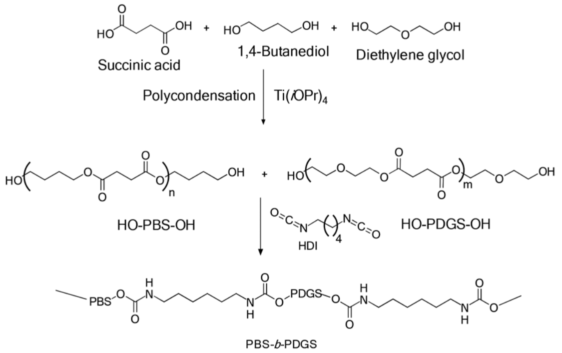


Scheme 54 Chain extension strategy for the synthesis of copolyesters using PBS and PCL diols.

PBS-*b*-PDGS copolymer

To enhance the properties of poly(butylene succinate), poly(diethylene glycol succinate) was introduced into the PBS backbone *via* the chain extension reaction of dihydroxyl-terminated PBS and PDGS precursors in the presence of a chain extender (hexamethylene diisocyanate (HDI)) (Scheme 55). PBS and PDGS units are found to be miscible in the copolymers. The incorporation of PDGS segments increases elongation at the break of PBS and a slight decrease in melting and crystallization temperatures is observed. Furthermore, the crystallization rate and spherulitic growth rate tend to decrease with an increase in PDGS content.

In addition, the glass transition temperature and cold crystallization temperature were found to increase with an increase in PDGS content. However, the melt and melting crystalliza-



Scheme 55 Synthesis of PBS-*b*-PDGS copolymer.

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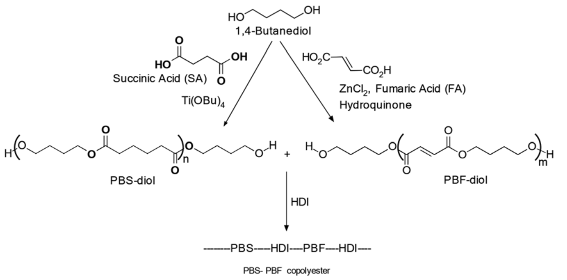
tion temperatures as well as the crystallinity decrease with an increase in PDGS content. Finally, when compared to neat PBS, the PBS-*b*-PDGS copolyester displayed interesting mechanical properties with higher strength and toughness.[37]

PBS-PBF copolymers

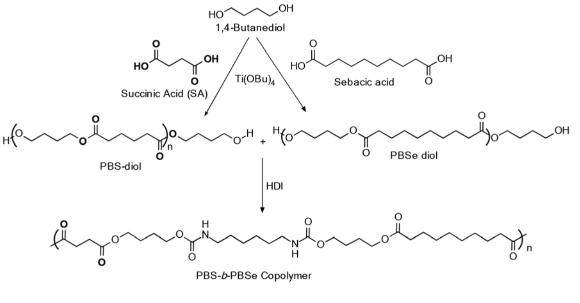
Copolymers synthesized by the chain extension reaction of polybutylene fumarate diol and polybutylene succinate diol exhibited good mechanical properties similar to those of the corresponding homo-polymers, PBS and PBFu (Scheme 56). Tensile strength increases with an increase in PBS content, whereas elongation at the break ranges from 120% to 156%. Flexural strength, flexural modulus and elongation at the break remain almost unaltered with respect to composition.[107]

PBS-*b*-PBSe copolymer

Novel PBS based, biodegradable and double crystalline poly (butylene succinate)-*b*-poly(butylene sebacate) multiblock copolymers were synthesized from PBS-diol and dihydroxyl terminated PBSe (PBSe-diol) using HDI as a chain extender (Scheme 57). The synthesized multiblock copolymers were found to be thermally stable and the thermal decomposition temperature was found to be above 340 °C. Both PBS and PBSe blocks crystallized separately during the cooling process. There was a gradual decease in the melt crystallization temperature and melt crystallization enthalpy of one block with an increase in the content of the other block. Furthermore, there was a slight and significant decrease in the crystallinity value for the PBS block and the PBSe block when compared to the corresponding homopolymers.



Scheme 56 Synthesis of PBS-PBF copolymer.



Scheme 57 Synthesis of poly(butylene succinate)-*b*-poly (butylene sebacate) multiblock copolymers.

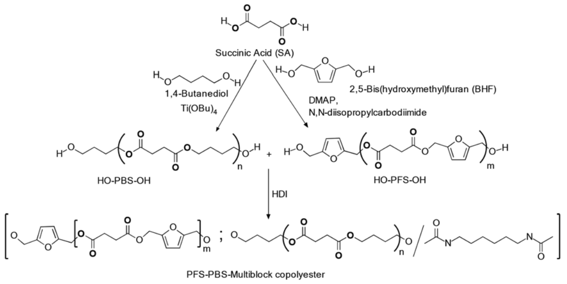
Furthermore, the effect of PBS block crystals towards the crystallization of the PBSe block was found to be significant. The melting point temperatures of the two blocks were slightly lower than those of the corresponding homopolymers and these two blocks were found to be miscible in the amorphous phase. In addition, an enhancement in the mechanical properties was observed for the copolymers with respect to the PBS homopolymer, which was evident from the significant increase in the elongation at the break values (51.7 ± 0.8% for the PBS homopolymer to 299.2 ± 16.7% for PBS-*b*-PBSe$_2$ (f_{PBS} 77.4% and f_{PBSe} 19.3%) and 673.6 ± 22.2% for PBS-*b*-PBSe$_4$ (f_{PBS} 56.5% and f_{PBSe} 40%)). However, there is a slight decrease in the tensile strengths and Young's modulus values.[27]

PFS-PBS multiblock copolymer

HO-PBS-OH (PBS diol) prepolymer was synthesized by the reaction of BDA and SA using TBT as a catalyst, which, in turn, was converted into the PFS-PBS multiblock copolymer by treatment with HO-PFS-OH (PFS diol) using HDI as a chain extender (Scheme 58). The PBS block exhibited better thermal stability than that of the PFS block. Two stages of thermal degradation (PFS followed by PBS) were observed for PFS-PBS copolyesters. The incorporation of the PFS blocks into PBS displayed a single T_g, which increased with an increase in the content of the PFS block. In addition, copolyesters showed a single crystallization peak and the crystallization of the PFS-PBS multiblock copolyesters was due to the formation of crystals from the PBS block.

An increase in the PFS content decreases the crystallization rates and degree of crystallinity without affecting the crystallization mechanism. A gradual decrease in T_c was observed with an increase in the PFS content of the copolyesters. The exclusion of amorphous PFS blocks from crystalline PBS blocks during crystallization led to a decrease in the crystallinity of copolyesters.

In addition, the mechanical properties of the PFS-PBS copolyesters were found to be composition dependent and an increase in the PFS content resulted in a decrease of the modulus, tensile strength, T_c and crystallinity of the copolymer. However, T_g and elongation at the break tend to increase with an increase in PFS content. A single T_g was observed for



Scheme 58 Synthesis of PFS-PBS multiblock copolymer.

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all the synthesized PFS-PBS copolymers. Thus, PFS-PBS copolyesters could be tuned from crystalline thermoplastics to elastomer-like polyesters by changing the amorphous PFS content from low to high respectively in the copolyester.[108]

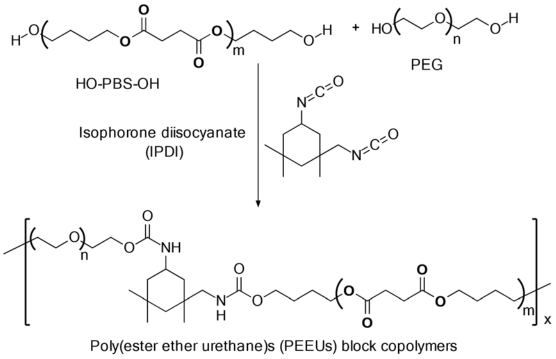
Copolymers with both hydrophilic and hydrophobic parts

A series of poly(ester ether urethane) (PEEU) block copolymers consisting of both a hydrophobic part (poly(butylene succinate) and a hydrophilic part (poly(ethylene glycol)) were prepared *via* the chain extension reaction using dihydroxyl terminated PBS and PEG in the presence of isophorone diisocyanate (IPDI) as a chain extender (Scheme 59).

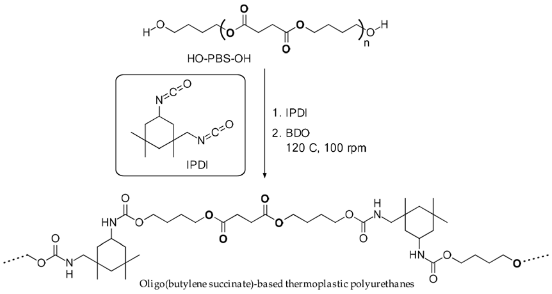
At a high concentration of PEG units in the copolymer, both the PBS segment and the PEG segment tended to form a single crystalline region and this behavior had a small impact on each segment within the copolymer. All the PEEU copolymers with different PEG contents exhibited ring-spherulite morphology, and then the size and distance between the spherulites increased with an increase in PEG content. The presence of PEG enhanced the crystallization ability of the PEEU copolymer without affecting the crystallization morphology. PEG and PBS segments were found to be miscible in the copolymer. In terms of the mechanical properties, an increase in the PEG content in the copolymer led to an increase in the tensile strength at first followed by a slight decrease. Whereas, the elongation at the break was found to increase gradually with an increase in PEG content. Flexibility of the PEG segment was greater than that of the PBS segment and therefore an increase in the PEG soft segment led to a gradual decrease in the tensile strength. On the other hand, a higher content of the PEG soft segment in the copolymer led to enhanced phase separation, which in turn increased the elongation at the break.[76]

Oligo(butylene succinate)-based TPU

Higher strain at the break was observed for oligo(butylene succinate)-based thermoplastic polyurethanes (TPUs) (Scheme 60) when compared to that of the corresponding homopolymer (PBS). Hydrogen bonging increased with an increase in isocyanate content, which in turn increases the Young's modulus of the corresponding polymer without limiting the strain at the break. However, the introduction of chain extenders resulted in a reduction of the degree of crystallization and subsequent decrease in the storage modulus when compared to that of PBS. The presence of hard segments within TPUs acted as defects and reduced the crystallization ability of the PBS-based TPUs. A reduction in T_c and T_f for TPUs of about 10 °C was observed due to the irregularities induced by the hard segments.



Scheme 59 Synthesis of poly(ester ether urethane) (PEEU) block copolymers with both hydrophilic and hydrophobic parts.



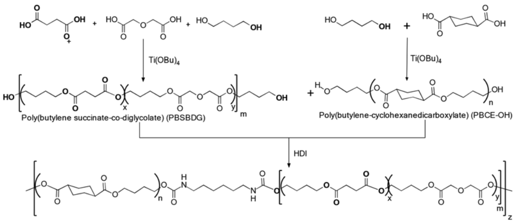
Scheme 60 Synthesis of oligo(butylene succinate)-based thermoplastic polyurethanes (TPUs).

Thermal stability studies indicated that, due to a broader range of thermal degradation, PBS-based TPUs had a lower thermal stability compared to that of homo-PBS. However, the maximum rate of decomposition (T_d max) was lower for TPUs than that of the corresponding homopolymer. Furthermore, TPUs with more urethane linkages (isocyanate index) displayed lower thermal stability.[51]

High molecular weight poly(ester urethane)s

High molecular weight poly(ester urethane)s were prepared by the chain extension reaction of the corresponding hydroxyl terminated poly(butylene cyclohexanedicarboxylate) (PBCE-OH) and poly(butylene succinate-*co*-diglycolate) random copolymers with two different compositions using hexamethylene diisocyanate (HDI) as a chain extender (Scheme 61).

A higher amount of BDG content in the PBS-based blocks resulted in a lowering of the crystallizability of the PBS phase. Copolymers with equimolar concentrations (P(BS50BDG50) exhibited higher elongation at the break and a lower elastic modulus when compared to that of copolymers with a high PBS content P(BS70BDG30). Copolymers with equimolar concentrations exhibited lower crystallinity than that of the P(BS70BDG30) copolymer.[109]



Scheme 61 Synthesis of high molecular weight poly(ester urethane)s.

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PES-*b*-PBS multiblock copolymers

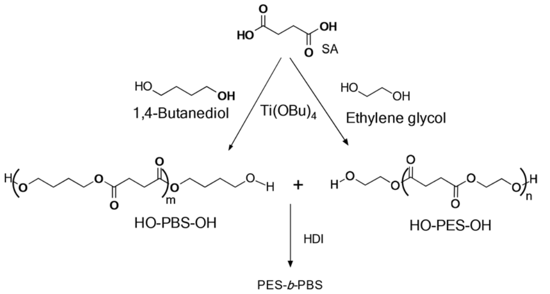
PES-*b*-PBS multiblock copolymers were prepared by the chain extension reaction of the corresponding dihydroxyl terminated prepolymers using HDI as a chain extending agent (Scheme 62).

The miscibility of the copolymers was greatly enhanced by the block lengths of the corresponding copolymers. The miscibility of the PBS and PES blocks in the amorphous phase increased when the block lengths were smaller and the miscibility decreased with an increase in block length. Crystallization behaviors (crystal structure and morphologies) were not affected by copolymerization, but the crystallizability of the copolymer increased with an increase in block length. Thus, PES and PBS blocks in the copolymers were able to crystallize and the PES block crystallized within the interlamellar regions of PBS spherulites.[110]

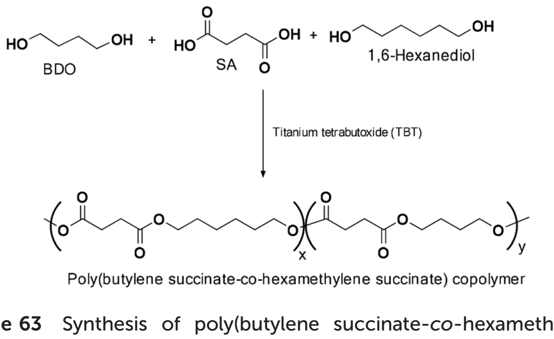
Aliphatic copolymers

P(BS-*co*-HS) copolymers

The synthesis of poly(butylene succinate-*co*-hexamethylene succinate) (P(BS-*co*-HS)) with various molar ratios of butylene succinate (BS)/hexamethylene succinate (HS) *via* direct melt poly-condensation was also reported in the literature (Scheme 63). The possibility of tuning the physical properties of the polymer by changing the monomer composition was explored in detail. All the synthesized polyesters exhibited good thermal stability and the degradation temperature ranged form 300 °C to 450 °C. Monomer composition played a significant role in enhancing the degradation temperature at 10% weight loss (T_d – 10%) of the polyesters, which increased from 336 °C for neat PBS to 376 °C for PHS. In comparison with pure PBS, T_d – 10% was enhanced by around 10 °C for BS-enriched copolyesters, and by around 30 °C for HS-enriched co-polyesters.



Scheme 62 Synthesis of PES-*b*-PBS multiblock copolymers.



Scheme 63 Synthesis of poly(butylene succinate-*co*-hexamethylene succinate) (P(BS-*co*-HS)).

Moreover, all the P(BS-*co*-HS) copolyesters exhibited only one T_g between those of neat PBS and PHS, which decreased with an increase of HS content in the copolyesters. However, the melting point temperature and equilibrium melting point temperature of P(BS-*co*-HS) were reduced significantly. Additional HS content initially decreased the Young's modulus and yield stress followed by an increase upon further addition of HS. Conversely, the elongation at the break tended to increase with an increase in comonomer content. Furthermore, P(BS-*co*-HS) copolyesters exhibited elastomeric behavior when compared to the brittle nature of pure PBS or ductile plastic nature of pure PHS.[35]

The crystal structures of P(BS-*co*-HS) copolyesters were found to be same with respect to that of neat PBS, which clearly indicated that the HS unit remained in the amorphous region, furthermore, incorporation of the HS comonomer reduced the crystallinity values compared to those in neat PBS. In addition, at the same crystallization temperature, the spherulitic growth rates of P(BS-*co*-HS) were smaller than that of neat PBS. It is also observed that the spherulitic growth rates of P(BS-*co*-HS) copolyester decreased with an increase in HS composition.[111]

Incorporation of the HS unit into neat PBS not only modified the crystal structures of PBS, but also slightly changed the crystal size and the degree of crystallinity (Scheme 63). Thus, copolyesters had bigger crystal sizes and lower degrees of crystallinity compared with those of neat PBS. Furthermore, the structure of the copolymer chains was found to be disordered, which resulted in the suppression of T_c, T_m and ΔH_m. Furthermore, the elongation at the break for copolyesters increased with an increase in HS content compared to that of the corresponding homo-polymers. However, the Young's modulus of the copolyesters decreased with the introduction of HS units.[112]

PHBS copolymers

The thermal properties and crystallization behavior of novel poly(hexamethylene succinate-*co*-6 mol% butylene succinate) (PHBS) (Scheme 64) have been extensively studied and compared with those of the corresponding homopolymer PHS. The introduction of a small amount of PBS into PHS resulted in a reduction of the melting point and the equilibrium melting point of the copolymer but there was no significant change in the glass transition temperature.

Both the homopolymer and the copolymer crystallized through the same crystallization mechanism and the crystallization rate of the copolymer was lower than that of the corresponding PHS homopolymer. It was also observed that a reduction in crystallization temperature increased the crystalli-

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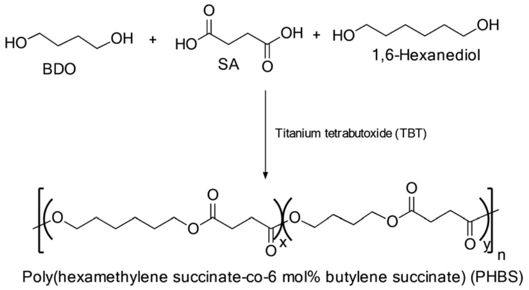


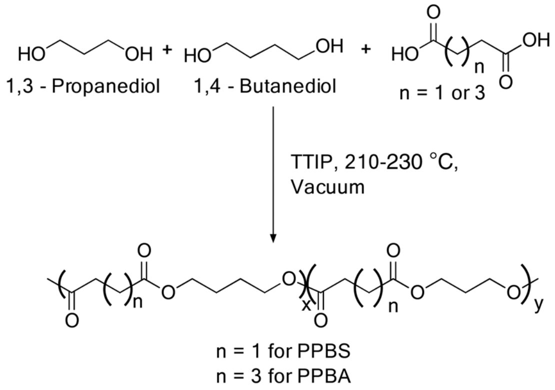
Scheme 64 Synthesis of PHBS copolymers.

zation rate for both the homo- and copolymer. Spherulite morphologies were observed in both the homo- and copolymer, but the nucleation density was found to be smaller in the copolymer than that in the corresponding homopolymer.[113]

PP-*r*-BS and PPBA copolymers

Aliphatic copolyesters [poly(1,3-propylene succinate-*ran*-1,4-butylene succinate) (PP-*r*-BS) and poly(1,3-propylene adipate-*ran*-1,4-butylene adipate) (PPBA)] were synthesized using 1,3-propanediol (1,3-PDO) and 1,4-butanediol with different molar ratios and examined for their mechanical and thermal performances (Scheme 65).

All the synthesized copolyesters exhibited good thermal stability below 260 °C and maximum degradation occurred above 315 °C and 325 °C respectively for PP-*r*-BS and PPBA copolyesters. The thermal stability of all adipate based copolyesters was found to be high and the thermal stability depended on the diacid monomer. Furthermore, the structural framework and length of the diol had no effect on the thermal stability. An isodimorphic co-crystallization behavior of both copolymers was very clear from the pseudo-eutectic melting behavior and the presence of only one crystalline phase, except for PPBA copolyesters with high 1,3-PDO contents. The succinic acid and 1,3-PDO contents in the copolyesters decreased the chain mobility and thereby increased the T_g of the corresponding copolyesters. The decrease in chain mobility might be due to an increase in the density of ester functional groups in the copolymer.[114]



Scheme 65 Synthesis of PP-*r*-BS and PPBA copolymers.

PBSPS copolymer

The effect of glycerol on the crystallization growth rates in poly(butylene succinate-*co*-propylene succinate) (PBSPS) copolymers was systematically examined. Isothermal crystallization kinetic studies indicated that PBSPS copolymers grew three dimensionally; this was initiated by heterogeneous nucleation. Furthermore, the crystallization growth rates were faster in the presence of glycerol than in the absence of glycerol. The presence of glycerol in lower amounts (0.01%) in PBSPS formed a nucleation site and thereby increased the packing ability of the molecular chains. However, an increase in the glycerol content decreased the relative crystallinity due to restricted movement of the molecular chain. Thus, a small amount of glycerol could improve the relative crystallinity and crystallization rate of the PBSPS copolymer.[115]

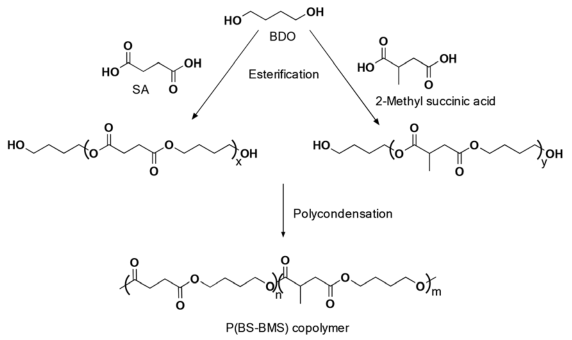
P(BS-BMS) copolymer

Copolymers of poly(butylene succinate-*co*-butylene 2-methylsuccinate) (P(BS-BMS)) were synthesized using succinic acid (SA), 2-methylsuccinic acid (MSA) and 1,4-butanediol (BDO) *via* a two step esterification and poly-condensation process (Scheme 66).

The thermal stability of PBS and P(BS-BMS) was barely affected by the introduction of MSA and it was found that $T_{d,5}$ (decomposition temperature at 5% weight loss) and $T_{d,max}$ (maximum rate) of pure PBS and P(BS-BMS) copolymers ranged from 337.1 to 340.0 °C and 397.6 to 399.4 °C, respectively. Furthermore, these copolymers possessed tunable melting temperatures and degrees of crystallinity. The crystallinity ranged from highly crystalline to amorphous in nature. An increase in the MSA content increased the amorphous region in the copolyester, due to destruction of the chain regularity and thereby this reduced the crystallinity.[116]

PBBS copolymer

The influence of regio isomers on the copolymers was studied using poly(1,4-butylene succinate-*ran*-2,3-butylene succinate) (PBBS) copolymer (Scheme 67). An increase in the 2,3-BDO content of the copolymers increased the T_g but decreased the chain mobility and degree of crystallinity of the corresponding



Scheme 66 Synthesis of poly(butylene succinate-*co*-butylene 2-methylsuccinate) (P(BS-BMS)) copolymers.

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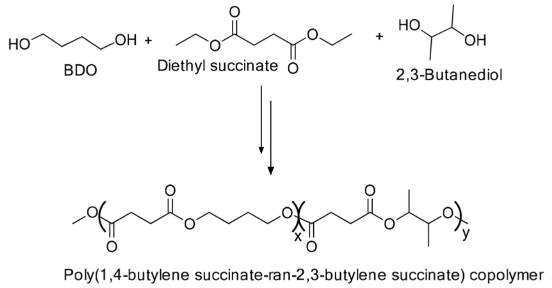


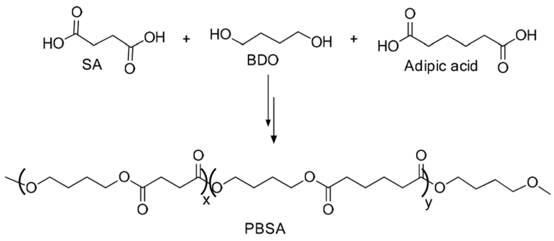
Scheme 67 Regio-isomeric polyalkylene succinate.

copolyesters. Polymers with an amorphous nature were obtained when the 2,3-BDO content was higher than 47%. Interestingly, all copolyesters displayed excellent thermal stability.[96]

PBSA copolymer

DSC and WAXS analysis of poly(butylene succinate-*ran*-butylene adipate) random copolymers (PBSA) (Scheme 68) indicated that PBSA random copolymers were isodimorphic in nature and each phase permitted the inclusion of the minority comonomer. In all copolymer compositions, the PBA-rich phase tended to crystallize in the β-PBA phase (kinetically favored) due to the inclusion of PBS repeating units in the cocrystals.[21]

Additional investigations into the crystallization conditions for comonomer exclusion/inclusion balance in PBSA random copolymers indicated that fast crystallization (*i.e.*, non-isothermal tests) favored BA inclusion inside the PBS phase crystals, whereas slow crystallization (*i.e.*, isothermal test) strongly limited it. Interestingly, a combination of fast and slow crystallization conditions demonstrated intermediate behavior due to the inclusion of BA comonomers during the conditioning step, whereas the annealing steps permitted less incorporation. However, both fast and slow crystallization of PBA resulted in the formation of the β-PBA phase with BS unit inclusion irrespective of the cooling conditions. It was also observed that expansion of the PBS crystal unit cell permitted accommodation of the BA comonomeric unit. Consequently, BS inclusion expanded the β-PBA unit cell along both the *a*- and *b*-axes whereas the combination of both expansion and shrinkage along the *a*- and *b*-axes occurred in the α-PBA unit cells (Fig. 13).[117]



Scheme 68 Synthesis of PBSA copolymer.

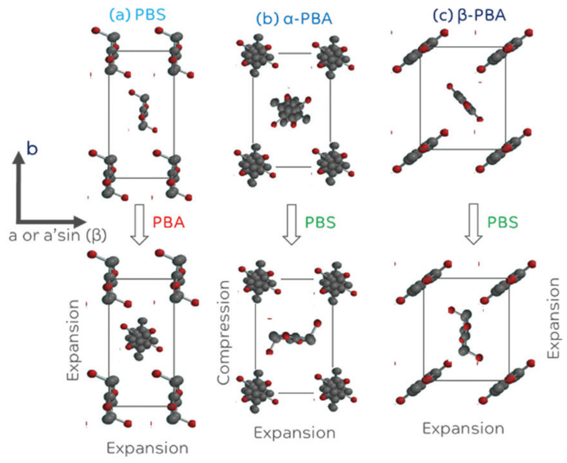


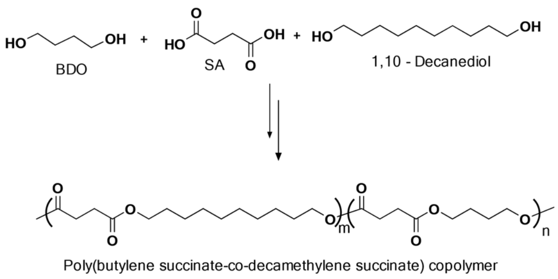
Fig. 13 Representation of isodimorphism.

PBDS copolymer

An investigation of the thermal and mechanical properties as well as crystal structures of poly(butylene succinate-*co*-decamethylene succinate) (PBDS) copolyesters (Scheme 69) clearly indicated that the glass transition temperature, melting point temperature, nonisothermal melt crystallization peak temperature and equilibrium melting point temperature were lower than those of the corresponding PBS and tended to decrease further with an increase of the DS composition. Furthermore, an increase in DS composition significantly increased the elongation rate at the break of PBDS co-polyesters; however, there was a gradual decrease in yield stress, Young's modulus, and tensile strength.[43]

P(BS-*co*-BAz) copolymers

Poly(butylenesuccinate-*co*-butyleneazelate) (P(BS-*co*-BAz)) copolyesters (Scheme 70) displayed good thermal stability up to 230 °C. All P(BS-*co*-BAz)s started to decompose in the range 230–260 °C and their thermal degradation followed a two-stage decomposition and ended at ~490 °C. An increase in the number of BAz units decreased the weight loss in the first stage of decomposition and increased during the second stage of degradation. Furthermore, it was realized that increasing the BAz unit content in the copolymers decreased the elastic



Scheme 69 Structure of poly(butylene succinate-*co*-decamethylene succinate) copolyesters.

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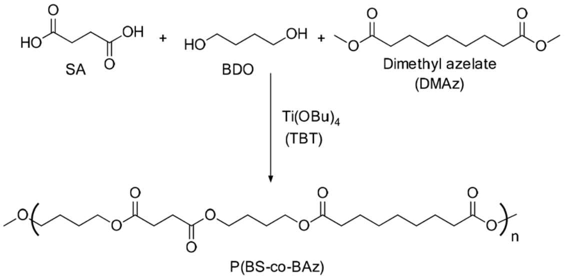
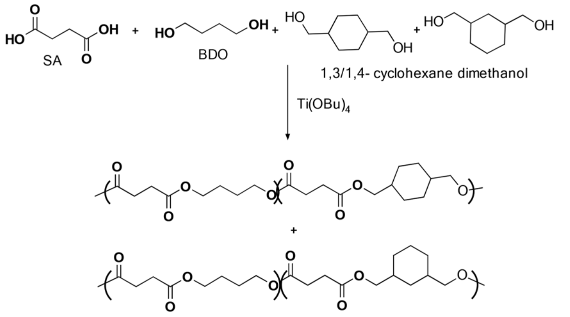


Scheme 70 Synthesis of P(BS-*co*-BAz).



Scheme 71 Synthesis of CHDM based alicyclic/aliphatic copolyesters.

response of P(BS-*co*-BAz)s and increased the flexibility with a maximum close to 50 mol% BAz. This might be due to the formation of random copolymers with uniform composition along the chain.[118]

(PBS-*ran*-PBAz) copolymers

The crystallization behavior of poly(butylene succinate-*ran*-butylene azelate) copolyesters (PBS-*ran*-PBAz) depended on the copolymer composition and it was found to be isodimorphic in nature, *i.e.*, there was a small degree of comonomer inclusion in the crystalline phases that are formed in the copolymers. Thus, in PBS-*ran*-PBAz copolymers, where, PBS rich units are observed, a small amount of BAz units is present in PBS like crystalline units and *vice versa*. However, in a random copolymer that had a composition near the pseudo-eutectic point, the formation of two crystalline phases with the inclusion of a small amount of the second co-unit was observed. Furthermore, during crystallization, the amount of comonomer inclusion was much lower than the comonomer exclusion; this drives the fractionation ability of the copolymer.[119]

An investigation of nucleation kinetics, spherulitic growth rates and overall crystallization kinetics of poly(butylene succinate-*ran*-butylene azelate) random copolyesters (PBS-*ran*-PBAz) indicated that the introduction of BAz-units into the PBS polymer chain significantly affected the crystallization of PBS-rich compositions. Furthermore, increasing difficulty in incorporating BAz units into the PBS crystals resulted in an increased density of nuclei and thereby decreased the spherulitic growth rate. However, in PBAz-rich compositions, the introduction of BS units did not affect crystallization and instead an anti-nucleating effect was observed. Moreover, it was concluded that the incorporation of comonomer within PBS crystals in the PBS rich composition was much lower when compared to PBAz-rich compositions.[120]

PBSC copolyesters

An array of 1,3/1,4-cyclohexanedimethanol based alicyclic/aliphatic copolyesters (PBSCs) at various molar ratios of monomers were also synthesized using SA, 1,4-BD and 1,3/1,4-CHDM (Scheme 71), to study the influence of these compositions on crystallinity, biodegradability and the mechanical properties of the copolyester. The glass transition temperature (T_g) of PBSCs was found to increase with respect to an increase in 1,3/1,4-CHDM content, due to restriction of the polymer chain movement by the bulky and cyclical moiety of 1,3/1,4-CHDM. Conversely, the melting temperature, degree of crystallinity, ultimate stress and initial modulus decreased significantly with an increase of the 1,3/1,4-CHDM content. Moreover, the strain at the break increased as the 1,3/1,4-CHDM content increased, indicating the influence of the alicyclic moiety in improving the ductility of the copolyester by reducing the degree of crystallinity.[121]

The crystalline structure and morphology analysis revealed that the copolymer changed its morphology from ring-banded spherulites at a low cyclohexanedimethylene succinate (CS) content to a regular spherulite morphology at a high cyclohexanedimethylene succinate (CS) content. It was also evident that the cyclohexyl group of CHDM not only influenced crystal formation, but also altered the morphology of the copolymers during crystallization. The hot crystallization temperature (T_c) of PBCS copolymers decreased with an increase of CS content and no significant changes were observed with a further increase in CS content and this phenomenon could be due to the low crystallization rate. Furthermore, T_g of the copolymer increases with an increase in CS content and only one T_g was observed for all the copolymer compositions indicating that the copolymers were completely miscible at all compositions.[121]

Furthermore, an increase in CS up to 50% resulted in a decrease of the melting point, melting enthalpy and size of the spherulites for the PBCS copolymers and the opposite trend was observed for a further increase in the CS content above 50%. A comparison of temperature and shear rate on the viscosities of the copolymers indicated that the copolymers were more sensitive to temperature than the shear rate in the molten state.[75]

PBS-*ran*-PCL polymer

Poly[(butylene succinate)-*ran*-(ε-caprolactone)] copolyesters (PBS-*ran*-PCL) (Scheme 72) were found to be isodimorphic in nature and exhibited spherulitic superstructures, in which its nucleation depended on the copolymer composition. Properties such as T_m, T_c and lamellar thickness were insensitive to large molecular weight variations. Nevertheless, the degree of crystallinity and T_g varied significantly with respect

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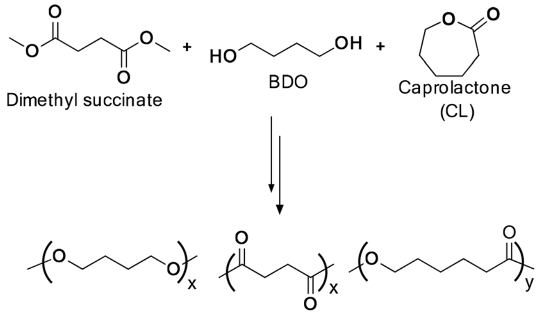


Scheme 72 Synthesis of PBS-*ran*-PCL copolymer.

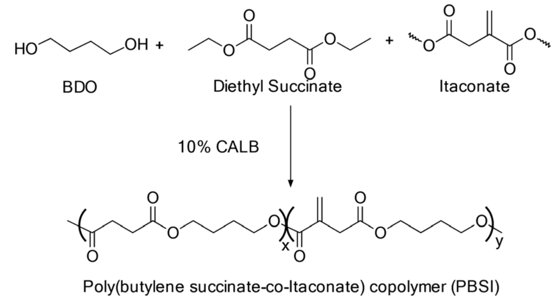
to an increase in molecular weight. Moreover, the average length of the crystallizable sequences was controlled by comonomer exclusion and thus, a decrease in the average lamellar thickness (l_c) at each side of the pseudoeutectic region was observed with an increase in comonomer addition.

Furthermore, the amount of crystals that could be formed was also dictated by comonomer exclusion and hence, the degree of crystallinity decreased with an increase in comonomer content, while the amorphous layer thickness (l_a) increased on both sides of the pseudoeutectic region. The copolyester with $BS_{45}CL_{55}$ composition exhibited double crystalline properties, in which space filling spherulites were formed by the PBS rich phase at higher temperature and at lower temperatures, the PCL rich phase crystallized in the interlamellar amorphous regions.[122]

The composition of the copolymers strongly influenced the spherulitic texture and nucleation density. Thus, an increase in the PCL content in BS-rich copolymers resulted in an increased nucleation density and decreased spherulitic size. Conversely, an increase in PBS content in the copolymer resulted in larger sized spherulites with decreased nucleation density. From WAXS analysis at −60 °C, it was realized that copolymers with BS contents greater than 60% displayed unique PBS reflections and, on the other hand, copolymers with CL contents greater than 60% showed PCL reflections. However, copolymers in the pseudo-eutectic region with BS content (54%) and CL content (46%) displayed reflections corresponding to combined crystal types.[95]

PBSI copolymer

TGA and DSC analysis of the poly(butylene succinate-*co*-itaconate) (PBSI) copolymers indicated that the concentration of itaconate in the PBSI copolymer (Scheme 73) did not have any influence on T_g and the thermal stability of the copolymers. The glass transition temperatures of the homopolymer (PBS) and copolymer (PBSI) were found to be −35 and −38 °C respectively. Both the homopolymer and the copolymer degraded with a maximum at around 400 °C. T_m of the copolyesters was significantly influenced by the itaconate content in PBSI and decreased almost linearly with respect to the mole percentage of itaconate.[98]



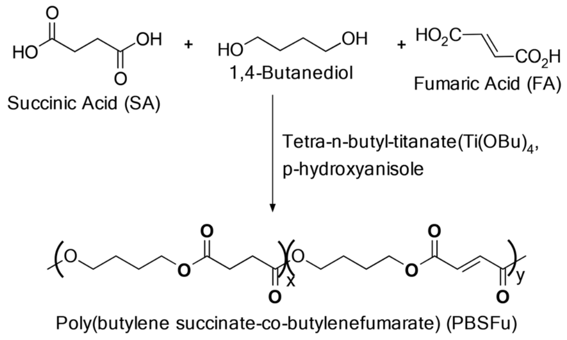
Scheme 73 Synthesis poly(butylene succinate-*co*-itaconate) (PBSI) copolymers.

PBSF copolymer

The introduction of *trans*-unsaturated comonomer (fumaric acid) units into saturated PBS polyester resulted in the isolation of poly (butylene succinate-*co*-butylene fumarate) (PBSFu) copolymer, which followed strict isomorphism by adopting the same crystal modification with slight differences in the crystal lattice parameters. A linear change in the melting point of the copolymers was observed with respect to copolymer composition and there was no significant change in the melting enthalpy. The introduction of *trans*-unsaturated comonomer units into PBS enhanced the total crystallization rate as well as the radial growth rate of the spherulites. In addition, PBF and PBSF tended to exhibit nucleating effects for PBS and its copolymers.[74]

Poly(butylene succinate-*co*-butylene fumarate) (PBSFu) copolymers with various molar ratios of butylene fumarate (BFu) from 1% to 40% were synthesized (Scheme 74) and their corresponding single crystals were prepared using a self-seeding method. Single crystals of copolymers changed from a regular hexagonal shape to round with respect to an increase in BF content. However, the degree of supercooling of the PBSF single crystals with different BF contents increased with an increase of the BF content, which resulted in an increased crystalline density and a decrease in tee size of the single crystals.

Selected area electron diffraction (SAED) analysis of PBSFu single crystals indicated an isomorphism between butylene succinate and butylene fumarate in the PBSFu copolymer. Furthermore, a close similarity in crystalline structures with



Scheme 74 Synthesis of PBSFu copolymer.

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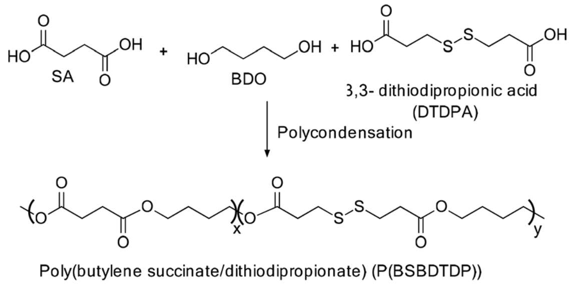
slight changes to the unit cell parameters was observed for PBS and the PBSFu copolymer. Ring banded spherulites were observed in PBSFu copolymers at suitable crystallization temperatures. The band spacing of PBSFu increased with the isothermal crystallization temperature and subsequently decreased with an increase in BF content at the same crystallization temperature. The crystallization temperature range for forming ring-banded spherulites broadened with an increase in the BFu molar ratios.[123]

P(BSBDTDP) copolymer

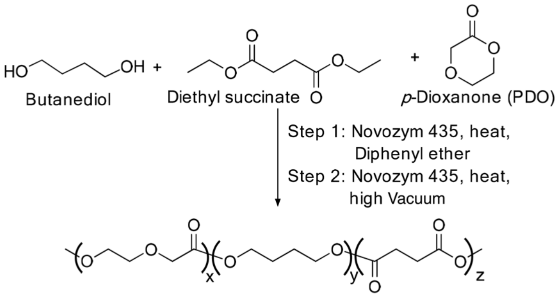
The hydrophobicity and thermal stability of poly(butylene succinate/dithiodipropionate) (P(BSBDTDP)) copolymer (Scheme 75) seemed to be unaltered, but the crystallinity of the copolymer was found to be lower when compared with the corresponding homopolymer. This reduced crystallinity resulted in faster degradation of the copolymer under physiological conditions.[26]

PPBS copolymer

Good compatibility was realized between PBS and the PDO chains in the PPBS copolymer (Scheme 76), which was evident by the single T_g. Furthermore, PDO chains in the PPBS copolyester restricted the movement and packing of PBS units, which resulted in inhibited crystallization and decreased melting points (T_m) of the copolyester. A change/increase in the crystallization temperature for the PPBS copolyester resulted in the corresponding changes to the spherulite structures from a well-rounded shape to straight-stalk dendrites. The distance between the interlamellar region of the PPBS copolyester was highly affected by the crystallization temperature, which led to the segregation of the PBS chain and subsequent breakdown of faceted crystals into dendritic morphologies. All the copolyesters with different compositions exhibited dendritic morphologies irrespective of the thickness of the films produced from the respective copolyester.[97]



Scheme 75 Synthesis of P(BSBDTDP) copolymer.



Scheme 76 Synthesis of PPBS copolymer.

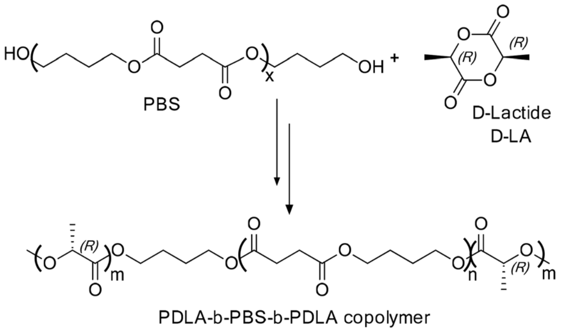
PBS copolymers with hydroxy acid units

An investigation into the isothermal crystallization and subsequent melting behaviors of PDLA and PBS blocks clearly indicated that at higher crystallization temperatures, the incorporation of longer PDLA blocks into the copolymer increased the crystallization rate at first and then it decreased. Furthermore, longer PDLA blocks covalently bonded to PBS resulted in an increased crystallization enthalpy before levelling off accompanied by a gradual increase in melting temperature. In general, PDLA crystallized slower in the tri-block copolymer than in the corresponding PLA homopolymer. On the other hand, there was a gradual decrease in crystallization and melting enthalpies for the PBS block when a considerable amount of PDLA was incorporated into the copolymer (Scheme 77).[54]

PBS copolymers with rigid monomeric units

PBIS copolymer

A series of PBS copolyesters (PBIS) were synthesized through two-step melt polymerization by using isosorbide (IS), one of the most significant carbohydrate-derived rigid and hydrophilic comonomers (Scheme 78). Because of its rigidity and chirality, incorporation of the IS unit into the PBS backbone linearly enhanced the T_g values of the copolyesters (PBIS). However, crystallinity, melting temperature and crystallization/melting enthalpies tended to decrease with an increase in IS content.[73a]



Scheme 77 Synthesis of PDLA-*b*-PBS-*b*-PDLA copolymer.

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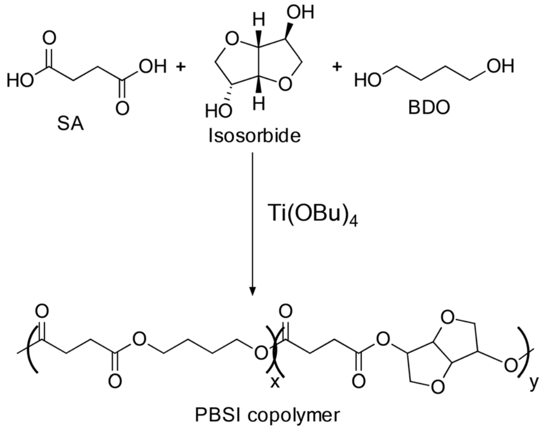


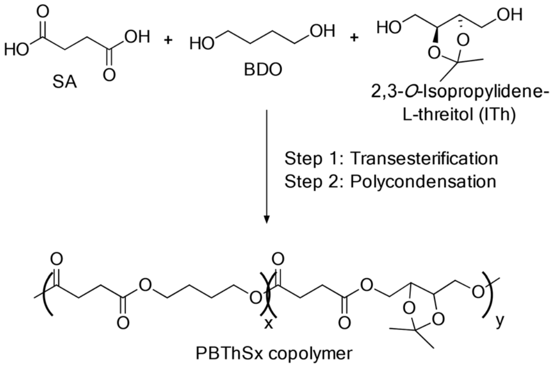
Scheme 78 Synthesis of PBIS copolymer.

The use of rigid bio-based comonomers, namely, isosorbide and 2,5-furandicarboxylic acid, in PBS was also examined. Interestingly, all the copolymers exhibited an increased glass transition temperature. The largest increase was observed for 20 mol% of isosorbide in which the glass transition increased from −30 °C for the PBS homopolymer to −11 °C.

In general, a decrease in the melting temperature and crystallization temperature was observed with an increase in the comonomer content. This decrease is due to irregularities incorporated into the polymer chain. Furthermore, the crystalline content decreased with an increase in comonomer content, which resulted in reduced stickiness of the film. Although the incorporation of rigid units increased the melt strength of the polymer, its low crystallization rate restricted its processing application, especially in film extrusion blowing. However, a large increase in the elongation at the break of the polymer was observed, when considering the final film properties.[56]

PBISx and PBThSx copolymers

To improve the mechanical and barrier properties as well as biodegradability of PBS, two series of copolyesters with different rigid sugar units, isosorbide (IS) (Scheme 78) or 2,3-*O*-isopropylidene-L-threitol (ITh) (Scheme 79), as co-monomers were synthesized. The M_n values of PBISx and PBThSx were found to be 1.6–8.3 × 10^4 g mol^{-1} and 1.6–3.7 × 10^4 g mol^{-1} respectively and M_n values decreased with an increase in Is or ITh content owing to their low reactivity. It was also found that the thermal stability of the copolyesters was higher than that of PBS especially when the Is unit content was 5 or 11 mol%. However, a decrease in T_{max} was observed, which could be due to low molecular weight. With respect to PBThSx copolyesters, T_{max} was found to be lower than that of PBS and decreased with an increase in ITh content.



Scheme 79 Synthesis of PBThSx copolymer.

Moreover, it is observed that copolyesters with bicyclic IS units exhibited similar thermal stability to that of PBS. Furthermore, the substitution of flexible butylene units with rigid bicyclic sugar units increased T_g of the copolyester, due to the fact that the bicyclic structure of IS conferred greater stiffness to the polymer chain and restricted its mobility. However, the influence of mono-cyclic ITh was slightly lower than that of bi-cyclic IS.

The incorporation of bicyclic sugar units increased the hydrophilicity of the copolyesters compared to the corresponding monocyclic sugar units. Incorporation of the IS comonomer unit increased the tensile strength and elongation at the break initially and a further increase in IS units led these to decrease. For a copolyester with ITh sugar units, the tensile strength decreased with an increase in ITh content; however, elongation at the break seems to be comparable to that of PBS.

It is evident that the introduction of the rigid bicyclic Is sugar unit into aliphatic polyesters led to better mechanical properties and decreased melting temperature, crystallinity, and crystallization rate compared to the corresponding monocyclic ITh sugar units. Furthermore, the introduction of the rigid IS comonomer, initially decreased and then increased the barrier properties of the copolyester.[124]

PB_xManx_yS and PB_xGlux_yS copolymers

Substitution of the butanediol units with 2,4 : 3,5-di-*O*-methylene-D-mannitol (Manx) in PBS (Scheme 80) increased T_g from −29 °C to 51 °C respectively for $PB_{95}Manx_5S$ and $PB_{30}Manx_{70}S$ copolymers. This increase in T_g of these copolymers would find wider application in the packaging industry. Insertion of Manx units into the PBS backbone significantly reduced T_m and ΔH_m and dropped to a minimum for the copolymer with 30% Manx content. The crystallinity was reduced with an increase in Manx content, which resulted in the formation of copolymers with a narrower crystallization window ($T_m - T_g$). An increase in Manx content in the copolymer was associated with the steady increase in both the elastic modulus and tensile strength and a decrease in ductility values.[49]

On the other hand, the introduction of 2,4 : 3,5-di-*O*-methylene-D-glucitol (Glux-Diol) resulted in a gradual decrease in T_m until the PB_xGlux_yS copolyesters became amorphous and this might be due to the asymmetric structure of Glux-diol. However, the PBxGluxyS copolymer exhibited a higher T_g due to its corrugated structure, which strongly hindered chain mobility of the polymers.[73b]

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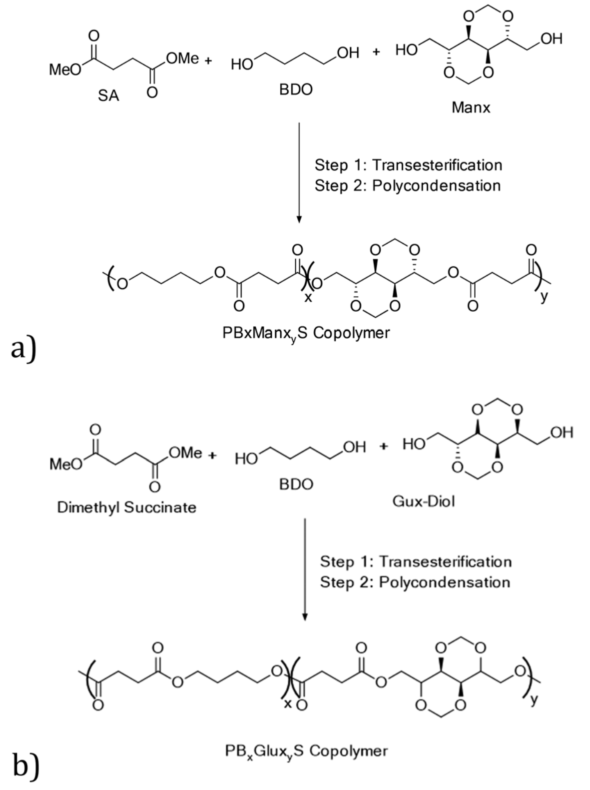
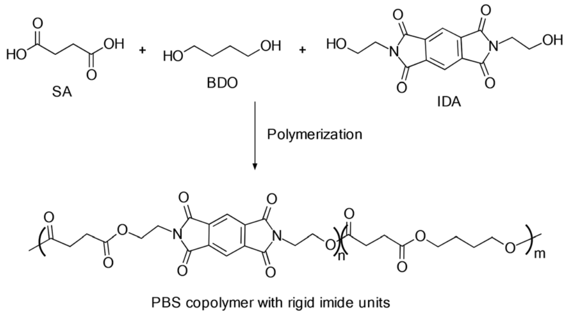


Scheme 80 Synthesis of (a) PB$_x$Manx$_y$S and (b) PB$_x$Glux$_y$S copolymers.

It is believed that the difference in T_m between PB$_x$Manx$_y$S and PB$_x$Glux$_y$S copolymers might be due to the symmetric and asymmetric nature of the corresponding comonomers.

PBS copolymer with rigid imide units (PBSIr)

The introduction of rigid imide units into the PBS polymer chain (Scheme 81) decreased the melting temperature (T_m) of the copolyesters from 117.5 °C (PBS) to 90.6 °C. Furthermore, there was a small change in the decomposition temperature of PBSIr when compared to that of PBS (345.5 °C). The tensile strength of PBSIr decreased while the elongation at the break increased. Destruction of the chain regularity of the copolymers by the rigid imide units also reduced the crystallinity.[64]



Scheme 81 Synthesis of PBS copolymer with rigid imide units (PBSIr).

PBS copolymer with rigid acetylenedicarboxylic acid units

Furthermore, the introduction of a rigid acetylene dicarboxylic acid (AD) unit into the PBS polymer (Scheme 82) decreased the crystallization temperature and crystallinity without affecting the crystallization kinetics.

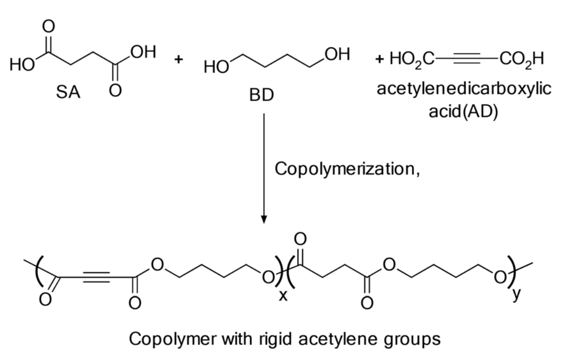
Even at a low concentration, the presence of AD units significantly enhanced the primary nucleation and this nucleation capability constantly improved with respect to AD content, which in turn supported the recovery of the total crystallization rate of PBSAD copolymers under the same supercooling conditions. Furthermore, the existence of weak interactions between the AD units supported the melt memory effect at elevated temperatures. As the temperature decreased, this weak interaction between C≡C units continuously strengthened, which resulted in the growth of a heterogeneous aggregation of AD units, and after certain point it induced the formation of a considerable amount of crystal nuclei. It was observed that the introduction of AD units enhanced nucleation and at the same time reduced the crystallinity.[25]

Aliphatic–aromatic PBS copolyesters

PBSFr copolymer

The introduction of aromatic rigid monomers into polyesters enhanced the mechanical and thermal properties. However, the biodegradability of the copolyester decreased significantly. The properties of aliphatic–aromatic random poly(butylene succinate-*co*-butylene furandicarboxylate) (PBSFr) copolyesters synthesized using 2,5-furandicarboxylic acid, succinic acid and 1,4-butane diol (Scheme 83) were investigated.

Interestingly, copolyesters exhibited excellent thermal stability and the glass transition temperature, crystallizability and T_m of the copolyesters tended to decrease initially and then increase with an increase in butylene furandicarboxylate (BF) content (ϕBF). In general, both BS-rich and BF-rich copolyesters were crystalline in nature. Conversely, copolyesters with intermediate composition (ϕBF 40–60%) were close to being amorphous polymers. Furthermore, the tensile modulus and strength decreased with ϕBF in the 0–40% range, but increased again in the 50–100% range. However, the elonga-



Scheme 82 Synthesis of PBS copolymer with rigid acetylenedicarboxylic acid units.

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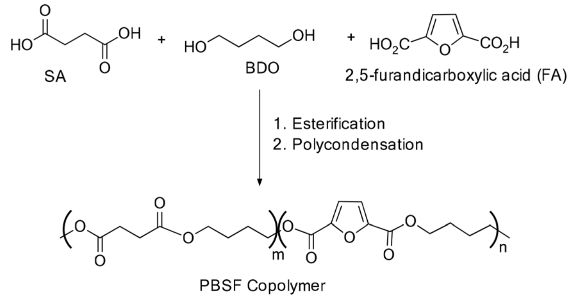


Scheme 83 Synthesis of aromatic–aliphatic PBS copolyester.

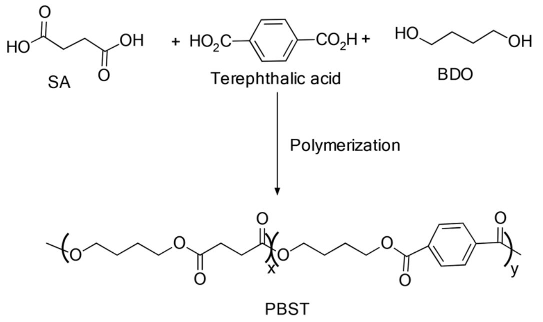
tion at the break tended to follow the opposite trend with respect to the tensile modulus and strength.[67]

PBSFc copolymer

The presence of furanoate units in poly(butylene succinate-*co*-furanoate) (PBSFc) copolymer reduced the size of the spherulites and, in addition, retarded crystallization when compared to the corresponding homopolymers. A reduction in the size of the spherulites resulted in an increased nucleation density for the copolymer at all crystallization temperatures. Additionally, T_g (−29 °C) of the copolymer was found to be between the T_g of the corresponding homopolymers (T_g (PBS) = −36 °C and T_g (PBF) = 34 °C). A higher $t_{1/2}$ for the PBSFc copolymer indicated that furanoate units in the copolymer reduced the crystallizability and influenced the anti-nucleation or retardation effect during the crystallization process.[29]

PBST copolymer

Analysis of the structure–property relationship of poly(butylene succinate-*co*-butylene terephthalate) random copolymer (PBST) (Scheme 84) with a symmetrical composition clearly demonstrated a good balance between biodegradability and performance. Furthermore, the crystallizability of both components in the PBST copolymer was highly restricted. PBST copolymers with a symmetrical composition of PBT tended to possess a significantly higher Young's modulus (59 MPa), yield strength (8 MPa) and elongation to break ratio (1300%) than the corresponding widely used commercial PBAT with 44 mol% of PBT. Moreover, DSC and FTIR studies revealed that the crystals of PBS blocks formed by both quick stretching and slowly at room temperature for a non-deformed sample were immature in nature.[58]



Scheme 84 Synthesis of PBST copolymer.

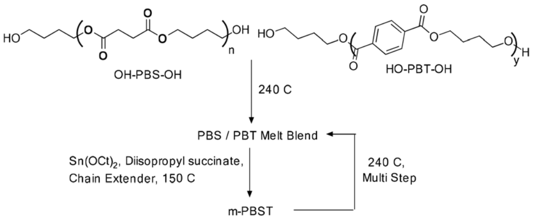
Aliphatic–aromatic PBS copolyesters *via* melt blending

A novel multi-block poly(butylene succinate)-multi-poly(butylene terephthalate) copolyester (*m*-PBST) was prepared by melt-blending of preformed PBS and PBT using tin octoate as a catalyst (Scheme 85). During melt-blend polymerization, a small amount of diisopropyl succinate was added to promote the ester-interchange reaction between the homopolymers to afford the corresponding required copolymer *m*-PBST.

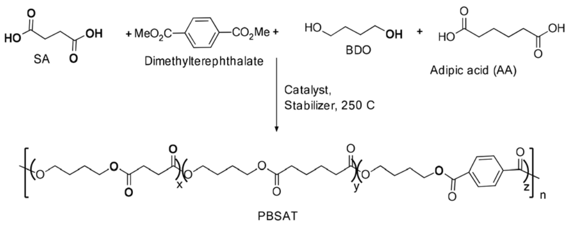
It was evident that films produced using *r*-PBST had a lower modulus and strength than those of the corresponding *m*-PBST, while the elongation at the break was found to be higher in *r*-PBST. Furthermore, *m*-PBST tended to mimic PBS and PBT in terms of strength and elongation and possessed average of these two homopolymers. Crystallization of the PBS segments in the *m*-PBST copolymer resulted in comparable elongation at the break with respect to the corresponding PBT homopolymer.[125]

Blended *vs.* synthesized copolymers

The difference in the mechanical properties of synthesized PBSAT15 (Scheme 86) and blended PBS/PBAT was also investigated in detail. Blended resin (PBS/PBAT) revealed a higher Young's modulus than that of the corresponding synthesized copolyester (PBSAT15) although the crystallinity of the blended resin was found to be higher than that of the synthesized copolyester. Furthermore, the increased elongation at the break



Scheme 85 Synthesis of PBST *via* melt blending.



Scheme 86 Synthesis of PBSAT copolymer.

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value for the synthesized copolyester clearly indicated that the synthesized copolyester was more flexible than the blended resin. Specifically, the compatibility between resins influenced the elongation at the break for both the synthesized copolyester and blended resin. Compatibility between PBS and PBAT in the blended resin was found to be lower and the phases tended to separate when compared to that of synthesized PBSAT15, which had a smooth surface.[126]

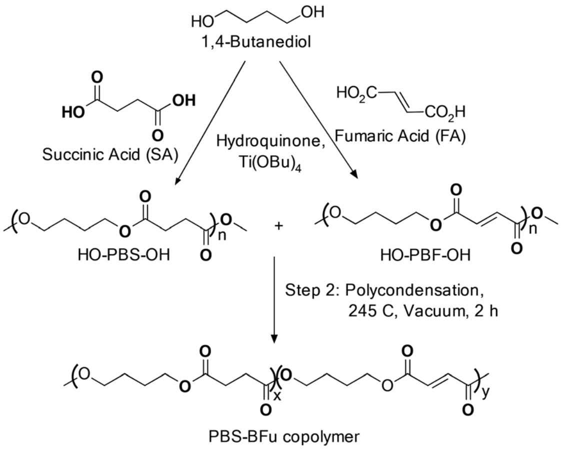
PBS copolyesters with cross-linking aids

Enhancement in the melting (T_m) and crystalline (T_c) temperatures was observed when pre-homopolymers of poly(butylene succinate) (PBS) and poly(butylene fumarate) (PBFu) were copolymerized (Scheme 87). The increase in the crystalline and melting temperatures was directly proportional to the copolymer fumarate content. Furthermore, the elastic modulus of the copolymers also increased with an increase in fumarate content; however, the tensile strength and elongation at the break tended to decrease with an increase in fumarate content.

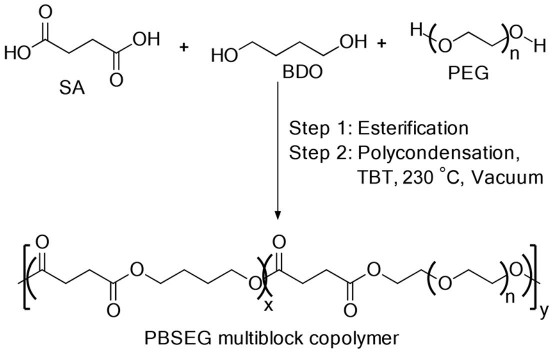
In addition, the properties of cross-linked and uncross-linked copolyesters were also investigated and it was found that rapidly cooled and cross-linked copolymer with 30% fumarate fraction exhibited the highest modulus of 393 MPa and lowest elongation at the break of 1.3% among all copolymers. In contrast, the rapidly cooled and uncross-linked copolymer with 10% fumarate fraction had the lowest modulus of 303 MPa and highest elongation at the break of 160%.[41]

PBS-PEG multiblock copolymers

The properties of poly(butylene succinate)–poly(ethylene glycol) multiblock copolymers, which were synthesized by a two step transesterification reaction, were investigated in detail (Scheme 88).



Scheme 87 Synthesis of PBS-BFu copolymer.



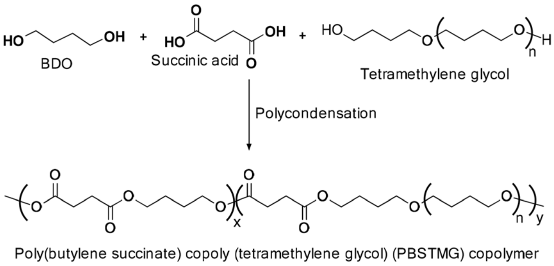
Scheme 88 Synthesis of PBSEG multiblock copolymer.

An increase in the PEG segment chain length tended to increase the chain lengths of both PBS and PEG segments. A slight increase in tensile strength was observed with an increase in PEG segment content. The crystallinity of the PEG segment was significantly enhanced when the PEG segment content was more than 36 wt%. Conversely, there was a gradual increase in the elongation at the break with increasing F_{PEG} segment content, which was due to greater phase separation with higher F_{PEG}. The hydrophilicity of the copolymers increased with the incorporation of PEG segments. Furthermore, the chain length of the PEG segment also played a significant role in altering the water contact angle, and lower water contact angles were observed for PBSEGs possessing PEG segments with shorter chain length.[127]

PBSTMG copolymers

To enhance the properties of poly(butylene succinate) (PBS), an array of poly[(butylene succinate)-*co*-poly(tetramethylene glycol)]s (PBSTMGs) with different compositions of poly(tetramethylene glycol) (PTMG) were synthesized (Scheme 89). An increase in the comonomer content resulted in a gradual decrease in melting temperature, crystallization temperature, and crystallinity of the PBSTMG copolymers.

Furthermore, the introduction of a third monomer into the PBS backbone resulted in a reduction of the sequence length of the crystallizable segments and comonomer units were excluded from the crystal lattice. However, increased incorpor-



Scheme 89 Synthesis of PBSTMG copolymer.

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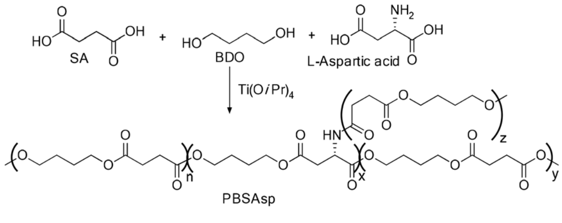
ation of the comonomer reduced the thickness of the PBS lamella and hence the melting point and crystallinity of the copolymer decreased. Thermal degradation and the crystal lattice were not affected by copolymerization; however, an increase in comonomer content gradually decreased the crystallinity of the copolymer. A change in the copolymer composition had a significant influence on the storage modulus and T_g. An increase in the comonomer content decreased T_g and the presence of phase separation in the copolymers was also observed. The tensile strength of the copolymer was reduced but the impact strength and elongation at the break were improved, especially when the comonomer content was less than 10%.

Furthermore, the copolymer composition played a key role in reducing the size of the spherulites and crystallinity of the copolymer, which, in turn, promoted phase separation and thereby enhanced the toughness, ductility and impact strength of the copolymer. In addition to copolymerization, blends of PBS and PBSTMG copolymers also exhibited improved elongation at the break, toughness and impact strength when compared to that of the corresponding PBS homopolymer.[38]

PBS copolyesters using amino acid monomers

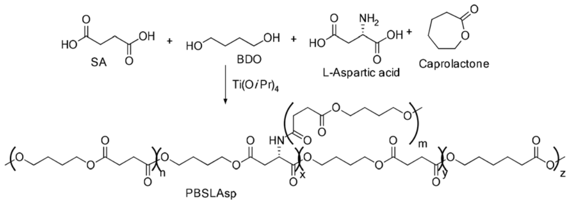
PBS copolymers of different amino acids were synthesized (Scheme 90) and the properties of the corresponding copolymers were investigated in detail. L-Aspartic acid displayed high reactivity when compared to other amino acids (glycine, L-alanine, L-aspartic acid, L-glutamic acid and L-phenylalanine). Furthermore, the time for the polymerization reaction increased with an increase in amino acid concentration, except for L-aspartic acid. There was no significant change in the thermal properties, such as the glass transition temperature (T_g), melting temperature (T_m), heat of fusion (ΔH_m) and 2% thermal decomposition temperature (T_{d2}). However, the mechanical properties of the copolymers, especially the break strain, tended to vary depending on the type of amino acid used. In particular, copolymers with alanine exhibited a slightly higher break strain than the corresponding PBS homopolymer.[128]

In addition, PBS copolymers with various amount of L-aspartic acid were synthesized and investigated for their thermal and mechanical properties. The concentration of L-aspartic acid shortened the reaction time to produce copolymers with M_w of 24.7×10^4 g mol^{-1}. Moreover, there was no remarkable change to the molecular weights and thermal properties when compared to that of PBS. However, the break strain increased from 289 to 548%, when the L-aspartic acid content was 0.3 mol% and a further increase in L-aspartic content led to a dramatic decrease in break strain.[128]



Scheme 90 Synthesis of PBSAsp copolymer.

The effect of the incorporation of L-aspartic acid into PBS copolymers containing caprolactone co-monomer units was also investigated (Scheme 91). It was found that the molecular weight distribution, M_w/M_n, increased with an increase in L-aspartic acid content. No significant changes to the thermal properties of the copolymers were observed with and without L-aspartic acid. However, the break strain changed with respect to changes in the L-aspartic acid content. Furthermore, PBS copolymers with 3-octadecyloxy-1,2-propanediol and L-aspartic acid were synthesized. The reaction time for polymerization decreased with an increase in amino acid content, whereas the PDI (M_w/M_n value) tended to increase with an increase in amino acid concentration.[128]

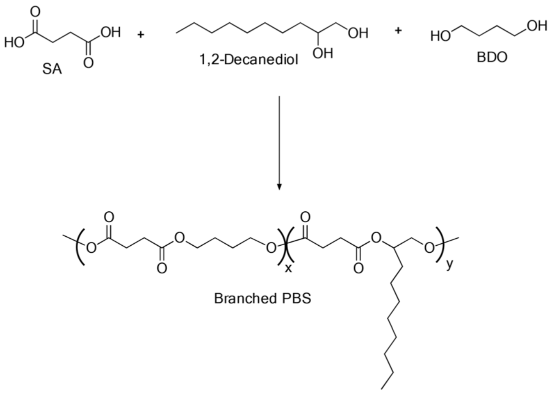


Scheme 91 Synthesis of PBSCLAsp copolymer.

PBS copolymers with long chain branching

Using 1,2-decane diol

Branched poly(butylene succinate) copolymers with 1,2-decane diol as a comonomer (Scheme 92) were synthesized and investigated for their thermal, mechanical and crystallization properties. The thermal stability of PBDS copolymers was similar



Scheme 92 Synthesis of PBS copolymers with long chain branching.

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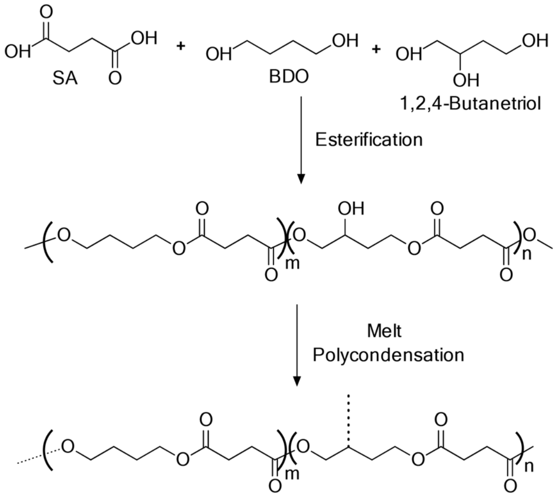
to that of PBS. An increase in decane diol decreased the crystallizability, T_g, T_m, and $T_m°$ of PBDS copolymers with respect to those of PBS.

However, regardless of the 1,2-decylene succinate (1,2-DS) content, the crystallization mechanism and crystal structure of the PBDS copolymers remained the same when compared to PBS. An increase in the 1,2-DS content increased branching in the polymer chain, which in turn increased the mobility of the polymer chain. Furthermore, an increase in the elongation at the break and a decrease in the Young's modulus were observed for PBDS copolymers with increased 1,2-DS content.[24]

Using 1,2,4-butanetriol

The influence of long-chain branching in PBS was also investigated using 1,2,4-butanetriol (1,2,4-BT) as a long chain branching agent (Scheme 93). From a systematic investigation of the physical and rheological properties, it was evident that an increase in the 1,2,4-BT segment resulted in a slight increase in crystallization and glass transition temperatures. A significant enhancement was observed with an increase in 1,2,4-BT segment content, which clearly indicated that long-chain branches would be advantageous towards enhancing the crystallization temperature and accelerating the crystallizability.

However, a gradual decrease in the relative degree of crystallinity was observed. Furthermore, long-chain branched PBS exhibited a higher tensile strength without a remarkable decrease in the elongation at the break when compared with that of linear PBS. Furthermore, the addition of 1 mol% 1,2,4-BT segments improved the tensile strength of long-chain branched PBS by 31% when compared with that of the linear PBS, which clearly indicated that long-chain branches could enhance the stiffness of linear PBS. Moreover, it is evident that the increase in 1,2,4-BT segments resulted in the formation of a low branching reaction. Triol monomer could also promote possible cross-linking reactions.[129]



Scheme 93 Synthesis of PBS copolymers with long chain branching using 1,2,4-butanetriol.

PBS-DLS-PEG copolymer

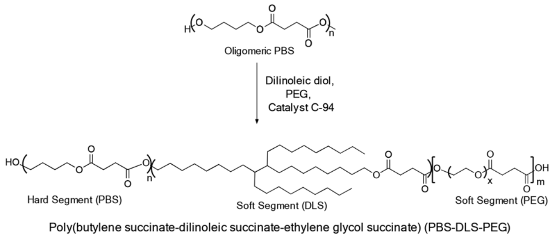
In addition, the introduction of the hydrophilic poly(ethylene glycol) unit with different molecular weights and amounts into poly(butylene succinate–dilinoleic succinate–ethylene glycol succinate) (PBS-DLS-PEG) copolymers (Scheme 94) resulted in different wettability and thus changed the hydrophobic copolymer to hydrophilic. Moreover, the presence of hard and soft segments resulted in low T_g and high T_m of the copolyesters. The presence of PEG units (up to 10%) in the copolymer improved the hydrophilicity without altering the thermal properties.[79]

The incorporation of dimeric linoleic diol (DLAOH) into the PBS backbone resulted in the formation of copolyesters with hard and soft segments. The synthesized copolymers were processed into electrospun mats without defects. During copolymer processing, it was observed that solvent and concentration played crucial roles in obtaining electrospun fibres without any defects. Furthermore, the thermal and mechanical properties were found to be comparable to those of the bulk copolymer synthesized *via* organometallic catalysis. The presence of a higher amount of hard segments in PBS : DLS 70 : 30 copolymer electrospun fibre mats led to a high Young's modulus (24.2 MPa) and tensile strength (4.0 MPa). However, there was a lower elongation at the break (63%) when compared to the copolymer synthesized *via* organometallic catalysis.[130]

Ternary random PBS copolyesters

Novel ternary or multiple random copolyesters containing various structural units were synthesized (Scheme 95), in order to understand the influence of chain length, aromaticity, symmetry, rigidity and short-chain branching of the structural units on crystallization, glass transition temperature and the tensile properties.

All the synthesized copolyesters tended to exhibit one T_g, indicating that they were all random copolymers in nature. Furthermore, it was evident that the incorporation of shorter chain aliphatic diacids, aromatic diacids (asymmetric ones, in particular) or short-chain branched diol suppressed copolyester crystallization and increased the glass transition temperature. With respect to aromatic diacids, asymmetry and/or rigidity of the aromatic ring played a significant role in influencing the T_g. However, the incorporation of aliphatic diacids with longer alkylene chains reduced the glass transition tempera-



Scheme 94 Synthesis of PBS-DLS-PEG copolymer.

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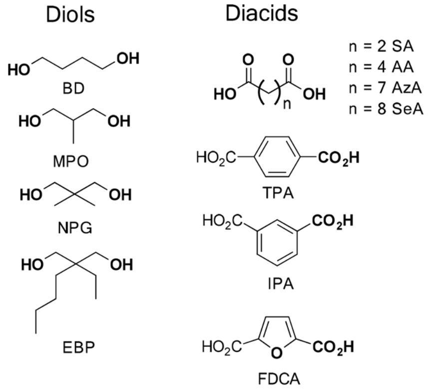


Scheme 95 Diol and diacid combinations for ternary random PBS copolyesters.

ture. Furthermore, it was clear that rigidity also contributed to higher T_g. The introduction of a terephthalate moiety into copolyesters improved the tensile properties; this was believed to be due to the presence of more intermolecular interactions between aromatic units. Furthermore, the introduction of isophthalate or furandicarboxylate tended to improve the elongation at the break because of lower crystallizability.[131]

Nucleating agents as crystallization aids

Major challenges associated with poly(butylene succinate) (PBS) are reduced mechanical properties, large spherulite size and relatively low crystallization rate. The use of nucleating agents to enhance the crystallization of poly(butylene succinate) (PBS), shorten the molding cycle as well as improve the mechanical properties has gained considerable interest for various applications. Extensive research has been carried out to develop suitable nucleating agents for PBS. As a result, various nucleating agents, such as organoclay, inorganic salts and oxides, carbon nanotubes, small organic molecules (cyclic aromatic or aliphatic acids), organo-phosphates, low-molecular-weight polyesters and α- or β-cyclodextrin, have been reported in the literature. However, the compatibility of all these nucleating agents with PBS was found lower and most of the nucleating agents were found to be larger in size (*e.g.*, 10 μm), which resulted in the nonuniform dispersion of the nucleating agents in the polymer matrix.[132]

Nevertheless, these nucleating agents increased the crystallization properties of PBS to some extent, but affected the most important mechanical properties, such as tensile strength and elongation at the break of the polymer. Recently, poly(butylene fumarate) and poly(butylene succinate-*co*-butylene fumarate) were also explored as polymeric nucleating agents to improve the crystallization of PBS with the aid of isomorphism.

Interestingly, the addition of nucleating agents like poly (vinyl butyral) (PVB) to the monomers prior to polymerization of poly(butylene succinate) (PBS), in order to accelerate crystallization and improve the mechanical properties, was also studied in detail. The addition of PVB to PBS significantly reduced the spherulitic sizes and increased the peak temperature of crystallization. An initial decrease in spherulitic size with an increase in PVB content was observed, followed by a minimum and then it increased finally. PVB with a low molecular weight resulted in smaller spherulitic sizes than the corresponding high molecular weight PVBs. Moreover, the nucleated PBS exhibited a significant improvement in tensile modulus (26%), tensile strength (30%), and elongation at the break (82%). It was observed that the size of the spherulites played a major role in deciding the tensile modulus, strength and elongation at the break. Enhanced mechanical properties were also observed when the spherulitic size was small.

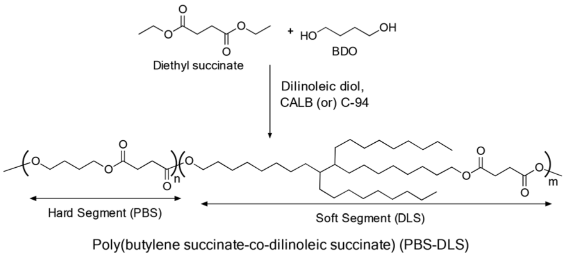
Pre-dispersion of nucleating agents into the monomers before polymer synthesis is believed to be an effective and consistent approach to improve the crystallization properties when compared to that of corresponding post-polymerization melt blending of nucleating agents.[132]

Role of catalysts in copolymer synthesis

The influence of the catalyst on the crystal structure of poly [(butylene succinate)-*co*-(dilinoleic succinate)] was investigated in detail (Scheme 96). The catalyst played a significant role in determining the polymer's intrinsic properties. From GPC analysis, the number average molecular weights were found to be 5.1×10^4 g mol^{-1} and 2.5×10^4 g mol^{-1} respectively for C-94-catalyzed and CALB-catalyzed copolyesters.

Thus, it ass clear that copolymerization under solvent free conditions resulted in the formation of high molecular weight polymers. In addition, a higher polydispersity index was observed for the CAL-B-catalyzed reaction (8.2) when compared to that of the C-94-catalyzed reaction (3.3). This difference in dispersity index values was due to the formation of more segmented block structures under enzyme mediated conditions, which led to the formation of the corresponding macromolecules.

The T_m, ΔH_m and T_g values were comparable for both PBS-DLS 70 : 30-E and PBS-DLS 70 : 30_M catalyzed copoly-



Scheme 96 Synthesis of PBS-DLS copolymer *via* enzyme and metal mediated polymerization.

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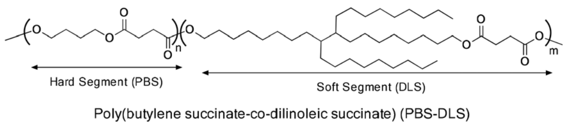
esters. However, the T_c value for the C-94-catalyzed copolymer (33 °C) was found to be lower than that of the corresponding CAL-B-catalyzed copolymer (53 °C). This could be attributed to the higher Xc,h (crystalline phase content in the hard segments) and Xc,tot (total crystalline phase content in the polymer) for the enzyme catalyzed copolymer when compared to that of the metal catalyzed polymer (66.0 *versus* 62.7% and 44.9 *versus* 40.2%, respectively). Moreover, the average sequence length of the hard segments in the enzyme catalyzed reaction was found to be twice that of the metal catalyzed reaction. Furthermore, crystalline forms of the metal catalyzed copolymers were found to be denser and the phase change was 20% greater than that of the corresponding enzyme catalyzed copolymers. However, a homogeneous density distribution was observed in the enzyme mediated copolymers.[39]

Differences in the thermal properties of the copolyesters produced with both an enzyme and a Lewis acid were negligible and could be correlated to the differences in the corresponding molecular weights.[98]

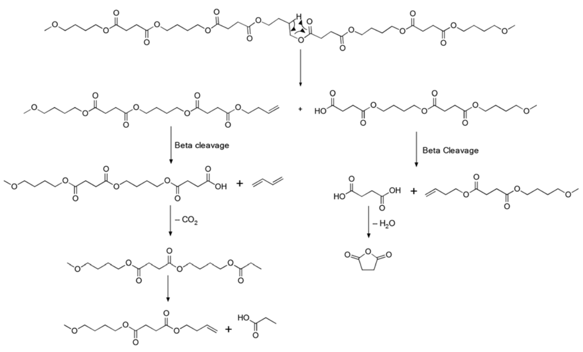
Thermoplastic elastomers with good processability were obtained by the incorporation of dimeric fatty acid soft segments into PBS (Scheme 97). Furthermore, an increase in the fatty acid soft segment resulted in lower water take up and mass loss, indicating slower degradation. Moreover, the effective surface area played a significant role in biodegradation.[133]

Thermal degradation of PBS copolymers

The thermal degradation mechanisms for poly(butylene succinate) (PBS) and PBS-rich poly(butylene succinate-*co*-propylene succinate) copolymers were investigated through FTIR analysis of the gases evolved from TGA (Scheme 98). The formation of olefin, ester, CO_2 and anhydride was observed from the analysis. Based on this observation, a plausible mechanism was proposed, which involved the β-hydrogen bond cleavage of the ester groups followed by dehydration to form the corresponding anhydrides, olefins and CO_2. Furthermore, the comonomer distribution was found to be random in the copolymer and this randomness did not alter the degradation mechanism.[134]



Scheme 97 Synthesis of PBS copolymer with fatty acid soft segments.



Scheme 98 Plausible mechanism for the thermal degradation of PBS.

Bio-degradation

The large dependence on polymer production from nonrenewable resources adds additional challenges to sustainable development. Conversely, chemical recycling of polymeric materials involves high energy consumption and longer downstream processing. Thus, the development of an efficient and eco-friendly method for recycling polymeric materials is much sought-after. As a result, research directed towards the synthesis, processing and degradability of biobased and/or biodegradable polymers has attracted increasing interest.

Aliphatic polyesters exhibit remarkable physicochemical, mechanical and processability properties, which are comparable with those of conventional polyolefins. Polyesters such as polycaprolactone (PCL), poly(3-hydroxybutyrate) (PHB), poly(ethylene succinate) (PES), poly(butylene succinate) (PBS), poly(butylene adipate), poly(hexylene succinate) (PHS), and poly(hexylene adipate) are some of the bio-alternatives to conventional polyolefins with the greatest potential. Among them, PES, PBS, and PHS have favorable biodegradability and biocompatibility, and hence they have found widespread applications in biomaterials, packaging materials, agriculture, gene delivery, drug delivery, tissue engineering, and the pharmaceutical, medical and biomedical industries. Particularly, poly(butylene succinate) (PBS) has found widespread applications and achieved rapid growth due to its balanced thermal and mechanical properties.

However, the use of PBS in the packaging and agriculture industries, especially for short lived products, is limited due to its relatively low degradability rate as well as the low ratio of PBS degrading microorganisms in the environment.[135]

Firstly, it is necessary to understand the biodegradation mechanism in order to improve the biodegradability of PBS under different degradation environments. It is well documented in the literature that various factors, such as the chemical structure, repeating units, hydrophilic/hydrophobic balance, molecular weight, solid-state morphology (*i.e.* crystallinity, crystal size and distribution), molecular mobility, thermal characteristics and other physical factors, greatly influence the biodegradation rate of a polymer. The biodegradation rate of the amorphous region is much faster than that of the crystalline zone. Absolute biodegradability also directly related to the nature, relative quantity, and distribution of the co-monomeric units along the polymer chain.

Polyester degradation can be categorized into two processes: endo-type scission (ester cleavage occurs at random

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points along the polymer chain) and exo-type scission (ester cleavage occurs at ends of the polymer chains). In this review, we tried our best to cover the extensive research that has been carried out to improve the biodegradability of bio-based polymers.

Aliphatic PBS copolyesters

PBS, PHS and P(BS-*co*-HS) copolymers

From the bio-degradability studies of various aliphatic copolyesters, such as poly(butylene succinate) (PBS), poly(hexamethylene succinate) (PHS), and poly(butylene succinate-*co*-hexamethylene succinate)s (P(BS-*co*-HS)s) with various hexamethylene succinate (HS) contents, it was realized that the hexamethylene content had a strong influence on biodegradability. The copolyester with increased HS content degraded faster than the corresponding copolyester with a low HS content.[112]

Co-polyesters tend to degrade faster than neat PHS and PBS. In particular, copolyesters with more of the HS component are more susceptible to lipase attack (*Candida rugose*) and degrade faster than copolyesters with more of the BS component. Furthermore, the mechanism of enzymatic degradation was found to be of the *endo*-type, which resulted in a steady decrease in molecular weight and also it was believed that the melting point and crystallinity were the main factors that controlled the degradation rate. However, since more equimolar P(BS-*co*-HS) (50/50) and (36/64) had T_m below the incubation temperature, there was likely to be a significant influence from chain motion and reorganization of the surface morphology.[136]

P(BS-*co*-CHDMS) and P(BS-*co*-BCHDA)

Enzymatic degradation of the homopolymer poly(butylene succinate) (PBS) and its copolymers containing 1,4-cyclohexane dimethylene succinate (CHDMS) or butylene 1,4-cyclohexanedicarboxylate (BCHDA) sequences with different molecular architectures (P(BS-*co*-CHDMS) and P(BS-*co*-BCHDA)) was investigated using *Pseudomonas cepacia* lipase (PCL) in chloroform. All the copolyesters degraded faster than pure PBS. However, the degradation rates were found to be higher in the presence of PCL in $CHCl_3$.

The introduction of monomers with a six-membered alicyclic group resulted in the destruction of the rigid spiral structure of PBS and thus improved the accessibility and stability of the copolyesters and enzyme (PCL) as well as enhancing the recognition of ester bonds by PCL, which in turn, accelerated enzymatic degradation. PBS modified by CHDM exhibited better enzymatic degradation than the corresponding PBS copolymer modified with CHDA. Molecular modeling studies have also shed some light on the interactions between residues at the active site of PCL and the polyester. It was very clear from the modeling studies that steric hindrance created by CHDA in the P(BS-*co*-BCHDA) copolymer reduced the accessibility of ester groups to the enzyme and thus inhibited the rate of enzymatic degradation.[34]

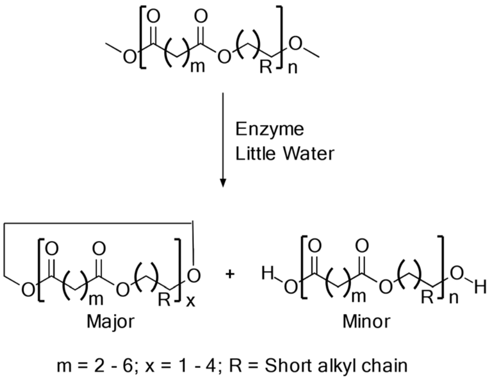
PBS, PBS-*co*-CL, PBS-*co*-CHDM and PBS-*co*-CL-*co*-CHDM copolymers

Investigation on catalytic degradation of poly(butylene succinate) (PBS) and its binary (PBS-*co*-CL), (PBS-*co*-CHDM) and ternary (PBS-*co*-CL-*co*-CHDM) and ternary copolymers by Immobilized Candida lipase (CA Novozym435), provided some mechanistic insights towards the formation of cyclic oligomers during the degradation (Scheme 99).

Copolyesters with M_w greater than 100 000 degraded into lower molecular weight copolymers. Enhanced degradation is observed in copolymers than the corresponding homopolymers. Copolymers with CHDM unit exhibits enhanced degradation due to increased gap between the polymer chains, which in turn provide easy access for enzymes to the corresponding ester bonds. Moreover, PBS modified with caprolactone also degrades faster than the corresponding PBS and this is due to the enhanced plasticity between the polymer chains. Degradation of CHDM-modified PBS copolymers and terpolymers of P(BS-*co*-CL-*co*-CHDM) exhibits small difference, which is due to the added advantage of both CHDM and CL units in the polymer backbone, which results in the formation of the cyclic oligomers.[137]

PBS-*co*-DEGS and PBS-*co*-BDGA copolymers

The importance of ether linkages at various positions in PBS towards biodegradability and the degradation mechanism was explored *via* enzymatic degradation of poly(butylene succinate-*co*-diethylene glycol succinate) (PBS-*co*-DEGS) and poly(butylene succinate-*co*-butylene diglycolic acid) (PBSco-BDGA) using lipase N435 in the THF/toluene mixed system. The rates of hydrolysis for all PBS-*co*-BDGAs were higher than that of PBS-*co*-DEGS, which clearly indicated that PBS-*co*-BDGA copolymers were more susceptible to hydrolysis. Except for PBS-*co*-BDGA15, the degradation rate increased with an increase in monomer content and the degradation rate of the PBS-*co*-BDGA copolymer was higher than that of PBS-*co*-DEGS. This was believed to be due to the presence of the ether linkage in the copolymer backbone. In PBS-*co*-BDGA, the ether bond was adjacent to the ester carbonyl bond of the diacids. Thus, it was more susceptible to hydrolysis than the corresponding PBS-*co*-



Scheme 99 Plausible degradation of polyesters by enzyme catalysis.

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DEGS, in which the ether bond was between the carbonyl groups of the diol part.[138a]

Moreover, an increase in the DEGS content in the poly(butylene succinate-*co*-diethylene glycol succinate) (P(BS-*co*-DEGS)) copolymer resulted in an increase in the glass transition temperature, hydrophilicity, ductility and degradation rate of the polymer under hydrolytic conditions. However, the tensile strength and modulus, melting temperature, crystallizability and degree of crystallinity tended to decrease with an increase in the DEGS content of the copolymer. Interestingly, the thermal stability of the copolymer was found to be unaffected by the composition.[138b]

PEEU copolymers

Enzymatic hydrolysis of the PEEU copolymers was studied using *Pseudomonas cepacia* lipase at 40 °C. The rate of enzymatic degradation was found to increase with an increase in the hydrophilic PEG segment in the PEEU copolymer. Furthermore, the copolymer with better hydrophilic properties underwent faster degradation.[76]

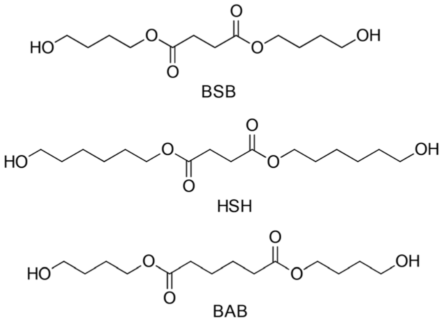
PES, PHS and PBS copolymers

The influence of hydroxy monomers on enzymatic degradation was examined using three different polymers, which were prepared using succinic acid and dihydric alcohols such as ethylene glycol (PES), 1,4-butanediol (PBS) and 1,6-hexanediol (PHS). From the experiment results, a very good correlation between the biodegradation behavior and the distance between ester groups (high methylene content), low crystallinity, low melt temperature and high hydrophilicity was realized. Thus, the biodegradability of the polymer PHS with six carbon atoms between the ester group exhibited maximum degradation and thus the order of enzymatic degradation was found to be PHS > PBS > PES.[139]

PBS, PBS-*co*-HS and PBS-*co*-BA copolymers

The enzymatic degradation of poly(butylene succinate-*co*-hexamethylene succinate) (PBS-*co*-HS), poly(butylenesuccinate-*co*-butylene adipate) (PBS-*co*-BA), and poly(butylene succinate) (PBS) was investigated using *Pseudomonas cepacia* (PC) to understand the influence of butylene adipate (BA) and hexamethylene succinate (HS) units in the PBS backbone (Scheme 100).

The PBS-*co*-HS copolymer degraded much faster and resulted in the formation of more oligomers than the corresponding PBS-*co*-BA copolymer. The formation of acyclic and cyclic oligomers was observed during the enzymatic degradation. Molecular modeling studies of enzymatic degradation indicated that the free energy of binding between the enzyme and the substrate in chloroform was higher for PBS-*co*-HS copolymers than those of the corresponding PBS-*co*-BA copolymer and PBS homopolymer. Moreover, the stability of the active sites of the enzyme containing HS units was greater than the other corresponding active sites.[140]



Scheme 100 Chemical structures of BSB, HSH and BAB units.

PBSCL copolymer

Lee *et al.* investigated the mechanism for the enzymatic degradation of PBS and poly(butylene succinate-*co*-6-hydroxycaproate) (PBSCL) using lipase PS® originating from *Pseudomonas cepacia*. The formation of 4-hydroxybutyl succinate (4HBS) during the enzymatic degradation of PBS indicated that biodegradation was believed to be an *exo*-type hydrolysis mechanism (Scheme 101).[135a]

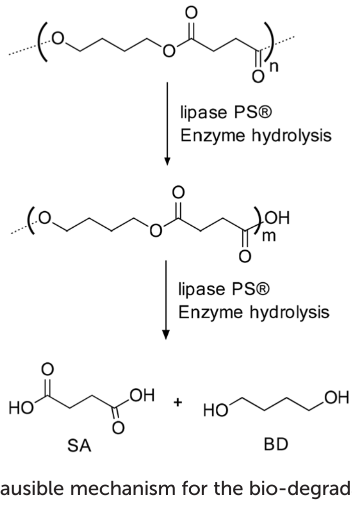
Aliphatic PBS copolyesters with unsaturated comonomers

PBSI copolymer

Biodegradability studies of poly(butylene succinate-*co*-butylene itaconate) copolymers indicated that copolymers with lower average molecular weight and lower degree of crystallinity degraded much faster than the other corresponding copolymers. Furthermore, it was observed that the introduction of an increased amount of unsaturated branched chain structure of the ITA monomer resulted in the reduced rate of biodegradation.[141]

PBS and PBFu copolymer

The biodegradability of a new class of multiblock copolymers composed of poly(butylene fumarate) (PBFu) and poly(butylene



Scheme 101 Plausible mechanism for the bio-degradation of PBS.

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succinate) was compared with those of the corresponding homo-polymers PBF and PBS. From the experimental investigation, it was found that PBS degraded much faster than PBF and the rate of degradation of the multiblock copolymer was significantly affected by the composition. An increase in the PBS content in the copolymer increased the biodegradability, especially when it was around or higher than 50 wt%. Molecular mobility, which determined the rigidity of the polymer chain, also played a significant role in biodegradation. Incorporation of the PBS segment into multiblock copolymers reduced the content of rigid carbon–carbon double bonds, and thus decreased the rigidity of the polymer. Thus, in the copolymer, the PBS segment was preferentially degraded and the PBS content decreased with the progress of degradation. Generally, the amorphous region degraded faster than the crystalline regions and thus, the PBS segment degraded preferentially compared to the PBF segment. Hence, the incorporation of PBS enhanced the degradation rate of the copolymers.[142]

Aliphatic–aromatic copolyesters

In general, due to resistance to fungi or bacteria, aromatic polyesters with rigid benzene rings, such as poly(ethylene terephthalate) and poly(butylene terephthalate), are very difficult to degrade in the natural environment. However, the degradability of aromatic polyesters could be enhanced by introducing aliphatic polyester units into the polymer chain. Biodegradability studies of various aliphatic–aromatic copolyesters resulting from different ratios of diols (ethylene glycol, 1,4-butanediol and 1,6-hexanediol) and diacids (succinic acid and dimethyl terephthalate) indicated that all the synthesized aliphatic–aromatic copolyesters were degradable and the copolyester with the highest content of aliphatic units showed the best degradability.

Moreover the biodegradability of copolyesters was also investigated through weight loss ratios and polymer morphology. Copolyesters with fewer aromatic units led to increased weight loss and thus, the degradation ability of copolyesters increased with an increase in the number of aliphatic units in the copolyesters. The importance of the aliphatic content to bio-degradation was realized during biodegradability studies on aliphatic–aromatic copolyesters. Copolymers with increased aliphatic content exhibited a higher biodegradation rate. Furthermore, the chemical structure of the copolyester played a more significant role in deciding the biodegradability than the degree of crystallinity of the copolyester.[65]

PBSFc copolymer

The bio-degradability of the aliphatic–aromatic copolyester poly(butylene succinate-*co*-furanoate) (PBSFc) clearly indicated that the amount of aromatic units influenced the degradation rate by enzymes. Thus, PBSFc copolyesters with a low furan dicarboxylic acid (FDCA) content of up to 15 mol% degraded as much as 90% in 180 days.[56]

*co*PBFS copolymer

The degradation of poly(butylene 2,5-furandicarboxylate-*co*-succinate) (*co*PBFS) copolyesters in the presence and absence of enzymes, clearly indicated that biodegradation depended on the composition of the copolymer and the degradation rate increased with an increase in butylene succinate units in the copolymer. Furthermore, enhanced degradation was observed for the copolyesters under enzymatic conditions.[99]

r- and *m*-PBST copolymers

Enzymatic hydrolysis of both *r*- and *m*-PBST (poly(butylene succinate)-multi-poly(butylene terephthalate)) increased with an increase in the number of butylene succinate units. Even at higher PBT concentrations, *m*-PBST exhibited a higher degradability than the corresponding *r*-PBST. This difference in degradation was due to the formation of a larger sized PBS domain in *m*-PBST than that in the corresponding *r*-PBST. Furthermore, the extent of degradation under enzymatic conditions was found to be greater than that in the absence of an enzyme.[125]

PBS and PBSA copolymers

Furthermore, a yeast strain, *Cryptococcus* sp. MTCC 5455, was utilized for the hydrolysis of poly(butylene succinate) (PBS) and poly(butylene succinate-*co*-butylene adipate) (PBSA) copolymers. Complete degradation of the polymeric films was observed after 72 h and 16 h respectively.[143] In addition, various microorganisms were examined for their activity towards the degradation of poly(butylene succinate-*co*-adipate) (PBSA). Among them, a newly isolated strain, S-32, was found to be more effective at degrading both solid and emulsified PBSA.[143]

P(BS-*co*-PeD), P(BS-*co*-20%HDO) (75%) and P(BS-*co*-PDO)

The enzymatic hydrolysis of poly(butylene succinate) (PBS) based random copolyesters consisting of a third monomer, 1,3-propanediol (PDO), 1,5-pentanediol (PeD) and 1,6-hexanediol (HDO), was studied using *Candida antarctica* lipase B (CALB) enzyme. The degradation of P(BS-*co*-20%PeD) (85%) polyester was found to be highest followed by P(BS-*co*-20% HDO) (75%) and P(BS-*co*- 20%PDO) (23%) polyesters. It was assumed that the presence of a third monomer resulted in the destruction of the spiral chain structure of PBS and thereby decreased the degree of crystallinity. This offered easy access for enzymes to attack the free hydrolysable ester bond segments in the copolymers. The order of degradation rates was found to be P(BS-*co*-PeD) > P(BS-*co*-HDO) > P(BS-*co*-PDO) > PBS. Furthermore, increased ester bond density in the P(BS-*co*-PeD) copolyester compared to other copolyesters could offer more ester bonds to CALB and thus result in enhanced degradation. This was further supported by molecular modeling studies, in which PeDSPeD-CALB had the lowest free energy of binding, and thus enhanced the degradability of the copolyester P(BS-*co*-PeD).[144]

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PBS, PBA and PBAS copolymers

Enzyme mediated hydrolysis of the poly(butylene succinate-*co*-butylene adipate) copolyester was investigated by Nikolic *et al.*, using *Candida cylindracea* lipase. It was observed that enzymes produced by microorganisms were *endo*-type enzymes and hence the bio-degradability was not dependent on the molecular weight of the polymers. It was very clear from the degradability studies that homopolymers of poly(butylene adipate) PBA and poly(butylene succinate) PBS, with a high degree of crystallinity, exhibited lower biodegradability than the corresponding copolyesters. The order of biodegradability was found to be PBAS-50 > PBAS-25 > PBAS-75. The copolyester with 50 mol% of butylene succinate units resulted in maximum biodegradability and this was believed to be due to a large decrease in the crystallinity of the corresponding copolyester.

Furthermore, the melting temperatures and entropy of fusion played a crucial in deciding the biodegradability of copolyesters. Thus, PBAS-25 and PBAS-75 with similar degrees of crystallinity exhibited different rates of biodegradability. This could be attributed to the difference in the melting temperatures of the copolyesters. The copolyester PBAS-25 had a low melting temperature and high entropy of fusion, which greatly affected the rigidity of the chain backbone and thereby increased the flexibility of the polymer chain. Polymers with increased chain flexibility could easily fit into the enzyme's active sites and hence they were more susceptible to biodegradation.[145]

Copolymers with different diols and diacids

The bio-degradability of co-polyesters synthesized from 1,4-butanediol and diacids with different chain lengths (succinic acid, azelaic acid, and sebacic acid) was also examined. Satisfactory results for enzymatic hydrolysis at temperatures 10–20 °C lower than the polymer's melting point were observed. Furthermore, PBAz and PBSe degraded faster that the corresponding PBS and this was due to differences in the crystallinity of the co-polyesters. The copolyester with high crystallinity degraded at a lower rate.[22a]

PBSTMG copolymer

Enzymatic and hydrolytic degradation of PBSTMG copolymers were found to be almost the same and the presence of the enzyme slightly enhanced the degradation of the copolymer. The introduction of the PTMG comonomer resulted in enhanced hydrolysis and degradation of the copolymer increased with an increase in PTMG content. This was due to increased hydrophilicity, chain flexibility and reduced crystallinity of the copolymer by the introduction of the soft PTMG segment.[38]

Aerobic bio-degradation

Aerobic biodegradation of PPS, PBS, PPAd and PBA using cellulose material as a reference in soil revealed that PBA and PBS showed slightly higher degrees of degradation (44% and 40%, respectively) when compared to that of PPAd and PPS (35% and 40% respectively). Moreover, no correlation between biodegradability and degree of crystallinity or melting temperature was observed. Furthermore, an increase in the number of methylene units between the diols and diacids played a crucial role in determining the biodegradability. Thus, diols with an increase in chain length from 3 to 4 carbons exhibited an increased degradation rate. However, the increase in chain length of the diacids had little effect on the biodegradation rate. It was believed that the increase in the number of methylene units in the diols increased the chain flexibility and thereby reduced the degree of crystallinity, which in turn influenced the biodegradability rate.[114]

Rigid hydrophilic units in bio-degradation

Both hydrolytic and enzymatic degradation of PBS copolyesters derived from isosorbide as a co-monomer (PBIS) were explored. PBIS degraded faster than the corresponding homopolymer under both hydrolytic and enzymatic conditions. The presence of the isosorbide unit in the PBIS copolymer increased the hydrophilicity and also reduced the crystallinity of the polymer. This facilitated the faster degradation of the PBIS copolyester than the corresponding homopolymer under enzymatic conditions. Furthermore, the degradation of polyesters derived from isosorbide units degraded substantially faster than other ester moieties derived from butane diol.[73a]

Bio-degradation by composting

Compost degradation experiments on poly(butylene succinate) based copolyesters with different ratios of Pripol 1009 moieties (Fig. 14) revealed that the biodegradability of copolymers was directly related to the incubation time and to the percentage of Pripol moieties in the copolymer. Interestingly, bacteria present in the compost attacked the butylene succinate units in the copolymer in a highly selective manner and thus resulted in an increased concentration of Pripol units in the decomposed polymer. The lower density of carboxylate groups in the copolymers with respect to PBS homopolymers might also be one of the reasons for the slower degradation of the Pripol segments.[146]

Blends derived from soy protein and chemically modified poly(butylene succinate) were also investigated for their biodegradability in compost. Blends with an increased PBS content

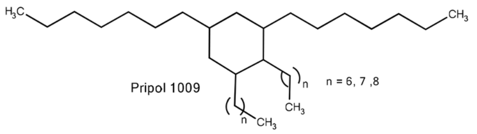

Fig. 14 Chemical structure of Pripol 1009.

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and increased molecular weight of PBS exhibited slow biodegradation rates. This could be correlated with the relatively low biodegradability of PBS. Furthermore, it was realized the biodegradation rate could be tuned by changing the structure and content of the PBS component.[147]

Biodegradation of the synthesized poly(ester urethane) copolymers under compost conditions indicated that crystallinity and surface hydrophilicity played key roles in determining the biodegradation of the co-polymer. Copolymers with high hydrophilicity and lower crystallinity (P(BS30BDG70)) underwent faster degradation than the other copolymer compositions. This further clearly indicated that polymers with more amorphous and labile functional groups that were easily accessible to the enzymes had increased biodegradability.[109]

Biodegradation of synthesized (PBSAT) and blended (PBS/PBT) aliphatic aromatic copolyester under compost conditions using microorganisms demonstrated that the monomer type and composition of the resins greatly influenced the biodegradability. Furthermore, PBS exhibited higher biodegradability due to its aliphatic segments, which were easily accessible to the microorganisms. The degrees of biodegradation of synthesized PBSAT10 and blended PBS/PBT were 19.9% and 28% respectively.[126]

Conclusion

In recent years, the availability of advanced technologies combined with increased interest in developing bio-alternatives to conventional petroleum based polymers have led to significant progress in the applications, development and industrialization of bio-based polyesters. Even though bio-degradable polymers are capable of mimicking synthetic polymers in various applications, only a few of them have found commercial importance. Among them, polybutylene succinate has gained significant importance owing to its improved mechanical and physical properties. However, cost and a lack of efficient methods for the synthesis of polybutylene succinate are the main challenges that restrict its application on a commercial scale. The development of cost effective methods for bio-based monomer synthesis as well as efficient and environmentally benign catalysts for polymerization are considered to be ideal solutions for commercializing polybutylene succinate.

Various catalyst systems, such as Lewis acids, organic acids, organo- and organo-metallic catalysts, as well as the combination of catalysts with thermal stabilizers, have also been explored for the synthesis of polybutylene succinate. The lack of hydrolytic stability of the catalyst and high temperature reaction conditions restrict the synthesis of high molecular weight PBS.

Among various catalyst systems that have been explored towards PBS synthesis, titanium alkoxides are found to be more efficient in synthesizing PBS. Furthermore, it is observed that the addition of a catalyst during the polycondensation reaction is more effective than catalyst addition during an esterification reaction (Table 4). This is believed to be due to the hydrolytic instability of the titanium based catalysts during the esterification reaction, in which water is found to be one of the by-products formed. Conversely, antimony(III) oxide (Sb_2O_3) is found to be more efficient than titanium alkoxides towards the synthesis of copolymers using less reactive and sterically crowded comonomers such as isosorbide.[70] Furthermore, under microwave conditions stannous chloride is found to be more efficient than titanium alkoxides.[86]

Table 4 Various catalyst systems for PBS synthesis

Catalyst	$M_n \times 10^4$ g mol^{-1}	$M_w \times 10^4$ g mol^{-1}	PDI ($Đ$)	Ref.
TBT	11.6	19.9	1.71	22*a*
TBT[a]	17.64	36.27	2.06	38
TBT[a]	8.62	18.33	2.12	85
TBT[a]	4.8	14.2	2.95	129
TBT/DPPA	—	11.6	—	43
CHTD	9.2	17.6	—	46
DBTO	—	11.2	2.2	48
Tin octoate	9.64	16.4	1.82	53
Zinc acetate/TBT[b]	7	16	2.2	66
TBT/La(acac)$_3$ [b]	6.4	10.48	1.62	68
*p*TSA/TBT[b]	8.8	21.3	2.41	70

[a] Catalyst added during the polycondensation step. [b] Dual catalyst system, in which one of the catalyst is added during the polycondensation step.

In the literature, various other techniques like copolymerization and the preparation of blends and composites have also been explored to improve the physical, mechanical and biodegradable properties of polybutylene succinate. In this regard, comonomers with aliphatic, aromatic, cyclic, acyclic and rigid backbones have been explored towards enhancing the properties of polybutylene succinate.

Although the polymerization of PBS with other comonomers led to an enhancement in either the physical or mechanical properties of the copolymer, there were compromises in its biodegradability (Table 5). Thus, the synthesis of high molecular weight PBS with balanced mechanical, physical and biodegradable properties still remains a challenging task. Thus, there is a lot of scope to develop mild and efficient polymerization catalysts as well as suitable comonomers to produce PBS with enhanced properties towards the commercialization of potential bio-degradable polymers, especially, polybutylene succinate.

The biodegradation of polymers depends on various parameters like chemical structure, repeating unit, hydrophilic/hydrophobic balance, molecular weight, solid-state morphology (*i.e.* crystallinity, crystal size and distribution), molecular mobility, and thermal characteristics. Moreover, amorphous and hydrophilic polymers degrade much faster than the corresponding crystalline and hydrophobic polymers. In addition, the nature, relative quantity, and distribution of the co-monomeric units along the polymer chain also have a significant influence on biodegradation.

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Table 5 PBS copolymer properties with respect to increase in comonomer content

Copolymer	T_g	T_m	T_c	Tensile strength	Elongation at break	Youngs modulus	Thermal stability	Bio-degradability	Ref.
PBESTU	++	– –	++	– –	** – –	– –	** ++		104
PBT – PBS	++^{r}	– –	– –						105
PBS-PCL	– –	– –	**	– –	+ +	—	– –		106
PDGS	**	– –	– –	+ +	++	– –			37
PBSe	– –	–	– –	–	++	–	–		27
PFS	++	– –**	– –	– –	++	– –	– –		108
PEG		**	– –	+ –	++	– –		++	76
P(BSBDG)(Diglycolic acid)	++	– –	– –	– –	++	– –	– –	++	109
P(BS-*co*-HS)	– –	– –	– –	– –**	+ –	–+	– –	++	111 and 112
P(BS-BMS)		– –	– –				**	++^{b}	116
2,3-BDO	++	– –	– –				– –		96
(PBDS)	– –	– –	– –	– –	–+	– –	**		43
P(BS-*co*-BAz)	– –	– –	– –				++		118
PBS-*ran*-PBAz	– –	– –	– –						119
PBSCs	++	– –	– –		++	– –	– –	++	121
PBS-*ran*-PCL	– –	– –	– –					–**	95 and 122
PBSI	**	– –	– –				**	– –	98 and 141
PBSFu	++	++	++						74 and 123
P(BSBDTDP)	– –	– –				– –	– –	++	26
PBIS	++	– –	– –		++	– –	–+	++	73*a*
PBST	++	– –	– –		––	––			56
PBSF	++	– –	– –		++	–**			56
PBISx & PBThSx	++	– –	– –	– –	++	– –	**	++	124
PBSGlux	++	– –	– –		– +	– +	++	++	73*b*
PBSManx	++	– –	– –	++	– –	++	++	++	49
FCDA	++	– –					–		29
PBSFr	++	– +	– +	– –	++	– –	–**	##	67
PFS-PBS	++	– **	– –	– –	++	– –	– –		108
PBS-BFu(Cross linked)	++	++	++	– –	– –	– –	– –	– –	41
PBS-BFu(Uncross linked)	++	++	++	– –	++	++	– –	– –	41
PBSTMGs	– –	– –	– –	– –	++	– –	– –	++	38
PBSTMGs (Blends)	– –	– –	– –	+–	+ –				38
1,2-DD	– –	– –	– –	– –	++	– –	– –	++	24
1,2,4-BT	++	**	++	++	– –				129
Glycerol	– –	– –	– –	– –	– –	– –			24
1,2-BDO	– –	– –	– –					++	24

– Slight decrease; ++ increases; – – decreases; + – increases initially and then decreases; – + decreases initially and then increases; $^{++r}$ increases with an increase in randomness; ** no significant change; – –** decreases and then no significant change; –** slight decrease and then no significant change; ** – – no significant change and decreases; $^{++b}$ degradation in the amorphous region is much faster than that in the crystalline region; ## composition dependent.

Abbreviation

PBS	Poly(butylene succinate)
CAGR	Compound annual growth rate
HDPE	High-density polyethylene
LDPE	Low-density polyethylene
LLDPE	Linear low-density polyethylene
MMT	Million metric tonnes
SA	Succinic acid
BDO	1,4-Butane diol
PBSAD	Poly(butylene succinate-*co*-butylene acetylenedicarboxylate)
p(BSBDTDP)	Poly(butylene succinate/dithiodipropionate)
TBT	Titanium tetrabutoxide
TTIP	Titanium tetraisopropoxide
PBSFu	Poly(butylene succinate-*co*-butylene fumarate)
PBFu	Poly(butylene fumarate)
PBSPS	Poly(butylene succinate-*co*-propylene succinate)
rPBSA	Poly(butylene succinate-*ran*-butylene adipate) random copolymers
PBS-*ran*-PCL	Poly[(butylene succinate)-*ran*-(ε-caprolactone)] copolyesters
BCHDA	Butylene 1,4-cyclohexanedicarboxylate
CHDMS	1,4-Cyclohexane dimethylene succinate
P(BS-*co*-HS)	Poly(butylene succinate-*co*-hexamethylene succinate)
P(BS-*co*-BAz)	Poly(butylene succinate-*co*-butylene azelate)
PBS-*b*-PDGS	Poly(butylene succinate-*b*-poly(diethylene glycol succinate)
PBSTMGs	Poly[(butylene succinate)-*co*-poly(tetramethylene glycol)]
PTMG	Poly(tetramethylene glycol)
PESu	Poly(ethylene succinate)
PPSu	Poly(propylene succinate)
PPA	Polyphosphoric acid
DPPA	Diphenylphosphinic
HTTD	

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	1-Hydroxy-3-thioisocyanate-1,1,3,3-tetrabutyldistannoxane
DCTD	1,3-Dichloro-1,1,3,3-tetrabutyldistannoxane
CHTD	1-Chloro-3-hydroxy-1,1,3,3-tetrabutyldistannoxane
CHTOD	1-Chloro-3-hydroxy1,1,3,3-tetraoctyldistannoxane
DBTO	Dibutyl tin oxide
PManxS	Bio-based PBS copolyesters obtained by partially replacing 1,4-butanediol in PBS with 2,4:3,5-di-*O*-methylene-D-mannitol
PEG	Polyethylene glycol
PDLA-*b*-PBS-*b*-PDLA	Poly(D-lactide)-*block*-poly(butylene succinate)-*block*-poly(D-lactide)
$La(acac)_3$	Lanthanum(III) acetylacetonate
HEPBP	2-Hydro-4-(2,3-epoxypropoxy) benzophenone
p-TSA	*p*-Toluenesulfonic acid
CS	Cyclohexanedimethylene succinate
BS	Butylene succinate
PBS-DLS	Poly(butylene succinate–dilinoleic succinate)
PBS-DLS-PEG	Poly(butylene succinate–dilinoleic succinate–ethylene glycol succinate)
SSP	Solid state polymerization
PBSM	Poly(butylene succinate-*co*-butylene malate)
PBST	Poly(butylene succinate-*co*-butylene terephthalate)
PBBS	Poly(1,4-butylene succinate-*ran*-2,3-butylene succinate)
PPBS	Poly(*p*-dioxanone-*co*-butylene-*co*-succinate)
ROP	Ring opening polymerization
PBSI	Poly(butylene succinate-*co*-itaconate)
PBSIr	PBS copolymer with rigid imide units
PETS-OH	Hydroxyl terminated poly(ethylene succinate-*co*-ethylene terephthalate)
PBS-OH	Hydroxyl terminated poly(butylene succinate)
TDI	Toluene-2,4-diisocyanate
PBT-PBS	Poly(butylene terephthalate)–poly(butylene succinate)
HO-PBT-OH	Dihydroxyl terminated PBT
PDGS	Poly(diethylene glycol succinate)
PBF	Polybutylene fumarate
PBSe-diol	Dihydroxyl terminated poly(butylene sebacate)
PFS diol	Poly(2,5-furandimethylene succinate)
IPDI	Isophorone diisocyanate
PEEUs	Poly(ester ether urethane)s
TPU	Thermoplastic polyurethanes
PBCE-OH	Hydroxyl terminated poly(butylene cyclohexanedicarboxylate)
HDI	Hexamethylene diisocyanate
PES-*b*-PBS	Poly(ethylene succinate)-*b*-poly(butylene succinate)
PHBS	Poly(hexamethylene succinate-*co*-6 mol% butylene succinate)
PP-*r*-BS	Poly(1,3-propylene succinate-*ran*-1,4-butylene succinate)
PPBA	Poly(1,3-propylene adipate-*ran*-1,4-butylene adipate)
1,3-PDO	1,3-Propanediol
IDA	Imide dihydric alcohol
P(BS-BMS)	Poly(butylene succinate-*co*-butylene 2-methylsuccinate)
MSA	2-Methylsuccinic acid
PBA	Poly(butylene adipate)
DS	Decamethylene succinate
BUP	Biodegradable unsaturated polyester
PBDS	Poly(butylene succinate-*co*-decamethylene succinate)
PBS-*ran*-PBAz	Poly(butylene succinate-*ran*-butylene azelate) copolyester
PBSCs	1,3/1,4-Cyclohexanedimethanol based alicyclic/aliphatic copolyesters
PBCS	Poly(butylene succinate-*co*-cyclohexanedimethylene succinate)
PCS	Poly(cyclohexanedimethylene succinate)
WAXS	Wide-angle X-ray scattering
CL	Caprolactone
PCL	Poly(caprolactone)
SAED	Selected area electron diffraction
PDLA	Poly(D-lactic acid)
PBIS	PBS copolyester derived from isosorbide as a co-monomer
IS	Isosorbide
ITh	2,3-*O*-Isopropylidene-lthreitol
Manx	2,4:3,5-Di-*O*-methylene-D-mannitol
Glux-Diol	2,4:3,5-Di-*O*-methylene-D-glucitol
AD	Acetylene dicarboxylic acid
BF	Butylene furandicarboxylate
PFS-PBS	Poly(2,5-furandimethylene succinate)-*b*-poly(butylene succinate)
PFS	Poly(2,5-furandimethylene succinate)
PBAT	Random copolymer of PBA and PBT
m-PBST	Multi-block poly(butylene succinate)–multi-poly(butylene terephthalate) copolyester
r-PBST	Random poly(butylene succinate)–multi-poly(butylene terephthalate) copolyester
PBSAT	Poly(butylene succinate-*co*-adipate-*co*-terephthalate)
PBSEG	Poly(butylene succinate)–poly(ethylene glycol)
PBSLAsp	PBS copolymer including e-caprolactone and aspartic acid
1,2-DS	1,2-Decylene succinate
1,2,4-BT	1,2,4-Butanetriol
DLAOH	Dimer linoleic diol
PVB	Poly(vinyl butyral)
FTIR	Fourier transform infrared spectroscopy
PHB	Poly(3-hydroxybutyrate)
PES	Poly(ethylene succinate)
PHS	Poly(hexylene succinate)
P(BS-*co*-CHDMS)	Poly(butylene succinate) (PBS) and its copolymers containing 1,4-cyclohexane dimethylene succinate

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P(BS-*co*-BCHDA)	Poly(butylene succinate) (PBS) and its copolymers containing butylene 1,4-cyclohexanedicarboxylate (BCHDA)
$CHCl_3$	Chloroform
SDMS	1,2-(Dimethoxycarbonyl)ethanesulfonate (sulfonated dimethyl succinate)
CHDM	1,4-Cyclohexanedimethanol
CHDA	1,4-Cyclohexanedicarboxylate
PBS-*co*-CL	Poly(butylene succinate-*co*-ε-caprolactone)
PBS-*co*-CHDM	Copolymer of PBS and 1,4-cyclohexane dimethanol
PBS-*co*-CL-*co*-CHDM	Ternary copolymer of PBS, PCL, and 1,4-cyclohexane dimethanol
PBS-*co*-DEGS	Poly(butylene succinate-*co*-diethylene glycol succinate)
PBS-*co*-BDGA	Poly(butylene succinate-*co*-butylene diglycolic acid)
HS	Hexamethylene succinate
BA	Butylene adipate
PBS-*co*-BA	Poly(butylenesuccinate-*co*-butylene adipate)
PBSCL	Poly(butylene succinate-*co*-6-hydroxycaproate)
FDCA	Furan dicarboxylic acid
PBT	Poly(butylene terephthalate)
PBSA	Poly(butylene succinate-*co*-butylene adipate)
PPAd	Poly(1,3-propylene adipate)
PBAS	Poly(butylene succinate-*co*-butylene adipate)
PBSFr	Poly(butylene succinate-*co*-butylene furandicarboxylate)
PBSFc	Poly(butylene succinate-*co*-furanoate) copolymer
PPS	Poly(1,3-propylene succinate)
PeD	1,5-Pentanediol
HDO	1,6-Hexanediol
CALB	*Candida antarctica* lipase B
P(BS-*co*-PeD)	PBS based random copolyester of a third monomer, 1,5-pentanediol (PeD)
P(BS-*co*-HDO)	PBS based random copolyester of a third monomer, 1,6-hexanediol (HDO)
P(BS-*co*-PDO)	PBS based random copolyester of a third monomer, 1,3-propanediol (PDO)
PBAz	Poly(butylene azelate)
PBSe	Poly(butylene sebacate)
(*co*PBFS)	Poly(butylene 2,5-furandicarboxylate-*co*-succinate)

Conflicts of interest

There are no conflicts to declare.

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